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Processing, Stability and High-Temperature Properties of Transition Metal Silicide-Refractory Oxide Composites for Electrical Applications

Gunes Alp Yakaboylu

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**PROCESSING, STABILITY AND HIGH-TEMPERATURE
PROPERTIES OF TRANSITION METAL SILICIDE-
REFRACTORY OXIDE COMPOSITES FOR ELECTRICAL
APPLICATIONS**

Gunes Alp Yakaboylu

**Dissertation submitted
to the Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Doctor of Philosophy
in
Material Science and Engineering**

**Edward M. Sabolsky, Ph.D., Chair
Konstantinos A. Sierros, Ph.D.
Xingbo Liu, Ph.D.
Nianqiang Wu, Ph.D.
Charter D. Stinespring, Ph.D.**

Department of Mechanical and Aerospace Engineering

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electrical conductivity, percolation, high-temperature preoxidation**

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Abstract

PROCESSING, STABILITY AND HIGH-TEMPERATURE PROPERTIES OF TRANSITION METAL SILICIDE-REFRACTORY OXIDE COMPOSITES FOR ELECTRICAL APPLICATIONS

Gunes Alp Yakaboylu

Many common electrical materials used in the current sensing applications suffer from structural and functional issues related to high operating temperatures (750°-1600°C), alternating reducing/oxidizing atmospheres, high pressures and corrosive environments. Therefore, there is a need for development of new materials, which are capable to operate under high-temperature and harsh-environments to provide real-time, accurate sensing during industrial processes such as coal gasification and power generation. In this study, electroconductive ceramic composites were fabricated by incorporating the 20-90 vol% of transition metal silicides (MoSi₂, WSi₂, NbSi₂, TaSi₂, CrSi₂) within refractory oxides (Al₂O₃, ZrO₂, Cr₂O₃), followed by sintering at 1370°-1600°C in argon. The densification, microstructural evolution, phase development and thermal stability of the composites were studied after sintering and further annealing by Archimedes, Scanning electron microscopy (SEM) and X-ray diffraction/Rietveld (XRD) techniques. Their non-isothermal and isothermal oxidation behavior was studied under ambient air using a thermogravimetric analyzer (TGA) at 50°-870°C to understand the key parameters influencing their high-temperature oxidation. The selected composites were also preoxidized at 1000°-1200°C for 10-120 minutes to better understand their high-temperature oxidation kinetics and surface layer formation, and hence, to enhance their oxidation resistance by forming a protective surface layer. XRD, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were used for structural and surface characterization. In addition, their 4-point DC electrical conductivities were measured up to 800°-1000°C to study their electrical performance as a function of the composition and processing. A microstructural image analysis method was also developed for quantitatively characterizing the degree of distribution (homogeneity) within the composites. Lastly, thick-film embedded thermocouples (e.g. MoSi₂-Al₂O₃//WSi₂-Al₂O₃) were fabricated using selected composites by a screen printing technique. Their thermoelectric properties were measured in argon by a typical hot-cold junction temperature measurements, while their structural and microstructural analyses were performed by XPS, XRD and SEM.

DEDICATION

To my wife...

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LIST OF SYMBOLS AND ABBREVIATIONS

CMOS	Complementary metal-oxide semiconductor
IUPAC	International Union of Pure and Applied Chemistry
wt%	Weight percentage
vol%	Volume percentage
T_g	Glass transition temperature
GPa	Gigapascal
MPa	Megapascal
ZT	Figure-of-merit
S	Seebeck coefficient
ρ	Electrical resistivity
K_{IC}	Fracture toughness
σ_f	Flexural strength
CTE	Coefficient of thermal expansion
SSA	Specific surface area
XRD	X-ray diffraction
FE-SEM	Field emission scanning electron microscopy
f. Al_2O_3	Fine-alumina
c. Al_2O_3	Coarse-alumina
h	Hour
sccm	Standard cubic centimeter per minute
min	Minute
MAUD	Material Analysis Using Diffraction
DC	Direct current
EDS	Energy dispersive spectroscopy
R-grey	Grey region
R-bright	Bright region
Sig	goodness of fit
Rwp	Weighted profile R-factor
D index	Degree (level) of distribution
CIF	Crystallographic information file
TGA	Thermogravimetric analyzer
CC	Chromium silicide-Chromium oxide (composite)
ASTM	American Standards for Testing of Materials
RPS	Relative particle size
MMCs	Metal matrix composites
β	Skewness index
s	Standard deviation
C_v	Coefficient of variation
N	Number of lines analyzed

pO ₂	Partial pressure of oxygen
HDPE	High-density polyethylene
//	A thermocouple being formed
XPS	X-ray photoelectron spectroscopy
E	Thermoelectric voltage
ΔT	Temperature difference (gradient)
S _A	Seebeck coefficient of a material-A
S _B	Seebeck coefficient of a material-B
S _{AB}	Difference in Seebeck coefficients of A-B materials
ΔV_{AB}	Electric potential across the interface of A-B materials
S _{MA}	Intrinsic Seebeck coefficient of a MoSi ₂ -Al ₂ O ₃ composite
S _{WA}	Intrinsic Seebeck coefficient of a WSi ₂ -Al ₂ O ₃ composite
S _{MAPt}	Effective Seebeck coefficient of a MoSi ₂ -Al ₂ O ₃ //Pt thermocouple
S _{WAPt}	Effective Seebeck coefficient of a WSi ₂ -Al ₂ O ₃ //Pt thermocouple
S _{MAWA}	Effective Seebeck coefficient of a MoSi ₂ -Al ₂ O ₃ //WSi ₂ -Al ₂ O ₃ thermocouple
NIST	National Institute of Standards and Technology
DAQ	Data acquisition
A,B,C,D	Fitting coefficients
MA//WA	MoSi ₂ -Al ₂ O ₃ //WSi ₂ -Al ₂ O ₃ composite thermocouple
PO	Preoxidation treatment
w/o PO	Non-preoxidized samples (without PO)
w/ PO	Preoxidized samples (with PO)

INTRODUCTION

Statement of Problem

High temperatures and extreme harsh environments are commonly described as one of the major challenges in a broad range of industries such as power generation, coal gasification, and steel and glass manufacturing. The main sources of these harsh conditions are known as very high operating temperatures, high pressures, and oxidative and corrosive atmospheres. To achieve better process control, high efficiency, less environmental impact and increased lifetime of the process units, it is required to closely monitor the process conditions such as temperature and pressure, as well as, the structural health and degradation (e.g. spallation) of the ceramic refractories widely used in the high-temperature reactors. However, commonly used materials (Pt, Rh as noble metals) and their alloys undergo structural and functional challenges, such as selective oxidation, compositional and mechanical degradation, microstructural changes, leading to their increased failure rate and highly reduced lifetime. Therefore, it is apparent that there is a great demand for the development of high-temperature electrical and sensing materials, which are capable to operate reliably and accurately for extended operation hours without any degradation.

Goals of Research

Due to the extensive material requirements of the high-temperature electrical applications, transition metal silicides (e.g. MoSi_2 , WSi_2) offer promising advantages due to their high melting points, excellent high-temperature oxidation resistance, low corrosion rates, thermal stability, sufficient mechanical properties, thermodynamic compatibility with potential ceramic reinforcements, and electrical conductivities at elevated temperatures. Therefore, the main focus of this research is to develop high-temperature electroconductive composites composed of transition metal silicides and refractory oxides for a broad range of electrical applications. In order to accomplish this, the following objectives were determined and completed:

- Preparation of highly stable and electrically conductive transition metal silicide-refractory oxide composites that are able to operate at high temperatures
- Study their densification as a function of composition and temperature
- Investigate their phase (thermal) stability and secondary phase formation at high temperatures
- Understand their microstructural evolution and effect of the oxide phase on grain growth mechanism
- Study their oxidation behavior in a wide temperature range in air atmosphere
- Improve their oxidation resistance via oxide phase addition and high-temperature preoxidation treatment
- Perform electrical measurements at high temperatures to study their electrical performance as a function of composition, processing and temperature
- Fabricate thick-film embedded thermocouples from the selected composites, and study their thermoelectric performance along with structural and microstructural analyses

Thesis Organization

This dissertation is composed of seven chapters. The *first chapter* provides a comprehensive literature review (background) reporting the needs for high temperature applications, importance of transition metal silicides, and earlier studies on intermetallics, transition metal silicides and their composites. *Chapter 2* presents the densification, phase stability, secondary phase formation, microstructural evolution, grain growth and high-temperature electrical properties for the molybdenum silicide- and tungsten silicide-based composites with the addition of alumina and zirconia phases. *Chapter 3* explores the processing of the niobium silicide- and tantalum silicide-based electroconductive composites, and their detailed characterization for phase (thermal) stability, microstructures, oxidation behavior, and electrical properties at elevated temperatures. *Chapter 4* discusses the fabrication of the chromium silicide-based composites via solid-state reactions, formation of various composites with different type of metal silicides, and their detailed characterization for phase stability, microstructures, oxidation behavior and

high-temperature electrical properties. *Chapter 5* presents the microstructural image analysis technique developed to quantitatively measure the mixedness (homogeneity) of the composite materials to help better understanding of the microstructure-property relations (e.g. homogeneity – percolation/electrical conductivity). *Chapter 6* provides the fabrication of the molybdenum silicide- and tungsten silicide-based thick-film ceramic composite thermocouples as deposited on alumina substrates via a screen printing technique, and their structural and thermoelectric characterization. *Chapter 7* explores the influence of the alumina phase addition and high-temperature preoxidation treatment on the oxidation behavior of the molybdenum silicide- and tungsten silicide-based composites for further improvement of their oxidation resistance.

CHAPTER 1: BACKGROUND

There has been a growing interest in the development of high temperature structural materials for a wide range of industrial and military applications such as gas turbine engines, combustion chambers, missile nozzles, diesel engine glow plugs, gas burners, lances for molten metal and glasses, and high temperature load bearing [1-3]. In such applications, different parts and components are all exposed to extreme physical conditions in various mechanical, corrosive, and oxidizing environments. For example, high operating temperatures, high thermal conductivities, high stiffness, high strength to weight ratio, and good resistance to oxidation and corrosion are required for the aerospace gas turbine engines [2-5]. In addition, structural materials used in industrial gas burners, and steel and glass manufacturing as lances need to have excellent oxidation and corrosion resistance at high temperatures due to their interaction with oxygen gas combustion environment, and their physical contact with molten metals and glasses [2,6]. Similar materials also require improved mechanical properties such as high yield strength, high fracture toughness, low creep rate, and high wear resistance at high temperatures [1,3,7].

In order to achieve those advanced properties that can withstand highly oxidizing and corrosive environments at elevated temperatures, many high temperature structural materials have been developed over the years. These structural materials, which consist of (1) nickel-base superalloys, (2) structural ceramics, and (3) intermetallics, are mainly classified and discussed based on operating temperatures at their applications [1,4,8]. For temperatures below 1200°C, nickel-base superalloys have been mostly used as gas turbine elements in aerospace applications due to their excellent oxidation and mechanical properties. However, these superalloys show some disadvantages such as requirement of cooling during the operation of the gas turbine engines, low operating temperature, high density, and low strength to weight ratio [1,8]. As alternatives of nickel-base superalloys, several nickel and titanium aluminides such as Ni_3Al , TiAl , and Ti_3Al in the class of intermetallics have been also utilized for similar applications in the range of 800°C and

1200°C due to their mechanical properties and lower densities [1,6,8]. But their poor oxidation resistance above 650°C and low melting temperature limits their use in structural applications. At higher temperatures above 1200°C, structural ceramics and intermetallics are known as primary candidates that can fulfill most of the required combination of properties for high temperature structural applications [4,6,8]. Structural ceramics, which are mostly silicon-based ceramic materials, such as SiC and Si₃N₄ are important high temperature structural materials since they present excellent resistance to oxidation and high strength at elevated temperatures with high melting points. Apart from their advantages, low ductility at high temperatures, difficulty of alloying and machining, cost of manufacture due to cost of starting materials/fabrication, and relatively lower fracture toughness are main limitations of these silicon-based structural ceramics [1,9,10]. Therefore, alternative materials called as intermetallics have been studied and developed for high temperature structural applications as alternatives to the other materials. In this field, high temperature intermetallics are generally divided into two groups which are (1) aluminides, and (2) silicides. Nickel-, niobium-, iron-, and titanium-aluminides such as NiAl, NbAl₃, Fe₃Al and Ti₃Al are mostly used intermetallics as high temperature structural materials in the group of aluminides [1-3]. Although these aluminide intermetallics have lower density and high operating temperature than nickel-base superalloys, they do not have significant advantages in comparison to the high temperature silicon-based structural ceramics. In addition, their use at high temperature structural applications are quite limited due to their low strength and creep resistance at the temperatures above 1000°C, as well as their low resistance to oxidation above 1200°C [1,8]. Another problem related to the use of aluminide intermetallics is their incompatibility with many reinforcing materials such as Nb, SiC, and Y₂O₃ resulting in unstable chemical reactions and thus formation of undesired phases, since their reinforcement is essential in this field for obtaining improved mechanical properties, creep and oxidation resistance.

As a second group of advanced intermetallics, transition metal silicides such as MoSi₂, WSi₂, Mo₅Si₃, and TiSi₂, that are silicides of refractory metals, have been

extensively studied as high temperature structural materials for applications in highly oxidizing and corrosive environments [1,3,4,11-15]. Transition metal silicides generally provide higher melting temperatures, similar densities, higher oxidation resistance (higher oxidation temperature), high thermal stability, and better mechanical properties than aluminide intermetallics [1,7]. In comparison to the silicon-based structural ceramics like SiC, metal silicides take advantages of ease of alloying with other structural silicides and thermodynamic compatibility with potential ceramic reinforcements (Al_2O_3 , SiC, Si_3N_4 , etc.), while they all have high melting temperatures, excellent oxidation resistance, high thermal conductivity, and good creep resistance. Another advantage of these high temperature structural metal silicides is the formation of a thin protective silica (SiO_2) layer on the surface up to 1700°C in highly oxidizing environments, which also acts as a great barrier against chemical attacks [4,11,13]. Their only weaknesses as high temperature structural materials are all stated as insufficient mechanical properties which are low toughness and reduced strength at elevated temperatures [1,11-13,16]. In addition to their use in high temperature structural applications, there has been a remarkable interest to transition metal silicides (MoSi_2 , WSi_2 , Ta_5Si_3 , CrSi_2 etc.) in high temperature electrical applications due to their high electrical conductivity, high chemical and thermal stability, excellent diffusion-barrier characteristics, low toxicity, and cost efficiency [2,17-19]. These electrical applications include interconnects and barrier layers in micro-electronic devices, and particularly high temperature thermoelectrics for generating electricity. Therefore, transition metal silicides also exhibit a great potential for high temperature electrical applications, and particularly thermoelectrics in comparison to the widely used, highly toxic, and expensive materials such as thallium-, germanium, and tellurium-based alloys [17,20]. In summary, it is required for advanced high-temperature materials to provide adequate combination of properties such as oxidation resistance, thermal stability, creep resistance, fracture toughness, strength, thermal conductivity and electrical conductivity at high temperatures, which make them capable to operate in highly oxidizing and corrosive environments for long terms. Among all potential high temperature structural materials, transition metal silicides as intermetallics are described as most promising candidates

[1,4,7,12,16,21,22] for high-temperature structural and also electrical applications due to their excellent high-temperature oxidation resistance, high melting point and operating temperature, high-temperature thermal/chemical stability and strength, relatively low density, good creep resistance, high thermal conductivity, high-temperature electrical conductivity, and also thermodynamic compatibility with potential ceramic reinforcements.

1.1 Transition Metal Silicides

Transition metal silicides have been implemented into a wide range of engineering and technological applications including heating elements, thin film coatings, molten metal lances, interconnects, gas burners, photovoltaics, CMOS devices, and thermoelectrics [2,23,24]. Transition metal silicides are generally described as intermetallic compounds of transition metals and silicon, which have diverse physical properties and crystal structures [24,25]. As a general review, all transition metal silicides that can be practically formed as compounds of transition metals, which are groups from IB to VIIIB of the periodic table (groups 3-11 based on IUPAC), and silicon are listed in Table 1 [24,26]. A broad set of transition metal silicides (binary metal silicides) such as monosilicides (TiSi, MnSi, and CoSi etc.) and disilicides (MoSi₂, WSi₂, and ZrSi₂ etc.) can be clearly seen. Therefore, they present a range of mechanical, chemical, thermal, and electrical properties depending on their constituent metals, stoichiometries, and crystal structures. Based on the literature, it can be generally seen that the main focus has been on disilicides of refractory metals in group IV, V, and VI (mostly MoSi₂, WSi₂, TiSi₂, TaSi₂, NbSi₂, and CrSi₂ as highlighted with bold letters in Table 1) because of their relatively higher melting temperature, good thermal and chemical stability at high temperatures, excellent oxidation resistance, good mechanical properties, relatively low density, and electrical conductivity at high temperatures, which make them best candidates for high temperature structural and also electrical applications in harsh (oxidizing and corrosive) environments [27-31]. Therefore, structure and properties of the refractory transition metal silicides, which have been mostly studied in the literature, are extensively reviewed in the following section.

Table 1. All transition metal silicide phases represented in the periodic table [24,26].

IVB (4)	VB (5)	VIB (6)	VIIB (7)	VIII B			IB (11)
				(8)	(9)	(10)	
(Ti-Si)	(V-Si)	(Cr-Si)	(Mn-Si)	(Fe-Si)	(Co-Si)	(Ni-Si)	(Cu-Si)
			Mn ₄ Si				
Ti ₅ Si ₃	V ₃ Si	Cr ₃ Si	Mn ₃ Si	Fe ₃ Si	Co ₃ Si	Ni ₃ Si	Cu ₃ Si
Ti ₅ Si ₄	V ₅ Si ₃	Cr ₅ Si ₃	Mn ₅ Si ₂	Fe ₂ Si	Co ₂ Si	Ni ₂ Si	Cu ₁₅ Si ₄
TiSi	V ₆ Si ₅	CrSi	Mn ₅ Si ₃	Fe ₅ Si ₃	CoSi	Ni ₃ Si ₂	Cu ₅ Si
TiSi₂	VSi₂	CrSi₂	MnSi	FeSi	Co ₂ Si ₃	Ni ₃₁ Si ₁₂	Cu ₇ Si
Ti ₃ Si	V ₂ Si		MnSi _{2-x}	FeSi ₂	CoSi ₂	NiSi	
			Mn ₆ Si			NiSi ₂	
(Zr-Si)	(Nb-Si)	(Mo-Si)	(Tc-Si)	(Ru-Si)	(Rh-Si)	(Pd-Si)	
Zr ₃ Si					Rh ₂ Si	Pd ₅ Si	
Zr ₂ Si	Nb ₄ Si	Mo ₃ Si	Tc ₄ Si	Ru ₂ Si	Rh ₅ Si ₃	Pd ₄ Si	
Zr ₅ Si ₃	Nb ₃ Si	Mo ₅ Si ₃	Tc ₃ Si	Ru ₅ Si ₃	Rh ₃ Si ₂	Pd ₃ Si	
Zr ₃ Si ₂	Nb ₅ Si	Mo ₃ Si ₂	Tc ₅ Si ₃	Ru ₄ Si ₃	RhSi	Pd ₂ Si	---
Zr ₆ Si ₃	NbSi₂	MoSi₂	TcSi	RuSi	Rh ₄ Si ₅	PdSi	
ZrSi	Nb ₅ Si ₃		Tc ₄ Si ₇	Ru ₂ Si ₃	Rh ₃ Si ₄	Pd ₉ Si ₂	
ZrSi ₂					Rh ₂₀ Si ₁₃	Pd ₄ Si ₂₀	
(Hf-Si)	(Ta-Si)	(W-Si)	(Re-Si)	(Os-Si)	(Ir-Si)	(Pt-Si)	
					Ir ₃ Si		
Hf ₂ Si	Ta ₃ Si	W ₃ Si	Re ₃ Si	OsSi	Ir ₂ Si	Pt ₃ Si	
Hf ₅ Si ₃	Ta ₂ Si	W ₅ Si ₃	Re ₅ Si ₃	OsSi ₂	Ir ₃ Si ₂	Pt ₁₂ Si ₅	
Hf ₃ Si ₂	Ta ₅ Si ₃	WSi₂	ReSi	Os ₂ Si ₃	IrSi	Pt ₂ Si	---
Hf ₅ Si ₄	TaSi₂		ReSi ₂	OsSi ₃	IrSi ₃	Pt ₆ Si ₅	
HfSi			ReSi _{1.75}	OsSi _{1.8}	Ir ₄ Si ₅	PtSi	
HfSi ₂					Ir ₃ Si ₄		

1.1.1 Structure of the refractory transition metal silicides

The refractory metal silicides are known as intermetallics compounds of transition metals in group IV, V, and VI (Ti, V, Cr, Zr, Nb, Mo, Hf, Ta, W) and silicon (Si). Therefore, they combine both metallic and covalent bonding in their structure. Although bonding between transition metals and silicon atoms are metallic in nature, covalent Si-Si bonds between silicon atoms also exist in these metal silicide structures [14,32]. The occupation of d- and f-electron shells of transition metals and fraction of transition metal and silicon atoms in the structure affects the contribution of these bonds determining the exact structure of the transition metal silicides and properties. For example; weak metallic bonds may form with increasing silicon content within a silicide structure. But formation of these metal silicides are different than some carbide and boride structures, which are called as interstitial compounds that can be obtained by dissolving the non-metals with small atomic radius into existing interstitial sites of the metal lattice. In the case of transition metal silicides, silicon atoms can only substitute (not interstitial) with transition metal atoms in the lattice positions since the ratios of silicon atom radius to the transition metal atom radius are all greater than 0.59 (for example; $r_{\text{Si}}/r_{\text{Mo}} = 0.84$ and $r_{\text{Si}}/r_{\text{Ta}} = 0.80$) as contrary to the Hagg's condition [32,33]. This can be also described as the origin of the complex structures of various refractory transition metal silicides.

To understand the formation of mostly studied and used refractory transition metal silicides, molybdenum-silicon (Mo-Si) binary phase diagram is presented in Figure 1 [7]. As seen in the Mo-Si binary phase diagram, there are three principal groups of refractory silicide compounds, which are (1) silicon rich, metal disilicides as MoSi_2 , (2) complex, 5-3 silicides as Mo_5Si_3 , and (3) metal rich, metal monosilicides as Mo_3Si , respectively. The crystal structure of Mo_3Si , which decomposes with a peritectic reaction at 2025°C , is A15 type cubic; while Mo_5Si_3 compound as 5-3 silicide exhibits a D8_m type tetragonal lattice structure [2,23]. In addition, it can be seen on the Mo-Si binary phase diagram that there are two polymorphs of molybdenum disilicide, which are stable $\alpha\text{-MoSi}_2$ with C11_b type tetragonal body-centered structure (space group I4/mmm), and metastable $\beta\text{-MoSi}_2$ with a

Figure 1. Molybdenum-silicon (Mo-Si) binary phase diagram [7].

C40 type hexagonal close-packed structure (space group $P6_222$) [21,23]. The tetragonal α - MoSi_2 phase is only stable up to 1900°C, while it transforms to the β -phase above this temperature. Although the crystal structures of both α - and β - MoSi_2 contain Mo-Si₂ layers, where six Si atoms exist around each Mo atom, their stacking sequences are different like AB and ABC for α - and β - MoSi_2 , respectively. In order to fully understand their structure, crystal structures of various refractory metal disilicides are discussed since they have been mostly studied and used in many applications. As shown in the projection of a pseudo-quaternary phase diagram with Si at the apex and base ternary of three groups of transition elements (Figure 2), refractory metal disilicides have different type of crystal structures such as C11_b, C40, C54, and C49 [7,27,34]. While WSi_2 exhibits the same tetragonal C11_b structure with MoSi_2 ; CrSi_2 , VSi_2 , NbSi_2 , and TaSi_2 present hexagonal C40 structure having same ABC stacking sequence with β - MoSi_2 . It is also shown that TiSi_2 and ZrSi_2 have orthorhombic C54 and C49 structures, respectively. These orthorhombic structures of

Figure 2. Projection of a pseudo-quaternary phase diagram summarizing the formation of mostly studied/used refractory metal disilicides [7].

disilicides differently contain four-layer of ABCD or two-layer of AB' stacking sequences depending on their types [27]. As a general review, the refractory metal disilicides can be classified based on their crystal structures as three main groups, which are (1) Mo and W disilicides with tetragonal C11_b structure, (2) Cr, V, Nb, and Ta with hexagonal (C40 type), and (3) Ti, Zr, and Hf with orthorhombic (C49 or C54 types) structure. The tetragonal and hexagonal crystal structures of refractory metal disilicides in terms of different stacking sequences of C11_b and C40 types can be seen in Figure 3 for better understanding of their structures [7,34]. Figure 3a presents the tetragonal C11_b crystal structure of α -MoSi₂ having I4/mmm space group and lattice parameters of $a = 3.2\text{\AA}$ and $c = 7.85\text{\AA}$ ($c/a = \sqrt{6}$). In this structure, molybdenum atoms are positioned at (0,0,0) and (1/2,1/2,1/2) positions, while silicon atom positions are (0,0,1/3), (0,0,2/3), (1/2,1/2,1/6), and (1/2,1/2,5/6) [2,26,35,36]. In addition, hexagonal C40 crystal structure of CrSi₂ has a P6₂22 space group and lattice

Figure 3. Crystal structure and stacking sequences of refractory transition metal disilicides: (a) tetragonal C11_b structure of MoSi₂, (b) hexagonal C40 structure of CrSi₂ [7,34].

parameters of $a = 4.43\text{\AA}$ and $c = 6.37\text{\AA}$ with a different stacking sequence (ABCABC) than tetragonal structure of MoSi₂ (ABAB) as shown in Figure 3b. As a review, it is essential to summarize different crystal structure parameters of the refractory metal disilicides, which are mostly studied as high temperature structural and electrical materials due to their excellent property combination and refractoriness. Therefore, their crystal systems, space groups, and lattice parameters are summarized in Table 2 [26]. It can be stated that α -MoSi₂ and WSi₂ exhibit quite similar tetragonal crystal structures, while CrSi₂, VSi₂, NbSi₂, β -MoSi₂, and TaSi₂ also have similar hexagonal crystal structures.

Table 2. Crystal system, space group and lattice parameters of the binary refractory metal disilicides as a primary group for the high temperature structural and electrical applications [21,26].

Metal Disilicides	Crystal Structure	Space Group	Lattice parameters (Å)		
			a	b	c
TiSi₂	Orthorhombic	Fddd	8.2687	8.5534	4.7983
VSi₂	Hexagonal	P6 ₂ 22	4.5723	---	6.3730
CrSi₂	Hexagonal	P6 ₂ 22	4.4281	---	6.3691
ZrSi₂	Orthorhombic	Cmcm	3.6958	14.7510	3.6654
NbSi₂	Hexagonal	P6 ₄ 22	4.7970	---	6.5920
α-MoSi₂	Tetragonal	I4/mmm	3.2000	---	7.8500
β-MoSi₂	Hexagonal	P6 ₂ 22	4.5960	---	6.5500
HfSi₂	Orthorhombic	Cmcm	3.6798	14.5562	3.6491
TaSi₂	Hexagonal	P6 ₂ 22	4.7835	---	6.5698
WSi₂	Tetragonal	I4/mmm	3.2110	---	7.8290

1.1.2 Mechanical properties of the refractory transition metal silicides

The mechanical behavior and properties of the refractory transition metal silicides have been extensively investigated in the literature due to their high potential for high temperature structural applications. Their fracture toughness, hardness, elastic modulus, yield strength, flexural strength and creep rate (resistance) have been mostly studied [37].

1.1.2.1 Fracture toughness

The main focus was on the molybdenum silicide structures and particularly the molybdenum disilicide (MoSi_2) in the literature [1-4,7,11-15,21-23]. For its use in high temperature structural applications, mechanical properties of MoSi_2 have been examined over the years to present their mechanical capability for such applications. It is known that polycrystalline MoSi_2 shows a brittle behavior at low temperatures like ceramic materials [16,38]. For their fracture behavior, Wade and Petrovic (1992) presented that transgranular fracture is dominant in the fracture mode of MoSi_2 at room temperature [39]. They also measured the fracture toughness of MoSi_2 at room temperature as $3.0 \text{ MPa.m}^{1/2}$. Zhang et al. (1999) reported a very low fracture toughness value for the MoSi_2 , since hot pressed MoSi_2 exhibited $2.0 \text{ MPa.m}^{1/2}$ fracture toughness at room temperature without any reinforcements [13]. In the study of Pan et al. (1998), the fracture toughness of monolithic MoSi_2 prepared by hot press sintering was measured at room temperature [40]. They reported the fracture toughness of the monolithic MoSi_2 at that temperature approximately as $4.3 \text{ MPa.m}^{1/2}$, which is relatively higher than the value provided by Wade and Petrovic. As reviewed by Mitra (2006), fracture toughness values measured at room temperature for polycrystalline MoSi_2 were all between 3.0 and $5.0 \text{ MPa.m}^{1/2}$ based on the published studies [37]. The low fracture toughness of MoSi_2 was explained by its brittle nature interrelated with the covalent character of Mo-Si bonds and existence of high number of cleavage planes in its structure. To overcome its brittleness and low fracture toughness, some elements such as niobium and aluminum have been used for alloying and reinforcing in low fractions [2,16,22], since it is known that the fracture toughness can be improved by incorporation of a ductile secondary phase to the matrix phase. Soboyejo et al. (1996) reported that fracture toughness of the MoSi_2 could be increased from 3.6 to $5.7 \text{ MPa.m}^{1/2}$ by addition of Mo, W, and Nb particles to the system [41]. As presented in the Figure 4, highest fracture toughness value for the MoSi_2 ($5.7 \text{ MPa.m}^{1/2}$) was achieved by using Nb particles as a secondary phase, which also resulted in the formation of Mo_5Si_3 , SiO_2 , and $(\text{Mo,Nb})_5\text{Si}_3$ phases in the system. However, in another study, no significant improvement has been achieved by addition of the Nb particles [42]. In the study of Zhang et al. (1999),

Figure 4. Comparison of the room temperature fracture toughness values (K_Q) of the monolithic MoSi₂ with the particulate (Mo, W, and Nb) reinforced MoSi₂ [41].

influence of the aluminum addition on the mechanical properties of MoSi₂ has been studied [13]. The room temperature fracture toughness of MoSi₂ increased from 2.0 to 2.8 MPa.m^{1/2} with the addition of 5 wt.% Al into the system, then slightly decreased approximately to 2.3 MPa.m^{1/2} with increasing Al content as shown in the Figure 5. In another study, molybdenum aluminosilicide, Mo(Si_{0.8}Al_{0.2})₂ as a ternary intermetallic compound was synthesized by alloying MoSi₂ with aluminum [16]. The indentation fracture toughness of alloyed MoSi₂ was calculated as 3.68 MPa.m^{1/2}, which is relatively higher than the data reported (2.0-3.0 MPa.m^{1/2}) for the MoSi₂ by Wade and Petrovic (1992), and Zhang et al. (1999). In such alloying studies with aluminum, they all proposed to improve the mechanical properties due to enhanced metallic character of MoSi₂ and presence of a C40-type Mo(Si_{1-x}Al_x)₂ phase [16,43,44].

On the other hand, there are only a several studies in the literature focusing on the mechanical properties and particularly the room temperature fracture toughness of the other refractory transition metal silicides such as WSi₂, NbSi₂, and TaSi₂ [30,45-48]. Ko et al.

Figure 5. Effect of aluminum addition on the room temperature fracture toughness and other mechanical properties of the MoSi₂ [13].

(2009) reported that average fracture toughness of the NbSi₂, that was calculated from the indentation data, was approximately 2.5 MPa.m^{1/2} at room temperature [45], which is relatively lower than the fracture toughness of MoSi₂. In another study, relatively higher fracture toughness value for the NbSi₂ was obtained as 3.0 MPa.m^{1/2} similarly from the indentation results [48]. The fracture toughness of the WSi₂ without and with 20 wt.% Nb reinforcements has been studied by Shon et al. (2000) [47]. At room temperature, pure WSi₂ and Nb-reinforced WSi₂ exhibited the fracture toughness values of 3.2 and 9.1 MPa.m^{1/2}, respectively, based on the indentation crack measurements. This result clearly indicates that WSi₂ has relatively higher fracture toughness than NbSi₂, and its fracture toughness can be substantially enhanced by addition of a ductile Nb particles. Furthermore, in the study of Ko et al. (2010), the fracture toughness of TaSi₂ was measured as 3.7 MPa.m^{1/2} [30], which is relatively higher than the average fracture toughness values of NbSi₂ and WSi₂, but similar to that of MoSi₂.

The fracture toughness of MoSi₂ has been also investigated at elevated temperatures as a function of temperature with/without existence of alloying and/or reinforcing elements. In the study of Maloy et al. (1992), mechanical properties of the MoSi₂ and alloyed MoSi₂ were studied up to 1400°C in order to determine the effect of carbon additions [49]. Therefore, MoSi₂ was alloyed with carbon (C) element up to 4 wt.%, and then their high temperature fracture toughness values were measured. As presented in the Figure 6, fracture toughness of the monolithic MoSi₂ (without addition of carbon) decreased approximately from 3.9 to 1.0 MPa.m^{1/2} with increasing temperature from 800° to 1400°C. This reduction in fracture toughness of MoSi₂ was found to be directly interrelated with the viscosity of silica grain boundary phase, which decreased with increasing temperature resulting in more grain boundary sliding with cavitation and low energy intergranular fracture via preferential path formed at high temperatures (above T_g of silica, 1200°C) [49,1,38]. This result revealed that high temperature fracture toughness of MoSi₂ is highly

Figure 6. High temperature fracture toughness of monolithic MoSi₂ and MoSi₂ alloyed with 1-4 wt.% of carbon as a function of temperature [49].

affected by base purity of MoSi₂ and existence of grain boundary phases. In addition, significant increases in the fracture toughness were observed for all carbon-alloyed MoSi₂ samples with increasing temperature up to 1200° and 1400°C due to removal of the grain boundary silica phase resulting in the change of fracture mode from intergranular to transgranular at high temperatures (Figure 6). The fracture toughness of the alloyed MoSi₂ with 2 wt.% carbon was increased approximately from 5.6 to 11.5 MPa·m^{1/2} with increasing temperature from 800° to 1400°C, which clearly presented the positive influence of alloying on the fracture toughness of MoSi₂.

1.1.2.2 Modulus of elasticity, yield strength and flexural strength

Modulus of elasticity or Young's modulus (E) is mainly described as a measure of a material's resistance to elastic deformation, and it is one of the mechanical properties studied for the refractory transition metal silicides [50]. In the study of Pan et al. (1998), room temperature mechanical properties of MoSi₂ were examined [40]. The modulus of elasticity of MoSi₂ was measured between 378 and 517 GPa, since different phases existing in the structure such as MoSi₂, Mo₅Si₃, and SiO₂ all affected its modulus of elasticity. However, they reported that the MoSi₂ matrix phase displayed approximately 440 GPa for its modulus of elasticity. Similar to this study, modulus of elasticity of the MoSi₂ was also reported as 430 GPa at room temperature [50]. The elastic properties of hexagonal C40 refractory metal disilicides such as polycrystalline NbSi₂ and TaSi₂ were studied by Chu et al. (1996) [51]. The average modulus of elasticity values of NbSi₂ and TaSi₂ at room temperature were determined as 362.8 and 359.0 GPa, respectively. Furthermore, relatively lower modulus of elasticity was reported for NbSi₂ as 255.1 GPa [50]. These results clearly demonstrated that the MoSi₂ has higher modulus of elasticity than NbSi₂ and TaSi₂ at room temperature. On the other hand, there is only a few studies in the literature reported the elastic modulus of the refractory metal silicides at high temperatures [7,44]. The average elastic modulus of several refractory metal silicides (MoSi₂, WSi₂, CrSi₂, VSi₂, TiSi₂, Ti₅Si₃, Cr₃Si, V₃Si, and Mo₅Si₃) as a function of temperature can be seen in the Figure 7 [44]. The elastic modulus of the MoSi₂ decreased approximately from 430 to 350 GPa with

Figure 7. Average elastic modulus (modulus of elasticity or Young's modulus) of several refractory metal silicides as a function of temperature [44].

increasing temperature up to 1100°C. Similar trends were observed for TiSi_2 , Ti_5Si_3 , Mo_5Si_3 , and Cr_3Si . It was also determined that WSi_2 , MoSi_2 , CrSi_2 , and VSi_2 have higher elastic modulus than other refractory metal silicides, but quite comparable to the nickel-base superalloys. It can be pointed out that the refractory metal disilicides such as MoSi_2 , VSi_2 , and CrSi_2 have relatively higher modulus of elasticity than that of their forms in monosilicides (Cr_3Si , V_3Si) and 5-3 silicides (Mo_5Si_3).

The yield strength, which is generally described as the stress value (yield stress or point) at which a material starts to deform plastically, of the refractory metal silicides has been also studied at both room temperature and high temperatures [1,7,23,38,40,44,52,53]. It is known that strength of a polycrystalline MoSi_2 is highly affected by silica content and grain size. Thus, grain boundary sliding, which can operate at lower stress levels than

dislocation plasticity, becomes more dominant in MoSi_2 as a deformation mechanism with increasing silica content and decreasing grain size [38]. The yield stress behavior of a large-grained, polycrystalline MoSi_2 was reported in that study as a function of temperature between 800° and 1400°C (Figure 8a). Under compressive deformation, it was found that the yield stress of MoSi_2 drastically decreased approximately from 730 to 180 MPa with increasing temperature. Besides, MoSi_2 exhibited a brittle-to-ductile transition temperature between 1300° and 1400°C in bending (flexural) deformation, since approximately 200 MPa yield stress was achieved at 1400°C for both compression and bending modes [38]. But, in another study, quite different yield stress data for the MoSi_2 was reported as a function of temperature [23]. In many intermetallic compounds, the yield strength increases with increasing temperature, and then starts to decrease drastically after a certain peak temperature, which is called as R feature. As shown in the Figure 8b, the yield strength of the MoSi_2 slightly increased up to around 1400°C , and then it drastically decreased to a very low level of yield strength (~ 100 MPa), which is not sufficient for high-temperature structural applications, and therefore, needs to be improved. It is also important to note that

Figure 8. (a) Yield stress of a polycrystalline MoSi_2 [38], and (b) R characteristic of MoSi_2 (change in yield strength) [23] as a function of temperature.

Figure 9. Yield strength of the pure MoSi₂ and MoSi₂ alloyed/doped with 1 at% Nb as a function of temperature (above 1500°C) [52].

there is a conflict between the high temperature yield strength values and trends obtained in these studies as compared in Figure 8. In the study of Pan et al. (1998), the compressive yield strength of monolithic MoSi₂ at 1200° and 1400°C were measured approximately as 370 and 80 MPa, respectively [40]. Therefore, there was a drastic decrease (76-78%) in yield strength of MoSi₂ at 1400°C, which is similar to the R characteristic of the MoSi₂. The yield strength of pure MoSi₂ and MoSi₂ alloyed with 1 at% Nb at high temperatures were studied by Sharif et al. (2005) [52]. It was determined that yield strength of pure MoSi₂ decreased approximately from 240 to 70 MPa with increasing temperature from 1600° to 1900°C. However, it is clear that yield strength of the MoSi₂ was substantially enhanced at elevated temperatures by alloying/doping with Nb as presented in Figure 9.

Another mechanical property studied for the refractory metal silicides (particularly MoSi₂) is flexural strength or bending strength, which can be described as material's ability to resist failure or deformation under bending [13,22,40,54]. Lee et al. (2005) reported that the flexural strength of the MoSi₂ was 324 MPa at room temperature [22]. It was also found

Figure 10. Flexural strength of (a) MoSi_2 [22], and (b) Mo_5Si_3 [54] as a function of temperature.

that the flexural strength of the MoSi_2 relatively increased up to around 800°C, and then significantly decreased approximately to 190 MPa with increasing temperature from 800°C to 1200°C (Figure 10a). This decrease in the high temperature flexural strength was attributed to the existence of a brittle-to-ductile transition temperature, since its brittle behavior at room temperature changed into ductile behavior without drastic fracture due to its softening above 1000°C [2,22]. In the study of Pan et al. (1998) [40], flexural strength of the MoSi_2 at room temperature was reported as 420 MPa, which is relatively higher than that the data presented by Lee et al. (2005). Also, as shown in the Figure 5, bending strength of the MoSi_2 was improved by the addition of aluminum into the matrix [13]. Although its bending strength did not change in the presence of up to 2 wt.% Al content, addition of more Al (2-10 wt.%) increased the bending strength of MoSi_2 at room temperature approximately from 200 to 350 MPa. In addition, mechanical properties and particularly flexural strength of Mo_5Si_3 as a 5-3 silicide phase have been investigated by Chen et al. (2014) [54]. The flexural strength of the Mo_5Si_3 was found to be quite stable up to 1000°C (around 470 MPa), but then it significantly decreased at higher temperatures (Figure 10b). Therefore, the flexural strength values of the Mo_5Si_3 at 1200° and 1400°C were obtained as 320 and 162 MPa. In comparison of the MoSi_2 with the Mo_5Si_3 phase in terms of their flexural strength values, it can be noted that Mo_5Si_3 exhibited higher flexural strength than the MoSi_2 at both room and elevated temperatures.

1.1.2.3 Creep properties

The time dependent strain that occurs under load at elevated temperatures is called as creep, and hereby creep resistance can be described as a material's ability to resist deformation over an extended time. Therefore, high temperature creep resistance and low creep rates are crucial for refractory metal silicides as high temperature structural materials [2,7,23]. In the study of Petrovic (1995), high temperature creep behavior of polycrystalline MoSi₂ at 1200°C has been studied as a function of stress and grain size values [38]. As presented in Figure 11, creep rate of the MoSi₂ increased with increasing applied stress, but decreased with increasing MoSi₂ grain size at high temperatures, which is not well understood. It is known that the temperature and stress values affect creep properties of the MoSi₂. While combination of grain boundary sliding and dislocation glide is dominant as a creep mechanism at high temperatures, grain boundary sliding becomes more dominant at low temperatures for MoSi₂ [23]. The creep behavior is also related with the applied stress,

Figure 11. Creep rate of the polycrystalline MoSi₂ at 1200°C as a function of the grain size [38].

Figure 12. Minimum creep rates in compression vs. stress for several refractory metal silicides at 1000°C, 1200°C, and 1400°C [7].

since dislocation slipping and grain boundary sliding mostly occur under high and low stress conditions, respectively. Furthermore, weak silica phase remaining in the grain boundaries can increase the degree of grain boundary sliding at high temperatures as well, which results in reduced creep resistance. Since the amount of the SiO_2 phase and grain size of the MoSi_2 matrix directly affect the degree of grain boundary sliding, the grain size effect on creep rate of the MoSi_2 observed in the study of Petrovic (1995) can be explained by this way [23,38]. On the other hand, minimum creep rate values of several refractory metal silicides (Cr_3Si , V_3Si , MoSi_2 , Mo_5Si_3 , Ti_5Si_3) in compression versus stress at 1000°C, 1200°C and 1400°C were reported [7,44]. Based on the given data (Figure 12), creep rate of the MoSi_2 is relatively lower than that of the Cr_3Si and V_3Si at 1200°C, which indicates that the MoSi_2 has better creep resistance than other intermetallics. At 1000°C, it is evident that the creep resistance of the Ti_5Si_3 and Mo_5Si_3 is similar to that of the superalloys [44]. Therefore, it can be concluded that Cr_3Si , MoSi_2 , and Mo_5Si_3 have very promising creep resistance values for high temperature structural applications.

1.1.3 Electrical properties of the refractory transition metal silicides

The electrical properties of the refractory transition metal silicides vary from metallic to semiconducting, and therefore, it is important to classify these silicides into two primary groups as metallic and semiconducting metal silicides [55,56]. Most of the refractory metal silicides, which are TiSi_2 , VSi_2 , V_5Si_3 , Cr_3Si , Cr_5Si_3 , NbSi_2 , Nb_3Si , MoSi_2 , Mo_3Si , TaSi_2 , HfSi_2 , and WSi_2 , are known as metallic silicides. In addition, CrSi_2 exhibits a degenerate semiconducting behavior, while some of the refractory metal silicides such as V_3Si , NbSi_2 , Mo_3Si , and TaSi_2 also have superconducting characteristics. Due to their various electrical properties and characteristics, refractory transition metal silicides have attracted a great attention for electrical applications, in addition to their high temperature structural applications. Thermoelectrics and gate electrodes, interconnects and barrier layers in micro-electronic devices are known as their major electrical applications of refractory transition metal silicides [2,17-20,57].

The refractory transition metal silicides have a great potential for high temperature thermoelectrics due to their high working temperature, low electrical resistance, high Seebeck coefficient, high thermal and chemical stability [18,20,21]. Other advantages of the transition metal silicides are their low toxicity and low cost compared to the mostly used thermoelectric materials, such as thallium-, chalcogen-, and germanium-based alloys. Due to their potential, the electrical properties of the CrSi_2 , MoSi_2 , WSi_2 , Ta_5Si_3 , and W_5Si_3 phases have been mostly investigated in the literature [17-21,58]. Since thermoelectric effect provides the direct conversion of heat into electrical energy (Seebeck effect), the figure-of-merit (ZT) is a function of electrical conductivity, Seebeck coefficient, and thermal conductivity. Therefore, high electrical conductivity, high charge carrier concentration, high density of state, metallic behavior, and poor thermal conductivity are required for achieving high thermoelectric performance with high ZT [18]. In the study of Yamada and Yamane (2011), thermoelectric properties of both α - MoSi_2 and β - MoSi_2 such as electrical resistivity (ρ), Seebeck coefficient (S), and thermoelectric power factor ($\alpha^2\sigma$) have been studied in detail [21]. Figure 13 displays the positive temperature

Figure 13. (a) Electrical resistivities, ρ , and (b) Seebeck coefficients, S of the polycrystalline α -MoSi₂ and β -MoSi₂ [21].

dependence of electrical resistivities and Seebeck coefficients for the samples, respectively. It was observed that the electrical resistivity of α -MoSi₂ increased from 0.74 to 1.1 $\text{m}\Omega \cdot \text{cm}$ with increasing temperature from 300 K to 725 K, while β -MoSi₂ exhibited electrical resistivity of 2.5-3.4 $\text{m}\Omega \cdot \text{cm}$, which is almost three times higher compared to the α -MoSi₂. These resistivities are relatively higher than the resistivities (0.06-0.43 $\text{m}\Omega \cdot \text{cm}$), which were presented for the α -MoSi₂ and β -MoSi₂ thin films at room temperature by Krontiras et al. (1987) [59]. As seen in Figure 13b, the Seebeck coefficients of the α -MoSi₂ were very low and in the range of 0.8 to 4.5 $\mu\text{V/K}$ at 330-725 K compared to the β -MoSi₂, which exhibited 60 $\mu\text{V/K}$ at 330 K, and 89 $\mu\text{V/K}$ at 725 K. These results imply that the α -MoSi₂ reveals higher electrical conductivity, but lower Seebeck coefficient. Furthermore, the temperature dependence of the electrical resistivity of the widely studied metallic silicides (MoSi₂, TaSi₂, TiSi₂, WSi₂) have been reviewed using their thin films [56]. As presented in Figure 14, electrical resistivity of the TiSi₂ linearly increased up to 0.088 $\text{m}\Omega \cdot \text{cm}$ with increasing temperature (1100 K) like a typical metallic-type of behavior. In addition, MoSi₂, WSi₂, and TaSi₂ thin films exhibited the electrical resistivities of 0.134, 0.093 and 0.119 $\text{m}\Omega \cdot \text{cm}$ at around 1100 K. Based on these results, it should be noted that WSi₂ and TiSi₂ thin films have higher electrical conductivity than the MoSi₂ and TaSi₂ thin films at

Figure 14. Temperature dependence of the electrical resistivity of MoSi₂, WSi₂, TaSi₂, and TiSi₂ refractory metal silicide thin films [56].

high temperatures, which provides a great advantage for their use in high temperature electrical applications. Furthermore, Viennois et al. (2011) reported a study with a focus on the high temperature thermoelectric properties of the Ta₅Si₃ and W₅Si₃, since they are known to be stable up to around 2000°C [17]. Figure 15 displays the electronic density of states for the Ta₅Si₃ and W₅Si₃ close to the Fermi energy level. More abrupt changes were observed in density of states of the W₅Si₃. In addition to that, they calculated the Seebeck coefficients (thermoelectric output) of the Ta₅Si₃ and W₅Si₃ from the Mott's relationship as -1.8 and -17 $\mu\text{V/K}$ at room temperature. These results all present that the W₅Si₃ is more promising candidate than Ta₅Si₃ for thermoelectric applications, although its thermoelectric power is relatively low. In addition to these refractory metal silicides, electrical properties of the Cr₃Si and Cr₅Si₃ have been also investigated by Mazzega et al. (1987) [55]. The electrical resistivities of these chromium silicides in their thin film forms as a function of temperature can be seen in Figure 16. Based on the data presented, the Cr₃Si provided a

Figure 15. The electronic density of states of Ta_5Si_3 and W_5Si_3 close to the Fermi level [17].

linear curve of electrical resistivity with increasing temperature up to 1100 K since its electrical resistance was measured as $\sim 0.1 \text{ m}\Omega\cdot\text{cm}$ at the maximum temperature. It was also determined that the Cr_5Si_3 has higher electrical resistivity ($\sim 0.16 \text{ m}\Omega\cdot\text{cm}$) than the Cr_3Si at this temperature, which clearly indicated that the Cr_3Si has higher electrical conductivity at high temperatures. As a review of these results, it is important to state that TiSi_2 , WSi_2 , and Cr_3Si have higher electrical conductivity than MoSi_2 , TaSi_2 , and Cr_5Si_3 at high temperatures ($\sim 1100 \text{ K}$).

The electrical properties of the semiconducting refractory transition metal silicides and particularly CrSi_2 phase have been also studied in the literature. It is known that the transition metal silicides are promising candidates in the field of thermoelectrics, and particularly for use in the microelectronic devices due to their wide range of energy gaps ($\sim 0.1\text{-}1.1 \text{ eV}$), ability to grow silicon dioxide as a native oxide, high thermal stability, and excellent diffusion-barrier characteristics [2,20,56]. In the study of Fedorov and Zaitsev [20], thermoelectric properties of the single crystal CrSi_2 have been investigated. The

Figure 16. Temperature dependence of the electrical resistivity of the (a) Cr_3Si , and (b) Cr_5Si_3 refractory metal silicide thin films [55].

Seebeck coefficient of the CrSi_2 single crystal along c-axis was determined approximately as in the range of 100-200 $\mu\text{V/K}$ (300-900 K). This provides a significant advantage for the use of the CrSi_2 in thermoelectric applications. In addition, its maximum thermoelectric figure-of-merit (ZT) was found to be 0.25, which was relatively low. A similar trend in the Seebeck coefficient of the CrSi_2 single crystals was also reported by Nishida (1972) [60]. On the other hand, Kobel et al. (2004) reported in their study for the development of $\text{MoSi}_2\text{-Al}_2\text{O}_3$ electroconductive ceramic composites that MoSi_2 exhibited a very high electrical conductivity ($\sim 6000 \text{ S/cm}$) at around 750°C [61]. However, it is important to point out that surprisingly studies are highly limited focusing on the electrical properties of the refractory transition metal silicides and their development for use in advanced high-temperature electrical applications (e.g. sensing, interconnects) [61,62].

1.1.4 Oxidation behavior of the refractory transition metal silicides

The oxidation resistance is one of the most important properties that need to be fulfilled by the refractory transition metal silicides for their particular use at high temperatures for extended operation hours. The oxidation resistance of the refractory metal silicides are mainly related with the formation of silica (SiO_2) layer on the surface, which is known to be highly protective due to its high thermodynamic stability and low diffusivity for molecular oxygen indicating low parabolic rate constants for its growth [37]. In order to understand the oxidation resistance mechanism of such metal silicides, MoSi_2 can be discussed in detail, since its low- and high-temperature oxidation behavior have been extensively studied [1,2,7,11,14,15,23,44,37]. Its oxidation behavior is generally studied in three temperature regimes as low temperature ($400^\circ\text{-}600^\circ\text{C}$), medium temperature ($600^\circ\text{-}1000^\circ\text{C}$), and high temperature (above 1000°C) regions. At low temperature region ($400^\circ\text{-}600^\circ\text{C}$), an accelerated simultaneous oxidation occurs in MoSi_2 structure by the following reaction (1), which results in a dramatic structural disintegration into a powdery product [2,11,37]. This oxidation phenomenon is referred as pest effect or pest oxidation, which is directly related with the formation of crystalline MoO_3 and amorphous SiO_2 clusters inhibiting formation of a dense protective SiO_2 layer and also substantial volume expansion

(molar volume increased by 250%). The disintegration of the MoSi_2 is also affected by the growth of the MoO_3 crystals from the grain boundary resulting in high stress, and thus, crack propagation [2]. Due to high volatility of the MoO_3 phase, loose SiO_2 layer remains on the surface, while oxygen continues to diffuse through these weak grain boundaries and finally causes the complete structural disintegration [23]. The oxidation behavior of porous and fully dense MoSi_2 at 500°C in air atmosphere has been studied by Kurokawa et al. (1999) [63]. The mass gain as a main indication of the oxidation was found to be highly low for the fully dense MoSi_2 , while the porous one showed a high mass gain and accelerated oxidation behavior, which was caused by high oxidation rates after initial oxidation stage (called as an induction time), as shown in Figure 17a. Due to this rapid oxidation, a substantial increase in the mass gain, cracking and structural disintegration of

Figure 17. (a) Oxidation behavior of fully dense and porous MoSi₂ at 500°C in air, and (b) SEM micrograph of the surface of porous MoSi₂ oxidized at 500°C for 360 ks (100 hours) [63].

the MoSi₂ (pest effect) were observed. In addition, mostly needle-like MoO₃ particles were formed on the surface, which then resulted in cracking and pesting at 500°C after 360 ks (100 hours) as seen in Figure 17b [63]. At the medium temperature (600°-1000°C) region, vapor pressure of the MoO₃ phase initially increased with increasing temperature, and then it started to evaporate at 500°-600°C [11]. Afterwards, formation and evaporation of the MoO₃ were balanced at around 770°C, which decelerated the volumetric expansion and internal stress level. Therefore, no disintegration and pest oxidation were observed for the MoSi₂ at this temperature region.

At higher temperatures above 1000°C, MoSi₂ has excellent oxidation resistance (up to 1600°C) due to the formation of a highly dense and protective SiO₂ layer on the surface [11,37]. Since the MoO₃ volatilizes rapidly with increasing temperature, a continuous SiO₂ layer could be formed as a protective barrier on the surface of the MoSi₂. In addition, further formation of the volatile MoO₃ phase could be prevented by low oxygen partial pressure at the interface between SiO₂ layer and MoSi₂, which improves the oxidation

resistance at high temperatures. Therefore, at this temperature region, there is only a formation of the Mo_5Si_3 and SiO_2 on the surface as presented in the reaction (2) [2,11]. The

oxidation resistance of the MoSi_2 was compared with several high temperature materials such as Nb-, Ti, and Ta-based intermetallic compounds and single crystal nickel superalloy (PWA1484) [1]. Based on the data presented in Figure 18, lowest weight gain and highest oxidation resistance was achieved by the MoSi_2 , particularly at the temperatures above 1100°C after 24 hours of exposure to air. Also, at the temperatures above 1700°C , it was presented that the oxidation resistance of the MoSi_2 decreased owing to the drastic decrease in viscosity of the SiO_2 phase and increase in the defect concentration [37]. Sharif (2010) studied the high temperature oxidation behavior of the MoSi_2 to determine the changes in the oxidation mechanism of the MoSi_2 above 1400°C [15]. As shown in Figure 19, the weight gain highly increased with increasing temperature from 1400°C to 1700°C after exposed to air up to 100 h. This result hereby implied that there is a change in the oxidation rate of MoSi_2 with increasing temperature and time. Although formation of the Mo_5Si_3 was

Figure 18. Comparison of the isothermal oxidation behavior of MoSi_2 with several intermetallic compounds and nickel superalloy (PWA 1484) [1].

Figure 19. The specific weight gain at high temperatures (1400°-1700°C) during isothermal oxidation of the MoSi₂ samples [15].

not observed at 1400°C and 1550°C, silica layer crystallized into β -cristobalite form at 1700°C, which caused a substantially high oxygen diffusion through the layer, and hereby reduced oxidation resistance at the temperatures approaching the melting point of the silica phase [15]. As a review of the high temperature oxidation resistance of the refractory transition metal silicides, it should be noted that the MoSi₂ and WSi₂ have significantly higher oxidation resistance than the other refractory metal silicides (TaSi₂, TiSi₂, Mo₅Si₃, W₅Si₃ etc.) as listed in the Table 3 [1]. It is known that volatility of the MoO₃ phase has an important role in the oxidation behavior of the MoSi₂, and WSi₂ exhibits a quite similar oxidation behavior to the MoSi₂ [7,37]. In addition, Ti₅Si₃ is known to have a reasonable oxidation resistance at high temperatures, compared to the other Mo-, Nb-, W-, Ta-based 5-3 metal silicides, since disintegration occurs within Mo₅Si₃ and Nb₅Si₃ at high temperatures [7,44]. Also, the Cr₃Si exhibits a good high temperature oxidation resistance, compared to the other monosilicides, while the least oxidation resistant silicides are W₅Si₃ and Ta₅Si₃.

Table 3. High temperature oxidation resistance of the several refractory transition metal silicides with high melting points based on the oxidation-induced mass changes [1].

Metal Silicide	Oxidation temperature (°C)	Oxidation time (h)	Mass change (mg/cm ²)
MoSi ₂	1200	4	+ 0.3
	1500	4	+1.3
WSi ₂	1200	4	- 17.0
	1500	4	- 23.0
NbSi ₂	1200	6	+ 40.0
TaSi ₂	1200	4	+ 60.0
TiSi ₂	1200	4	+ 22.0
Mo ₅ Si ₃	1500	4	- 67.0
W ₅ Si ₃	1500	4	- 205.0
Ta ₅ Si ₃	1500	1	+ 125.0
Ti ₅ Si ₃	1500	2	+ 32.0

1.2 Refractory Transition Metal Silicide Composites

Although the refractory transition metal silicides have a great potential for high temperature structural and electrical applications, they have some major disadvantages that restrict their use in some applications. These disadvantages could be summarized as (1) low fracture toughness below the ductile-brittle transition temperature (~1000°C), (2) low strength above the ductile-brittle transition temperature, (3) low creep resistance at high temperatures (above 1200°C), and (4) poor oxidation behavior (poor oxidation resistance) at around 600°C [1-4,12,54,64-66]. Therefore, composite approach has been extensively utilized to overcome such disadvantages of the refractory transition metal silicides, and hence, to make them capable to operate as high temperature structural materials more reliably and precisely. Based on the studies performed on the literature (mostly on the

MoSi₂-based composites), oxide and non-oxide ceramic materials, such as SiC, Si₃N₄, ZrO₂, Al₂O₃, AlN, TiC, and TiB₂, are mostly used as reinforcement materials to develop refractory transition metal silicide-based composites due to their high melting point, thermodynamic compatibility with refractory metal silicides, high thermal stability, good mechanical properties, and high oxidation and creep properties.

1.2.1 Mechanical properties of the refractory transition metal silicide composites

The mechanical behavior and properties of the refractory transition metal silicide composites have been examined in the literature due to their high potential for use in high temperature applications. The room temperature fracture toughness and creep properties of different composite compositions have been extensively reported over the years.

1.2.1.1 Fracture toughness

The fracture toughness of the MoSi₂-based composites has been studied in detail, since it is essential to improve the fracture toughness of the MoSi₂. Therefore, SiC, Si₃N₄, and TiC are mostly used as non-oxide ceramic reinforcements. Newman et al. (1999) performed a study with a focus on the development of mechanical properties of the MoSi₂ by the addition of the SiC and Al₂O₃ phases [4]. The room temperature fracture toughness of the MoSi₂-Al₂O₃ composites (~3.1-3.2 MPa·m^{1/2}) almost did not change compared to the pure MoSi₂, whereas MoSi₂-SiC composites exhibited relatively high fracture toughness depending on the volume fraction of the SiC. The fracture toughness of the MoSi₂ was increased from 3.2 to 5.8 MPa·m^{1/2} by utilizing the MoSi₂-SiC composite with 16 vol% SiC content, since it provided a crack deflection toughening. In addition, it is important to point out that less grain growth was observed in the MoSi₂-Al₂O₃ composites owing to the positive effect of the Al₂O₃ addition on the grain growth kinetics, which could be an additional advantage for long operation hours at high temperatures [4]. In the study of Pan et al. (1998), the mechanical properties of the MoSi₂-SiC composites prepared by hot press sintering (20 vol% α -SiC) and in-situ reaction sintering (24.5 vol% β -SiC) have been examined in detail [40]. As presented in Figure 20, room temperature fracture toughness

Figure 20. The room temperature fracture toughness (K_{IC}) and flexural strength (σ_{FS}) of the pure MoSi₂, hot pressed MoSi₂-SiC and in-situ MoSi₂-SiC composites [40].

values of the hot pressed MoSi₂-SiC and in-situ MoSi₂-SiC composites were measured as 5.95 and 4.94 MPa·m^{1/2}, respectively. These values are relatively higher than the fracture toughness of the pure MoSi₂ (~ 4.3 MPa·m^{1/2}), and thus, it could be clearly stated that the SiC-reinforced MoSi₂ composite has enhanced fracture toughness at room temperature. The result obtained for the hot pressed MoSi₂-SiC composite were found to be very similar to the data presented by Newman et al. (1999) [4,40].

Sun and Pan (2002) also presented that the room temperature fracture toughness values of the MoSi₂ composites reinforced with 20 vol% TiC- and SiC-whiskers were 5.2 and 5.5 MPa·m^{1/2}, respectively [67]. Therefore, these results demonstrated that fracture toughness of the MoSi₂ (3.2 MPa·m^{1/2}) was highly increased by reinforcing with SiC and TiC particles due to reduced crack propagation within the MoSi₂ structure with whiskers.

Figure 21. Effect of the TiC particle content on the fracture toughness (K_{IC}) and flexural strength (σ_f) of the MoSi₂-TiC composites [68].

These values are quite comparable to the data obtained for the MoSi₂-SiC composites in other studies [4,40]. In contrast, relatively lower room temperature fracture toughness values (4.0-4.4 MPa·m^{1/2}) were also presented for the MoSi₂ composites reinforced by 20 vol% SiC particles (e.g. whiskers) [38]. In the study of Sun and Pan (2002), effect of the TiC particle reinforcement on the room temperature fracture toughness of the MoSi₂-TiC composites has been investigated [68]. Figure 21 shows the change in fracture toughness as a function of the TiC volume fraction. The fracture toughness of the MoSi₂-TiC composites increased up to 4.9 MPa·m^{1/2} with the addition of 20 vol% TiC, which is much higher than the fracture toughness of the monolithic MoSi₂ (3.2 MPa·m^{1/2}). It was also identified that the fracture toughness slightly decreased when the TiC content was above 20 vol%, due to brittle fracture. In another study, room temperature fracture toughness of the MoSi₂ was increased from 3.2 to 5.2 MPa·m^{1/2} by reinforcing with 20 vol% TiC-whiskers [69]. Apart from the SiC and TiC, the Si₃N₄ was also used as a ceramic reinforcement. Wang et al. (2004) studied the mechanical properties of the MoSi₂-Si₃N₄ composites by using 20 vol% of Si₃N₄ rod-like crystals [70]. The room temperature fracture toughness of the MoSi₂-

Si_3N_4 composite was measured as $5.1 \text{ MPa}\cdot\text{m}^{1/2}$, which is relatively higher than that of the monolithic MoSi_2 ($3.6 \text{ MPa}\cdot\text{m}^{1/2}$). In the study of Petrovic et al. (1997), room temperature indentation fracture toughness of the MoSi_2 - Si_3N_4 composites was reported [10]. Figure 22 presents the changes in the fracture toughness as a function of the MoSi_2 volume percentage and particle size of the MoSi_2 . The MoSi_2 particle size was found to have a significant effect on fracture toughness, since improvements were achieved using MoSi_2 particles with $10 \mu\text{m}$ size. The maximum room temperature fracture toughness value was obtained as $8.3 \text{ MPa}\cdot\text{m}^{1/2}$ at the composition of (40-60) vol% MoSi_2 - Si_3N_4 having $10 \mu\text{m}$ sized MoSi_2 particles, which was higher than the MoSi_2 - Si_3N_4 composite with $3 \mu\text{m}$ sized MoSi_2 particles ($5.7 \text{ MPa}\cdot\text{m}^{1/2}$) and monolithic MoSi_2 ($3.0 \text{ MPa}\cdot\text{m}^{1/2}$). The improved fracture toughness was explained by the effect of thermal expansion coefficient mismatch between MoSi_2 and Si_3N_4 phases, providing internal stress-toughening mechanism [10,71].

Figure 22. Changes in room temperature fracture toughness of the MoSi_2 - Si_3N_4 composites as a function of the volume fraction and particle size of the MoSi_2 phase (MgO was used as a densification aid for Si_3N_4) [10].

As alternatives of the non-oxide ceramic reinforcements, Al_2O_3 and ZrO_2 oxide ceramics have been also used for the development of refractory transition metal silicide-oxide composites. Wang et al. (2014) studied the mechanical properties of the MoSi_2 -5 vol% Al_2O_3 composites at room temperature as a function of the sintering temperature [72]. The room temperature fracture toughness of the MoSi_2 - Al_2O_3 composites increased from 3.69 to 4.53 $\text{MPa}\cdot\text{m}^{1/2}$ with increasing sintering temperature from 1300°C to 1400°C, but then, decreased to 3.63 $\text{MPa}\cdot\text{m}^{1/2}$ at 1600°C. This result could be directly interrelated with a drastic increase in the MoSi_2 grain size approximately from 5 to 15 μm with increasing sintering temperature from 1400°C to 1600°C, which resulted in a decreased toughness. Therefore, volume percentage of the Al_2O_3 phase should be relatively higher for retarding the grain growth, and hence, enhancing the fracture toughness at the same time. In addition, room temperature fracture toughness of the MoSi_2 - Al_2O_3 composites has been studied [62]. The maximum fracture toughness was measured at around 4.8 $\text{MPa}\cdot\text{m}^{1/2}$ for (35-65) wt% MoSi_2 - Al_2O_3 , as presented in Figure 23. The room temperature fracture toughness of the Mo_5Si_3 -20 wt.% Al_2O_3 composite was reported as 6.53 $\text{MPa}\cdot\text{m}^{1/2}$ by Chen et al. (2014) [54], which is relatively higher than that of the MoSi_2 - Al_2O_3 composites. In addition, ZrO_2 has been also utilized as an oxide reinforcement. In the study of Yi and Li (1999), the mechanical properties of the MoSi_2 - ZrO_2 composites were reported by using both unstabilized (monoclinic) and yttria partially stabilized- ZrO_2 (tetragonal) particles [64]. Also, both commercial and mechanically alloyed MoSi_2 powders were used in this study. The maximum room temperature fracture toughness values were obtained as 6.66 and 6.75 $\text{MPa}\cdot\text{m}^{1/2}$ for the commercial MoSi_2 -20 vol% unstabilized- ZrO_2 and mechanically alloyed MoSi_2 -20 vol% unstabilized- ZrO_2 composites, respectively. The MoSi_2 -yttria partially stabilized- ZrO_2 composites all exhibited lower fracture toughness values (2.73-3.44 $\text{MPa}\cdot\text{m}^{1/2}$). These results clearly indicated that the unstabilized ZrO_2 is more effective as a reinforcement material owing to the existence of large number of microcracks initiating the microcracking as a dominant toughening mechanism [64]. Furthermore, Dogan and Hawk (1997) studied the mechanical properties of the MoSi_2 - ZrO_2 composites all having 20 vol% ZrO_2 content [73]. They also conducted their study by using the unstabilized, partially

Figure 23. Effect of the MoSi₂ weight percentage on the room temperature mechanical properties of the MoSi₂-Al₂O₃ composites [62].

stabilized, and fully stabilized ZrO₂ particles. Based on the data presented, the MoSi₂-20 vol% unstabilized ZrO₂ composite revealed higher room temperature fracture toughness with 6.7 MPa·m^{1/2} compared to the other composites (4.0-4.1 MPa·m^{1/2}). This result was found to be related to the large number of microcracks existing in the composite structure, which predominated the microcracking toughening mechanism. In another study, the fracture toughness of the MoSi₂-20 vol% ZrO₂ composite was measured as 7.8 MPa·m^{1/2} [38]. Ma et al. (2001) also reported a study with a focus on the effect of unstabilized ZrO₂, yttria partially stabilized ZrO₂, and SiC reinforcements on the mechanical properties of the MoSi₂-based composites [74]. Figure 24 shows the room temperature fracture toughness of the monolithic MoSi₂ and different MoSi₂-matrix composites. The highest fracture toughness values were found as 6.1 and 7.6 MPa·m^{1/2} for the MoSi₂-20 vol% unstabilized-ZrO₂ and MoSi₂-10 vol% SiC-10 vol% unstabilized-ZrO₂ composites, respectively. These results also demonstrated that the unstabilized-ZrO₂ and SiC are highly effective ceramic reinforcements, particularly compared to the yttria partially stabilized ZrO₂. It was additionally determined that the MoSi₂-(SiC+ZrO₂) composite is another highly promising candidate for enhancing the mechanical properties.

Figure 24. Room temperature fracture toughness of the monolithic MoSi₂ and different MoSi₂-matrix composites reinforced with unstabilized ZrO₂ (0YPSZ), yttria partially stabilized ZrO₂ (2.5YPSZ), and SiC (reinforcement content was 20 vol% for all) [74].

Apart from the MoSi₂-based composites, there are very limited number of studies, which conducted on the WSi₂- and NbSi₂-based composites in the literature. Muraoka et al. (1996) reported that room temperature fracture toughness values of the (40-60) mol% and (20-80) mol% WSi₂-yttria partially stabilized ZrO₂ composites were 7.7 and 12.4 MPa·m^{1/2}, respectively [75]. These values were found to be relatively higher than that of the MoSi₂-based composites. In the study of Ko et al. (2010), room temperature fracture toughness of the NbSi₂-Si₃N₄ composite was reported as 3.5 MPa·m^{1/2} [76]. Furthermore, fracture toughness of the NbSi₂-SiC composite was measured at room temperature as ~5.3 MPa·m^{1/2} [77].

1.2.1.2 Creep properties

The high temperature creep resistance of the refractory transition metal silicide composites has been investigated in the literature to determine the influence of different oxide (Al₂O₃, ZrO₂ etc.) and non-oxide (SiC, Si₃N₄ etc.) ceramic reinforcements, since it is known that the creep resistance of the refractory metal silicides need to be improved for

their reliable use in high temperature applications. Petrovic (1995) reviewed the high temperature creep behavior of the MoSi₂-SiC composites [38]. As presented in the Figure 25a, the high temperature (1200°C) creep resistance at different stress levels was significantly improved by addition of 40 vol% of the SiC particles into the MoSi₂ structure. On the other hand, the creep rates relatively increased, when volume percentages of the SiC were between 5 and 20 vol%. This was directly related to the reduced matrix grain size promoting the operation grain boundary sliding as a creep mechanism. In the study of Vasudevan and Petrovic (1992), the creep rates of the monolithic MoSi₂ and the MoSi₂-20 vol% SiC_w were compared as shown in Figure 25b [1]. It is apparent that the creep rates were highly decreased (creep strain increased) at 1200°C and 78 MPa stress level by using SiC whiskers as a reinforcement, while a rapid deformation was observed for the monolithic MoSi₂. The creep resistance of the MoSi₂-SiC composite was also found quite comparable to that of the Si₃N₄-SiC composite, which implied that the creep resistance of the MoSi₂ can be substantially improved by developing MoSi₂-SiC composites. In addition, Si₃N₄ has been also used as a particulate reinforcement for improving the high temperature creep resistance, since it is known that the pest problems existing at around 600°C could be relatively lowered by the Si₃N₄ reinforcement. Sadananda et al. (1999) reported a research

Figure 25. (a) Creep rate of the MoSi₂-SiC_w composites at 1200°C with different volume fractions of SiC phase [38], and (b) comparison of the creep deformation of the monolithic MoSi₂ and MoSi₂-20 vol% SiC_w at 1200°C and 78 MPa stress level [1].

Figure 26. (a) Effect of the Si_3N_4 volume fraction and stress on creep rate of the MoSi_2 - Si_3N_4 composites [78], and (b) improvements in the high temperature creep resistance of MoSi_2 -non-oxide composites over the years [3].

study with a focus on creep properties of the high temperature refractory metal silicides and their composites [78]. Figure 26a presents the effect of the Si_3N_4 volume fraction on the creep rate of the MoSi_2 . The creep rates for the MoSi_2 -50 vol% Si_3N_4 composites at 1200°C were very low compared to the MoSi_2 . The changes in the creep rate of the MoSi_2 and MoSi_2 -non-oxide composites (MoSi_2 - SiC and MoSi_2 - Si_3N_4) as a function of years were presented as a review, which clearly displayed improvements in the high temperature creep resistance [3]. Based on the plot presented in the Figure 26b, it can be noted that the creep rates of the MoSi_2 significantly decreased over years with the development of the refractory transition metal silicide-non-oxide composites, mostly with the addition of the SiC and Si_3N_4 particles. On the other hand, it is surprising that very limited studies were found, which investigated the high temperature creep resistance of the refractory metal silicide-oxide ceramic composites (MoSi_2 - Al_2O_3 , MoSi_2 - ZrO_2 etc.) in the literature. In the study of Dumont et al. (1999), high temperature creep behavior of the MoSi_2 - Al_2O_3 composites were reported [79]. Three MoSi_2 -based composites were prepared with 21.0, 56.1, and 68.1 vol% of the Al_2O_3 content. As presented in the Figure 27, creep rates at 1200°C decreased compared to the MoSi_2 by increasing the volume percentage of the Al_2O_3 . This result demonstrated that the Al_2O_3 can be efficiently used as an oxide ceramic reinforcement to improve the high temperature creep resistance of the MoSi_2 .

Figure 27. Creep rate of the C1 (MoSi₂-20 vol% Al₂O₃), C2 (MoSi₂-56.1 vol% Al₂O₃), and C3 (MoSi₂-68.1 vol% Al₂O₃) at 1200°C as a function of different stress levels, and their comparison with the pure MoSi₂ and Al₂O₃ [79].

1.2.2 Electrical and thermal properties of the refractory transition metal silicide composites

For high-temperature electrical applications, it is known that high operating temperature, electrical conductivity at high temperatures, high oxidation/corrosion resistance, close thermal expansion coefficients of different components (matrix and reinforcement), and good mechanical properties are essential for the composite systems [9,61,80]. Therefore, it is known that there is a high potential for the refractory transition metal silicide composites in such applications subjected to high temperatures due to their capability of fulfilling all the required properties and the compatibility of refractory metal silicides with many ceramic reinforcements. But, surprisingly, there are very limited studies conducted on the investigation of the electrical properties of the refractory transition metal silicides and the development of electroconductive ceramic composites in the literature.

Kobel et al. (2004) reported a study with a focus on development of the MoSi₂-Al₂O₃ electroconductive ceramic composites for high temperature applications [61]. They fabricated various MoSi₂-Al₂O₃ composites with 16-40 vol% MoSi₂ content, and measured

their high temperature electrical conductivity and coefficient of thermal expansion in their study. Figure 28a presents the electrical conductivities of the pure MoSi_2 , (40-60) vol% $\text{MoSi}_2\text{-Al}_2\text{O}_3$, and (25-75) vol% $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites as a function of temperature (50°C to 750°C). It was found that electrical conductivity of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites increased with increasing MoSi_2 volume percentage; while decreased with increasing temperature. It is important to point out that they have a high potential for high temperature electrical applications due to their high electrical conductivity values even at elevated temperatures. Another important criterion is the close thermal expansion coefficients of the different phases in the composite systems both for their processing and properties of the composite materials. As shown in Figure 28b, the thermal expansion coefficient (CTE) of the MoSi_2 is very close to that of the Al_2O_3 , which is essential to minimize thermal stresses, effect of interfacial cracks on mechanical properties, and also to improve the thermal shock resistance [61,1]. This is one of the major advantages (high temperature electrical conductivity, high operating temperature, chemical and thermal stability) of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites for high temperature electrical applications. In another study, thermal expansion coefficients (CTE) of several high temperature materials were summarized (Figure 29) [1]. Based on the data presented, it is apparent that CTE of the MoSi_2 ($\sim 8.2 \times 10^{-6} \text{K}^{-1}$) has a close match with that of the Al_2O_3 ($\sim 8.0 \times 10^{-6} \text{K}^{-1}$), particularly compared

Figure 28. (a) Electrical conductivity of pure MoSi_2 and $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites as a function of temperature, and (b) Coefficient of thermal expansion (CTE) for pure MoSi_2 , pure Al_2O_3 , and $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite [61].

Figure 29. Coefficients of thermal expansion (CTE) for high temperature materials [1].

to the other reinforcement materials such as SiC ($\sim 5.0 \times 10^{-6} \text{K}^{-1}$). Therefore, the MoSi₂-Al₂O₃ composite system has a higher potential compared to the other composite systems such as MoSi₂-SiC and MoSi₂-Si₃N₄ for high temperature electrical applications. In addition to the MoSi₂-Al₂O₃ composite system, there are also very limited studies on the electrical properties of the MoSi₂-SiC and MoSi₂-Si₃N₄, because the main focus in these studies was high temperature structural applications. In the study of Guo et al. (2007), high temperature electrical conductivity of the Si₃N₄-MoSi₂ composites (5 vol% Lu₂O₃ as a sintering additive) was reported with a focus on their use in high temperature electrical applications such as heating elements of ceramic glow plugs for diesel engines [9]. As shown in Figure 30, the MoSi₂-Si₃N₄ composites with 32, 40, and 60 vol% MoSi₂ content all exhibited high electrical conductivity at high temperatures up to 1250°C. But it is important to point out that their high temperature electrical conductivities are relatively lower than that of the MoSi₂-Al₂O₃ composites. As a review of the electrical and thermal properties of the refractory transition metal silicide composites, it can be concluded that the refractory metal silicide-oxide ceramic composites are very promising candidates for high temperature applications.

Figure 30. Electrical conductivity of the $\text{Si}_3\text{N}_4\text{-MoSi}_2$ composites with 32 vol% (SML-32), 40 vol% (SML-40), and 60 vol% (SML-60) MoSi_2 as a function of temperature [9].

1.2.3 Oxidation behavior of the refractory transition metal silicide composites

The improved oxidation resistance at elevated temperatures is very important for refractory transition metal silicide composites to be capable of functioning at high temperatures in highly oxidizing and corrosive environments for extended operation hours as structural and electrical materials. It is known that most of the refractory transition metal silicides exhibit high oxidation resistance, and particle reinforcement is the most commonly applied route to alter their mechanical and thermal properties. However, after particle reinforcement, oxidation resistance of these transition metal silicides must not be degraded [11]. Therefore, the oxidation behavior of the refractory metal silicide composites has been also investigated in the literature.

Medri and Bellosi (2004) conducted a study on degradation of the $\text{Si}_3\text{N}_4\text{-35 vol% MoSi}_2$ composite after long-term (100 h) oxidation in air atmosphere up to 1500°C [81]. It was determined that the oxidation-induced weight gain was less than 1.0 mg/cm^2 at the

temperatures up to 1300°C. Afterwards, there was a drastic increase from ~1.0 to ~5.2 mg/cm² with increasing temperature from 1300°C to 1500°C (Figure 31a). This result indicated that the oxidation rate for the Si₃N₄-MoSi₂ composites increased at temperatures above 1400°C, whereas they were highly resistant to oxidation up to 1400°C. In another study, oxidation behavior of the Si₃N₄ and Si₃N₄-6 vol% MoSi₂ at 1500°C was examined for a very long period of time (10000 h) [82]. Although they displayed a same oxidation behavior up to 1600 h, a slight difference between their oxidation rates was observed after that time period (Figure 31b). Therefore, it should be pointed out that the Si₃N₄-MoSi₂ composites may have relatively higher oxidation resistance than the Si₃N₄ for longer operation hours at 1500°C. In addition to that, SiC, TiB₂, ZrB₂, and HfB₂ have been used as reinforcement materials in the literature for the MoSi₂ structure. Vasudevan and Petrovic (1992) reported a review study on the cyclic oxidation behavior of several intermetallic compounds, superalloys, and refractory transition metal silicide composites [1]. It is evident that oxidation resistance of the MoSi₂-SiC composite is relatively higher than that of the pure MoSi₂ at 1200°C up to 144 h (Figure 32a). Additionally, oxidation resistance of the MoSi₂ significantly reduced after utilizing the TiB₂ as a reinforcement. The weight gain level for the MoSi₂-SiC composite at 1200°C after 100 h exposure to air was reported as less than 0.1 mg/cm². The weight gain for the MoSi₂-15 vol% SiC composite at 1600°C

Figure 31. Oxidation behavior of the (a) Si₃N₄-35 vol% MoSi₂ composite after 100 hours as a function of temperature [81], and (b) Si₃N₄ and Si₃N₄-6 vol% MoSi₂ composite at 1500°C as a function of time [82].

Figure 32. (a) Cyclic oxidation behavior of the pure MoSi₂, MoSi₂-based composites, and superalloys at 1200°C (24 hours) [1], and (b) Oxidation behavior of the pure MoSi₂ and MoSi₂-based composites as a function of temperature up to 1500°C (24 hours) [84].

after 100 h was also reported as 0.44 mg/cm² in another study [83]. Furthermore, Lee et al. (1991) studied the high temperature oxidation behavior of the pure MoSi₂ and MoSi₂-based composites reinforced with TiB₂, ZrB₂, HfB₂, and SiC up to 1500°C for 24 h [84]. The lowest weight gains were achieved by pure MoSi₂ and MoSi₂-SiC composite as presented in Figure 32b. MoSi₂-HfB₂ composite also exhibited comparable oxidation resistance up to 1400°C, but the oxidation rates were found to be very high for the MoSi₂-TiB₂ and MoSi₂-ZrB₂ composites above 1200°C and 800°C, respectively. These results clearly implied that the MoSi₂-SiC and MoSi₂-Si₃N₄ composites have higher oxidation resistance than the other MoSi₂-non-oxide composites at elevated temperatures.

The oxidation behavior of the refractory metal silicide-oxide ceramic composites has been also studied, but there are very limited studies in the literature [54,83,85]. Fei et al. (2010) reported a study on the oxidation behavior of the pure MoSi₂ and MoSi₂-Al₂O₃ composite coatings at 1500°C as a function of oxidation time up to 30 h [85]. As presented in Figure 33, oxidation behavior of the pure MoSi₂ and MoSi₂-10 vol% Al₂O₃ composite coatings was quite similar. However, the MoSi₂-30 vol% Al₂O₃ composite revealed relatively low oxidation resistance at 1500°C. The most detailed study on high temperature oxidation behavior of the particle-reinforced MoSi₂ composites was reported by Lohfeld et

Figure 33. Mass changes of the pure MoSi₂ (MA0), MoSi₂-10 vol.% Al₂O₃ (MA1), and MoSi₂-30 vol.% Al₂O₃ composite coatings at 1500°C as a function of time [85].

al. (2005) [83]. In this study, the Al₂O₃, Y₂O₃, ZrO₂, and HfO₂ were used as oxide ceramic reinforcements, while the TiB₂, ZrB₂, and HfB₂ were selected as non-oxide ceramic reinforcements with a fixed amount of 15 vol%. Table 4 presents the weight changes of the different MoSi₂-based composites after 100 h of exposure to air at 1600°C. Based on these results, the MoSi₂-SiC is the most oxidation resistant composite material in comparison to others. The MoSi₂-HfO₂, MoSi₂-Y₂O₃, and MoSi₂-TiB₂ also presented relatively good oxidation behavior at 1600°C. Although the MoSi₂-Al₂O₃ composite displayed poor oxidation resistance at this temperature, there are only a few studies in the literature for comparison. Therefore, further studies are essential for the determination of high temperature oxidation behavior of different refractory transition metal silicide-oxide composites. As a review of these research studies on the refractory transition metal silicide

Table 4. Weight changes for the pure MoSi₂ and several MoSi₂-based composites after 100 h of exposure to air at 1600°C [83].

Composite System	Weight Change (mg/cm ²)
MoSi ₂ / Al ₂ O ₃	+ 5.97
MoSi ₂ / ZrO ₂	+ 1.80
MoSi ₂ / HfO ₂	+ 1.00
MoSi ₂ / Y ₂ O ₃	+ 1.23
MoSi ₂ / SiC	+ 0.44
MoSi ₂ / TiB ₂	+ 1.33
MoSi ₂ / ZrB ₂	+ 3.98
MoSi ₂ / HfB ₂	+ 2.62
pure MoSi ₂	+ 0.11

composites, significant improvements have been achieved in both mechanical and electrical properties, particularly by developing the refractory transition metal silicide-oxide composites such as the MoSi₂-Al₂O₃ and MoSi₂-ZrO₂. The refractory metal silicide-oxide composites provided high operating temperature, high electrical conductivity at elevated temperatures, high oxidation/corrosion resistance, good mechanical properties, and high thermal stability. Furthermore, close match between the coefficients of thermal expansion of the refractory metal silicides and oxide ceramic reinforcements displayed an important advantage for minimizing thermal stresses and effect of interfacial cracks on mechanical properties, as well as, for improving the thermal shock resistance. The thermodynamic compatibility of the refractory transition metal silicides with many of the oxide ceramic reinforcements was also determined to be very beneficial for achieving high chemical stability. Additionally, the grain growth can be potentially minimized by use of the oxide ceramic reinforcements as grain growth inhibitors, which may improve the lifetime of

materials and performance under real operation for longer service hours. The electrical conductivity can be also tuned by adjusting the metal silicide/oxide content. Therefore, the refractory transition metal silicide-oxide electroconductive ceramic composites are very promising candidates for high-temperature electrical applications, such as interconnects, and high temperature and harsh environment sensors (e.g. thermocouple, thermistor). However, it should be pointed out that there are very limited studies conducted on their high-temperature electrical properties, related sensing applications and oxidation behavior/kinetics, and there are no studies on their thermal (phase) stability, sintering/phase transformations and grain growth kinetics.

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CHAPTER 2: PROCESSING AND PROPERTIES OF MoSi₂ - AND WSi₂ - OXIDE COMPOSITES

2.1 Introduction

Extreme harsh-environments are emphasized as one of the major challenges in many industries such as coal gasification, power generation, oil refineries and steel/glass manufacturing. These harsh conditions are due to the very high operating temperatures (1200°-1650°C), oxidizing/corrosive environments and high pressures [1,2]. Technologies are sought to monitor the process conditions such as temperature and pressure for these processes, and also the structural health and degradation of the ceramic refractories used in the high-temperature reactors. This is crucial for achieving better process control, improved efficiency, reduced environmental impact and increased lifetime of the process units. However, materials commonly used for real-time sensing in harsh-environments, like noble metals (Pt, Rh, Ir etc.) and their alloys, suffer from serious structural and functional issues such as selective oxidation via formation of volatile oxides, detrimental microstructural/compositional changes and mechanical degradation [1-4]. Therefore, there is a great demand for advanced sensing materials capable of operating under such extreme conditions reliably and precisely for long-term without high-temperature degradations [2,4,5].

Sensing applications in high-temperature and harsh-environments require advanced materials that can fulfill the required combination of physical, thermal, electrical and mechanical properties, such as a high melting point, good oxidation and corrosion resistance, high-temperature thermal/chemical stability and electrical conductivity at elevated temperatures [4,6,7]. Therefore, refractory transition metal silicides (MoSi₂, WSi₂, TaSi₂ etc.), which have been mostly studied for high-temperature structural applications along with silicon-based ceramics (SiC, Si₃N₄), offer great advantages for such sensing applications due to their high melting temperatures (>1900°C), very low oxidation and corrosion rates at high temperatures, high-temperature stability, good mechanical properties

and high-temperature electrical conductivity [8-10]. They are intermetallic compounds of transition metals in group IV, V, VI and silicon, so the bonding in these metal silicides is more metallic in nature [11,12]. Among all refractory transition metal silicides, molybdenum disilicide (MoSi_2) and tungsten disilicide (WSi_2) are the most promising candidate materials for advanced sensing applications, since they are more thermally/chemically stable and oxidation resistant at the temperatures between 1000°C and 1600°C under harsh environments. The weight gain level for the MoSi_2 and WSi_2 at around 1600°C in air was approximately measured as 0.007 and 0.2 mg/cm^2 per hour, respectively [4]. These low oxidation rates are directly attributed to the formation of highly stable, dense silicon oxide (SiO_2) layer on the surface that protects from further oxidation in highly oxidizing atmospheres at high temperatures [4,8,13]. It was also demonstrated that they are good metallic conductors even at high temperatures, which is necessary for high-temperature sensing applications. The electrical resistivity of the MoSi_2 and WSi_2 thin films were found as 134 and $93 \mu\Omega\cdot\text{cm}$ at around 830°C [14]. Kobel et al. (2004) also reported that the MoSi_2 exhibited very high electrical conductivity ($\sim 6000 \text{ S/cm}$) at around 750°C [15]. However, the poor low temperature toughness, pest effect (or accelerated oxidation at 400°C - 600°C), low mechanical strength and poor creep resistance at high temperatures ($\geq 1200^\circ\text{C}$) were identified as their major limitations that need to be addressed [8,15,16].

Therefore, a composite approach has been applied by some researchers to overcome such disadvantages and to enhance their performance/reliability at high temperatures, since MoSi_2 and WSi_2 are chemically compatible with many ceramic reinforcements including SiC , Al_2O_3 , ZrO_2 , TiC , Si_3N_4 and TiB_2 [16-18]. It was reported in studies that their mechanical strength, fracture toughness and high-temperature creep resistance could be substantially increased by reinforcing with Al_2O_3 , ZrO_2 , SiC and TiC [8,19-23]. The refractory oxide addition of choice is typically Al_2O_3 and ZrO_2 in these composite systems (mostly $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{MoSi}_2\text{-ZrO}_2$), since these materials have a close match of their thermal expansion coefficients ($\sim 8.0 \times 10^{-6} \text{ K}^{-1}$ for Al_2O_3 ; $9.6 \times 10^{-6} \text{ K}^{-1}$ for ZrO_2) with MoSi_2

($8.2 \times 10^{-6} \text{K}^{-1}$) and WSi_2 ($7.9 \times 10^{-6} \text{K}^{-1}$) in a wide temperature range from 20°C to 1400°C [12,24,25]. This is very beneficial in composite systems for minimizing thermal stresses and interfacial cracks, and thus, for improving their thermal shock resistance and stability at high temperatures [8,26]. In addition, it is anticipated that oxygen diffusion pathways may be blocked by reinforcing with these oxidation-resistant refractory oxides, and therefore, the high temperature oxidation resistance could be enhanced, while eliminating the problematic pest oxide formation [13,25]. Zmii et al. (2008) showed that the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ coatings with 5-30 wt% of alumina reinforcement have significantly higher oxidation resistance at 1800°C than monolithic disilicide coatings [27]. However, it was reported on the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite coatings that the oxidation rate at 1500°C slightly increased with 30 vol% of Al_2O_3 addition, which was explained by formation of mullite resulted in less protective, porous oxide layer on the surface [13]. But the effect of the Al_2O_3 and ZrO_2 reinforcements on the oxidation resistance of the MoSi_2 - and WSi_2 -based composites has not been well understood yet. Furthermore, it is well known from ceramic composite systems that grain growth can be efficiently retarded at elevated temperatures by grain boundary pinning of reinforcement (second-phase) particles such as alumina and zirconia [28-30]. This is also advantageous for achieving more stable microstructures that may improve the long-term stability and performance of the metal silicide/refractory oxide composites at high temperatures. It is important to note that grain growth kinetics and long-term stability of these composites have not been studied.

Metal silicide/refractory oxide ceramic composites (particularly $\text{MoSi}_2\text{-Al}_2\text{O}_3$, $\text{MoSi}_2\text{-ZrO}_2$, $\text{WSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-ZrO}_2$) are very promising high-temperature electroconductive materials for advanced sensing applications under harsh-environments, based upon their current and potential advantages discussed. Regarding to their electroconductive behavior and metallic nature, Yamamoto and Sendai developed a method for producing MoSi_2 -based composite heating elements and high-temperature thermistors with granular Al_2O_3 reinforcement [31,32]. The $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites exhibited an adequate low-temperature electrical conductivity even at alumina fractions above 80 wt%,

as well as, improved mechanical strength and high-temperature oxidation/erosion resistance. In the study performed by Kobel et al. (2004), electrical properties of the MoSi₂-Al₂O₃ composites with 16-40 vol% silicide contents were investigated as a function of temperature [15]. The electrical conductivity of the 25-75 and 40-60 vol% MoSi₂-Al₂O₃ composites at 750°C was approximately measured as 24 and 600 S/cm, respectively. However, there are very limited studies conducted on their high-temperature electrical properties and potential advanced sensing applications; there are no studies on their short/long-term thermal stability and grain growth kinetics. Therefore, the main objectives of this research were to fabricate the MoSi₂- and WSi₂-based ceramic composites reinforced by Al₂O₃ and ZrO₂ particles, and to investigate their chemical/thermal stability, microstructural evolution, grain growth kinetics and electrical properties at high temperatures.

2.2 Experimental Procedure

2.2.1 Materials and method

Commercial MoSi₂ (99.5% metals basis), WSi₂ (99.5% metals basis) and ZrO₂ (99+%) powders, all purchased from Alfa Aesar (Tewksbury, MA, USA), were used as starting powders. In addition, fine-Al₂O₃ (99.8%, 8.6 m²/g SSA) and coarse-Al₂O₃ (99.6%, 1.2 m²/g SSA) powders used were purchased from Almatix (Leetsdale, PA, USA); and they are abbreviated as f.Al₂O₃ and c.Al₂O₃, respectively, for simplicity. Prior to the processing of the composites, phase and microstructure analysis of the starting powders were completed by X-ray diffraction (XRD, Panalytical X'Pert Pro, Westborough, MA, USA) and field emission scanning electron microscopy (FE-SEM, Hitachi S-4700F, Tokyo, Japan), respectively. Figure 34 presents the XRD patterns of the starting MoSi₂ and WSi₂ powders. It was found that 5-3 metal silicides (Mo₅Si₃, W₅Si₃) and metals (Mo, W) exist along with the major MoSi₂ (tetragonal, I4/mmm, #01-080-0544) and WSi₂ (tetragonal, I4/mmm, #00-011-0195) phases. In addition, the XRD results of the refractory oxide powders (not shown) demonstrated that both Al₂O₃ powders have the corundum structure with rhombohedral symmetry (R3c, #01-078-2427), while the ZrO₂ displayed a monoclinic

Figure 34. XRD patterns of the commercial (a) molybdenum disilicide (MoSi_2), and (b) tungsten disilicide (WSi_2) starting powders.

structure (P21/c, #00-024-1165). Also, SEM microstructures of the starting powders are presented in the Figure 35. The results showed that the MoSi_2 and WSi_2 particles have random-shaped morphology with average sizes of 4.2 and 5.3 μm , respectively. The average sizes of equiaxed-shaped $\text{f.Al}_2\text{O}_3$ and random-shaped $\text{c.Al}_2\text{O}_3$ particles were measured by using the ImageJ software [33] as 0.4 and 2.5 μm , respectively. It was also found that the ZrO_2 had both equiaxed and elongated particles with 12.1 μm average size.

The fractions of the metal silicide powders in the composite compositions were all determined based on the volume, thus only the volume percentages (vol%) were used to describe the composites as 20-80 and 60-40 for simplicity. The 20-80 and 60-40 volume fractions were selected in this study to work in the regions (1) near percolation and (2) above percolation, respectively. MoSi_2 - and WSi_2 -based ceramic composite powders reinforced by Al_2O_3 , $\text{c.Al}_2\text{O}_3$ and ZrO_2 were prepared by ball-milling in ethanol for 24 h followed by drying at room temperature in a fume hood. The as-prepared composite powders were uniaxially pressed into small (13 mm diameter) and large (26 mm diameter) cylindrical pellets having 2-4 mm thickness by using a stainless steel die under the pressure of 13.8 MPa. These pellets were then sintered at 1400°-1600°C in a tube furnace in flowing argon gas (50 sccm). The rate of heating was set as 3°C/min. The samples were held for 2 h at that temperature and subsequently cooled to room temperature at a rate of 3°C/min. After sintering of the composites was completed, three small pellets of each composition were further annealed at 1400°C for 24 and 48 h, respectively, in order to investigate their thermal stability, microstructural evolution and grain growth kinetics at high temperatures.

2.2.2 Characterization

Characterization studies were performed regarding their density, phase development, microstructure/grain growth and electrical properties. Densities of the sintered composite samples were measured by employing the Archimedes principle using ethanol (0.789 g/cm³) as the immersion liquid. The volume fractions of the secondary phases formed after sintering were not included in the theoretical density calculations.

Figure 35. SEM microstructures of the commercial (a) MoSi_2 , (b) WSi_2 , (c) $\text{f.Al}_2\text{O}_3$ (fine- Al_2O_3) (d) $\text{c.Al}_2\text{O}_3$ (coarse- Al_2O_3), and (e) ZrO_2 starting powders.

Figure 35. (continued) SEM microstructures of the commercial (a) MoSi_2 , (b) WSi_2 , (c) $\text{f. Al}_2\text{O}_3$ (fine- Al_2O_3) (d) $\text{c. Al}_2\text{O}_3$ (coarse- Al_2O_3), and (e) ZrO_2 starting powders.

Figure 35. (continued) SEM microstructures of the commercial (a) MoSi₂, (b) WSi₂, (c) f.Al₂O₃ (fine-Al₂O₃) (d) c.Al₂O₃ (coarse-Al₂O₃), and (e) ZrO₂ starting powders.

Phase analyses of the composite samples were performed both after sintering and annealing by XRD with CuK α radiation source. Additionally, quantitative phase analysis studies via Rietveld method were performed by using the MAUD software [34] to determine the fractions of secondary phases formed after sintering and annealing. Sample preparation for microstructural analyses was carried out by cutting of the samples with a diamond saw, and then fine polishing with SiC sanding papers (600-1200 grits) and diamond paste (0.5 μ m). Chemical etching was also utilized by soaking the samples in 2 M HCl or 1:1:1 HCl:HNO₃:H₂O acid solutions for 2 min. Afterwards, field emission scanning electron microscopy (FE-SEM, Hitachi S-4700F, Tokyo, Japan) was used to examine the microstructures of composite samples, and also to study the grain growth of the metal silicides. Average grain size of the metal silicides were determined from their SEM micrographs by using the ImageJ. For electrical measurements, a high temperature test rig was made using a high purity 4-bore alumina tube and platinum connection leads. The

rectangular bar samples, with average dimensions of 20×4×4 mm, were prepared from the large cylindrical pellets for a standard measurement (ASTM B193-16) [35], and then, they connected to the test rig and the entire system was sealed in a tube furnace. Electrical resistance of the sintered composite samples was measured with a digital multimeter (Keithley 2100, Tektronix, Beaverton, OR, USA) by the DC four-probe method. A B-type of thermocouple was also used to monitor the temperature. The electrical measurements were conducted at temperatures up to 900°-1000°C in argon atmosphere to avoid material degradation. The resistance data was acquired as a function of time and temperature by LabView and Keithley programs, and lastly, the electrical resistivity/conductivity were calculated by using the specific sample dimensions.

2.3 Results and Discussion

2.3.1 Densification, chemical stability and microstructures after sintering

MoSi₂- and WSi₂-based composites were all prepared by reinforcing with different refractory oxides based on the metal silicide-refractory oxide volume fractions of 20-80 and 60-40. Then, these twelve composites were sintered at the temperatures range from 1400°C to 1600°C in order to determine their densification as a function of composition and temperature, as well as, to define the optimum sintering temperature for further studies. Table 5 and Table 6 presents the relative density, apparent density and apparent porosity of the MoSi₂- and WSi₂-based composites as a function of sintering temperature. The results showed that all composites except for 60-40 WSi₂-f.Al₂O₃ have relative densities lower than 74.7% at 1400°C. With increasing temperature to 1500°C, there was a 4.8-6.2% increase in relative densities of the MoSi₂-c.Al₂O₃, MoSi₂-ZrO₂ and WSi₂-c.Al₂O₃ composites. But it is clear that MoSi₂- and WSi₂-based composites reinforced with fine-alumina particles (f.Al₂O₃) exhibited higher relative densities ranging from 77.8 to 98.0% at 1500° and 1600°C, particularly at low metal silicide fractions. The relative densities of the 20-80 MoSi₂-f.Al₂O₃ and WSi₂-f.Al₂O₃ at 1600°C were 98.0 and 92.6%, respectively. The increase in their relative densities ranged from 17.9 to 26.5 with increasing sintering temperature from 1400° to 1600°C. The lowest apparent porosity values (1.2-2.9%) were

Table 5. Relative densities of the MoSi₂-based and WSi₂-based composites reinforced by f.Al₂O₃, c.Al₂O₃ and ZrO₂ particles as function of sintering temperature.

Composite	Relative density (%)		
	1400°C	1500°C	1600°C
20-80 MoSi ₂ -f.Al ₂ O ₃	71.5	92.5	98.0
20-80 MoSi ₂ -c.Al ₂ O ₃	66.8	71.5	74.1
20-80 MoSi ₂ -ZrO ₂	69.6	76.3	89.7
60-40 MoSi ₂ -f.Al ₂ O ₃	71.6	81.7	90.9
60-40 MoSi ₂ -c.Al ₂ O ₃	63.1	68.4	77.7
60-40 MoSi ₂ -ZrO ₂	68.9	74.3	87.9
20-80 WSi ₂ -f.Al ₂ O ₃	74.7	92.5	92.6
20-80 WSi ₂ -c.Al ₂ O ₃	67.2	73.4	74.3
20-80 WSi ₂ -ZrO ₂	72.3	73.4	72.9
60-40 WSi ₂ -f.Al ₂ O ₃	78.1	77.8	88.6
60-40 WSi ₂ -c.Al ₂ O ₃	70.8	72.0	79.8
60-40 WSi ₂ -ZrO ₂	74.0	72.5	85.0

also achieved by these composites sintered above 1500°C. Similar density results (86.5-98.2%) were reported on the MoSi₂-Al₂O₃ composites in the literature [26,36]. Besides, a similar effect was also observed by reinforcing the metal silicides with larger zirconia particles (~12.1 µm), which improved the densification mostly at 1600°C. Although the MoSi₂-ZrO₂ and WSi₂-ZrO₂ composites (except for the 20-80 WSi₂-ZrO₂) revealed high

Table 6. Apparent density and apparent porosity of the MoSi₂-based and WSi₂-based composites reinforced by f.Al₂O₃, c.Al₂O₃ and ZrO₂ particles as function of sintering temperature.

Composite	Apparent density (g/cm ³)			Apparent porosity (%)		
	1400°C	1500°C	1600°C	1400°C	1500°C	1600°C
20-80 MoSi₂-f.Al₂O₃	4.52	4.17	4.37	26.7	2.4	1.2
20-80 MoSi₂-c.Al₂O₃	4.32	4.40	4.44	31.8	28.3	26.5
20-80 MoSi₂-ZrO₂	5.99	5.97	5.92	32.8	26.0	12.3
60-40 MoSi₂-f.Al₂O₃	5.14	4.90	5.33	25.8	11.2	9.2
60-40 MoSi₂-c.Al₂O₃	5.18	5.23	5.34	35.1	30.3	22.5
60-40 MoSi₂-ZrO₂	6.03	6.28	6.18	31.2	28.9	14.5
20-80 WSi₂-f.Al₂O₃	5.09	4.78	4.79	26.3	2.8	2.9
20-80 WSi₂-c.Al₂O₃	5.06	5.11	5.05	33.4	27.9	26.2
20-80 WSi₂-ZrO₂	6.71	6.67	6.66	31.1	29.6	29.9
60-40 WSi₂-f.Al₂O₃	6.68	5.90	7.40	15.7	5.6	14.2
60-40 WSi₂-c.Al₂O₃	7.19	7.30	7.54	29.5	29.4	24.3
60-40 WSi₂-ZrO₂	8.27	8.30	8.10	29.7	31.5	17.6

relative densities above 85.0% at 1600°C, their densities were found to be significantly low (68.9-76.3%) at the lower temperatures. The porosity level was also significantly higher (26.0-32.8%) for these composites sintered at 1400°-1500°C, but a drastic decrease was observed at 1600°C. Therefore, their low densities at 1400°-1500°C could be explained by insufficient thermal energy for sintering and possible formation of microcracks due to the ZrO₂ monoclinic-tetragonal phase transition at around 1170°C, respectively [37,38]. Matsuo and Homma (1964) similarly showed that densities of the MoSi₂-ZrO₂ composites increased at the sintering temperatures above 1500°C [39]. The lowest relative densities (72.9-79.8%) for the composites sintered at 1600°C were measured by the MoSi₂-c.Al₂O₃ and WSi₂-c.Al₂O₃ along with the 20-80 WSi₂-ZrO₂. They also displayed higher apparent porosities (22.5-29.9%) among all the composites.

It is known that densification of the composites could be highly influenced by volume fraction, particle size and distribution of the reinforcement particles (second phase) [40,41]. It was reported that densification could be improved by increasing the particle size ratio of the reinforcement to the matrix, which could result in more efficient particle packing [42]. The zirconia/metal silicide particle size ratios (2.3-2.9) were significantly higher than coarse-alumina/metal silicide particle size ratios (0.5-0.6), which would lead to more efficient particle packing and higher densification for the zirconia/metal silicide composites. However, it was difficult to calculate the fine-alumina/metal silicide particle size ratios due to the agglomeration of fine-alumina particles after milling. However, if the fine-alumina/metal silicide particle size ratios are assumed relatively higher due to that agglomeration, enhanced densification in the silicide-f.Al₂O₃ composites could be explained with the same effect. Additionally, it is known that matrix-matrix (silicide-silicide or oxide-oxide) locations within the composite sinter and grow faster than the matrix-reinforcement (silicide-oxide) locations due to the difference in surface energy between the two grains and due to potentially higher transport along the grain boundaries of the contacts with similar chemistry and structure [40,42,43]. The number of matrix-matrix contacts significantly decreases with addition of the reinforcement particles within

the composite structures. Therefore, homogeneous particle distribution may not be beneficial for improving the densification due to the formation of more dissimilar silicide-oxide contacts throughout the microstructure resulting in constrained sintering (i.e. lower densification kinetics). The number of silicide-silicide and oxide-oxide contacts was higher in the silicide-f. Al_2O_3 composites due to agglomeration of the fine-alumina particles; thus, large regions of these composites contained a higher concentration of single-phase grain boundaries leading to local densification kinetics controlled by single-phase sintering mechanisms. As a review of the results, it can be concluded that the densification of the composites was highly affected by sintering temperature, reinforcement material, particle size ratio of the reinforcement to the matrix, particle agglomeration and distribution level of particles. The higher relative densities were generally achieved by sintering of the composites at 1600°C , and therefore, further studies were conducted on the composite samples sintered at that temperature.

The phase analysis studies of the composites were initially performed after sintering in order to determine the chemical stability of the metal silicides within different refractory oxide ceramics. The XRD patterns of the 60-40 MoSi_2 -based composites sintered at 1600°C are presented in the Figure 36a. The phases identified for the MoSi_2 -f. Al_2O_3 and MoSi_2 -c. Al_2O_3 were MoSi_2 , Al_2O_3 and Mo_5Si_3 . Similarly, the Mo_5Si_3 phase was also observed for the MoSi_2 - ZrO_2 composite. In addition, it is clear that Mo_5Si_3 peaks are more intense in the MoSi_2 -c. Al_2O_3 and MoSi_2 - ZrO_2 . This result demonstrates that the interaction between MoSi_2 and coarse-grained ($\geq 2.5 \mu\text{m}$) refractory oxides was relatively higher, which may be related to the high number of silicide-oxide contacts within these composites. However, the agglomeration of the fine-alumina particles may highly lower the number of silicide-oxide contacts, and thus, the related particle interaction. The secondary phase formation was also found to be related to interaction of MoSi_2 with residual oxygen that may remain in the starting silicide powder [44,45]. It is well known that MoSi_2 reacts with oxygen to form Mo_5Si_3 and SiO_2 at high temperatures (above the boiling point of MoO_3) based on its thermodynamics and enhanced reaction rate [10,46,47]. Furthermore,

Figure 36. XRD patterns of the (a) 60-40 MoSi₂-based composites, and (b) 60-40 WSi₂-based composites reinforced by f.Al₂O₃, c.Al₂O₃ and ZrO₂ particles after sintering at 1600°C for 2 h.

existence of the Mo_5Si_3 phase in the system may not constitute an issue, since it has a higher melting point (2160°C), relatively low oxidation resistance and higher creep resistance [8,9]. Figure 36b shows the XRD patterns of the 60-40 WSi_2 -f. Al_2O_3 , WSi_2 -c. Al_2O_3 and WSi_2 - ZrO_2 composites all sintered at 1600°C . Similar results can be clearly seen for these composites as well. It is determined that only W_5Si_3 secondary phase formed in all three composites after sintering, since WSi_2 also has a high-temperature oxidation process similar to MoSi_2 [11]. This formation was explained differently by the decomposition of WSi_2 into W_5Si_3 and Si during hot isostatic pressing at 1500°C and 196 MPa [22,48]. But it is important to note that the oxidation rate of W_5Si_3 at high temperature (1500°C) is high, particularly compared to the WSi_2 , as well as MoSi_2 and Mo_5Si_3 ; therefore, the low fraction of W_5Si_3 should be preferred as a secondary phase in these composites [8]. As a review of the XRD results, it can be concluded that both MoSi_2 and WSi_2 are found to be chemically stable within Al_2O_3 and ZrO_2 oxide ceramics at 1600°C , proving the high stability of these composites at high temperatures only with formation of 5-3 silicides.

For mixtures of the conductive and insulating materials like the MoSi_2 - Al_2O_3 composite system, it is well known that the homogeneous distribution of conductive particles within an insulating material is essential when seeking to achieve consistent electrical properties and an electrical network near the critical percolation threshold [15,17,49]. Therefore, SEM microstructural analyses were performed after sintering of the composites at 1600°C . Figure 37 presents the backscattered SEM microstructures of all 60-40 MoSi_2 - and WSi_2 -based composites reinforced by f. Al_2O_3 , c. Al_2O_3 and ZrO_2 . The bright and dark regions within all microstructures refer to the metal silicide and refractory oxide particles, respectively. It is demonstrated that MoSi_2 and WSi_2 particles were distributed very homogeneously within the coarse-alumina and zirconia particles; therefore, a better percolating network was obtained particularly in the MoSi_2 -c. Al_2O_3 , WSi_2 -c. Al_2O_3 and WSi_2 - ZrO_2 composites (Figure 37b-e-f). However, agglomerated regions of molybdenum disilicide, tungsten disilicide and fine-alumina grains can be clearly seen in Figure 37(a-d),

Figure 37. SEM microstructures of the (a) $\text{MoSi}_2\text{-f.Al}_2\text{O}_3$, (b) $\text{MoSi}_2\text{-c.Al}_2\text{O}_3$, (c) $\text{MoSi}_2\text{-ZrO}_2$, (d) $\text{WSi}_2\text{-f.Al}_2\text{O}_3$, (e) $\text{WSi}_2\text{-c.Al}_2\text{O}_3$, and (f) $\text{WSi}_2\text{-ZrO}_2$ composites all having 60-40 metal silicide-refractory oxide fractions after sintering at 1600°C for 2 h.

Figure 37. (continued) SEM microstructures of the (a) $\text{MoSi}_2\text{-f.Al}_2\text{O}_3$, (b) $\text{MoSi}_2\text{-c.Al}_2\text{O}_3$, (c) $\text{MoSi}_2\text{-ZrO}_2$, (d) $\text{WSi}_2\text{-f.Al}_2\text{O}_3$, (e) $\text{WSi}_2\text{-c.Al}_2\text{O}_3$, and (f) $\text{WSi}_2\text{-ZrO}_2$ composites all having 60-40 metal silicide-refractory oxide fractions after sintering at 1600°C for 2 h.

Figure 37. (continued) SEM microstructures of the (a) $\text{MoSi}_2\text{-f.Al}_2\text{O}_3$, (b) $\text{MoSi}_2\text{-c.Al}_2\text{O}_3$, (c) $\text{MoSi}_2\text{-ZrO}_2$, (d) $\text{WSi}_2\text{-f.Al}_2\text{O}_3$, (e) $\text{WSi}_2\text{-c.Al}_2\text{O}_3$, and (f) $\text{WSi}_2\text{-ZrO}_2$ composites all having 60-40 metal silicide-refractory oxide fractions after sintering at 1600°C for 2 h.

which are highly associated with the initial agglomeration of the fine-alumina particles (0.4 μm) possessed a higher surface area after ball-milling. In addition, more porous regions were observed in the MoSi_2 - and WSi_2 -based composites reinforced by c. Al_2O_3 and ZrO_2 particles (Figure 37b-c-e-f). These results imply that particle distribution in the composite systems is highly influenced by matrix/reinforcement particle size ratio and particle size of reinforcement itself, which could also affect the electrical properties. It is reported that improved distribution, particles with large aspect ratios and also lower size ratio of conductive to insulating particles could provide significant advantage for formation of continuous percolating network and also for lowering the percolation concentration [15,50,51]. Therefore, achieving highly homogeneous microstructures is very important to lower the critical percolation concentration and to fabricate metal silicide-refractory oxide composites that are electrically conductive even at low metal silicide contents.

In addition to the SEM studies discussed above, some of the composite samples were chemically etched after sintering in order to increase the contrast between different phases and, by this way, to observe the formation of secondary 5-3 silicide phases on the microstructures. Figure 38(a-b) show the SEM images of the 60-40 MoSi_2 -c. Al_2O_3 and WSi_2 -f. Al_2O_3 composites that were previously soaked in HCl and $\text{HCl}:\text{HNO}_3:\text{H}_2\text{O}$, respectively. The bright, grey and dark regions indicate 5-3 silicides (Mo_5Si_3 , W_5Si_3), metal disilicides (MoSi_2 , WSi_2) and alumina grains, respectively. It was found that secondary 5-3 silicide phases mostly formed around alumina grains. Similar observation was also reported on the MoSi_2 - Al_2O_3 composite consisting only 5 vol% alumina by Wang et al. (2014) [12]. Additionally, energy dispersive spectroscopy (EDS) was performed on the SEM microstructure of the 60-40 WSi_2 -f. Al_2O_3 composite, which is presented in the Figure 38c. For the grey region (*R-grey*), only W and Si peaks were obtained except for the gold (Au) peak coming from the sputtered coating made just for SEM analysis. The atomic percentages (at%) of W and Si elements were quantified as 37.3 and 62.7, which implied the WSi_2 composition in the grey region. However, 15.4 at% oxygen (O) was determined in addition to the W and Si elements in the bright region (*R-bright*). The atomic percentage

Figure 38. SEM microstructures of the (a) 60-40 MoSi₂-c.Al₂O₃, and (b) 60-40 WSi₂-f.Al₂O₃ composites after sintering (chemically etched), and (c) EDS analysis results of the grey (*R-grey*) and bright (*R-bright*) regions specified on the 60-40 WSi₂-f.Al₂O₃ composite microstructure.

Figure 38. (continued) SEM microstructures of the (a) 60-40 MoSi₂-c.Al₂O₃, and (b) 60-40 WSi₂-f.Al₂O₃ composites after sintering (chemically etched), and (c) EDS analysis results of the grey (*R-grey*) and bright (*R-bright*) regions specified on the 60-40 WSi₂-f.Al₂O₃ composite microstructure.

of W element increased to 49.3, but Si decreased to 35.3 at%, as expected for the secondary 5-3 silicide phase formed. These results clearly established the presence of W₅Si₃ with a small amount of glassy SiO₂ grain boundary phase in the bright region. But it is important to note that silica phase could not be detected by XRD due to its very low amount on the grain boundaries, since it mostly formed on the surface as a protective layer to further oxidation [8]. Therefore, the formation of the 5-3 secondary phases could also be associated with the reaction of metal disilicides with oxygen that may be residual in the system or may penetrate into the system through silica layer in the existence of

microcracking, because it is known that Mo_5Si_3 and W_5Si_3 mostly form in small amounts and beneath the silica layer [46,52,53]. Therefore, such studies reported the difficulty of identifying the presence of these 5-3 metal silicide phases by XRD in most cases.

2.3.2 Thermal stability and grain growth kinetics at high-temperatures

Due to the high operating temperatures (1200°C - 1650°C), harsh environments and long operation hours experienced in many industries, advanced sensing materials like electroconductive ceramic composites need to be thermally stable at high temperatures both for short- and long-term without any compositional decomposition [2,4]. Therefore, the MoSi_2 - and WSi_2 -based composites reinforced by alumina and zirconia particles were further annealed (after sintering) at 1400°C for 24 and 48 h for better understanding their thermal stability at significantly high temperatures. Figure 39 presents the XRD patterns of these six composites (60-40) after sintering at 1600°C and annealing at 1400°C for 24-48 h. The XRD results of these composites after sintering were used only for a better comparison, and defined with “0 h” indicating zero annealing time as a starting point. For all composites, no thermal decomposition was observed after annealing at 1400°C up to 48 h. The major phases were metal disilicides (MoSi_2 , WSi_2) and refractory oxides (Al_2O_3 , ZrO_2), while the 5-3 silicides (Mo_5Si_3 , W_5Si_3) still existed in the composite systems as secondary phases. In addition, peak intensities of the Mo_5Si_3 and W_5Si_3 phases slightly increased in all 60-40 composites as a function of annealing time, but this increase was relatively higher in the MoSi_2 - and WSi_2 -based composites reinforced by coarse-alumina and zirconia, as shown with arrows in the Figure 39(b-c-e-f). This may be related with more interaction between metal disilicide and coarser oxide grains. It is important to point out that no significant changes were observed after 24 h annealing period. All these results imply that amount of the secondary 5-3 silicide phases may have slightly increased as a function of annealing time, but eventually all these composites exhibited excellent thermal stability at 1400°C , particularly after 24 h, without undergoing any decomposition. No studies on the high-temperature thermal stability of the metal silicide-refractory oxide bulk composites were found in the literature for a comparison. Only the thermal stability of the

Figure 39. XRD patterns of the (a) MoSi_2 -f. Al_2O_3 , (b) MoSi_2 -c. Al_2O_3 , (c) MoSi_2 - ZrO_2 , (d) WSi_2 -f. Al_2O_3 , (e) WSi_2 -c. Al_2O_3 , and (f) WSi_2 - ZrO_2 composites all having 60-40 metal silicide-refractory oxide fractions after sintering at 1600°C , and then annealing at 1400°C for 24-48 h (sintered sample was defined as “0 h” indicating zero annealing time as a starting point).

Figure 39. (continued) XRD patterns of the (a) MoSi₂-f.Al₂O₃, (b) MoSi₂-c.Al₂O₃, (c) MoSi₂-ZrO₂, (d) WSi₂-f.Al₂O₃, (e) WSi₂-c.Al₂O₃, and (f) WSi₂-ZrO₂ composites all having 60-40 metal silicide-refractory oxide fractions after sintering at 1600°C, and then annealing at 1400°C for 24-48 h (sintered sample was defined as “0 h” indicating zero annealing time as a starting point).

Figure 39. (continued) XRD patterns of the (a) MoSi_2 -f. Al_2O_3 , (b) MoSi_2 -c. Al_2O_3 , (c) MoSi_2 -ZrO₂, (d) WSi_2 -f. Al_2O_3 , (e) WSi_2 -c. Al_2O_3 , and (f) WSi_2 -ZrO₂ composites all having 60-40 metal silicide-refractory oxide fractions after sintering at 1600°C, and then annealing at 1400°C for 24-48 h (sintered sample was defined as “0 h” indicating zero annealing time as a starting point).

mechanically alloyed and then milled $\text{MoSi}_2\text{-Al}_2\text{O}_3$ powders was studied by annealing at 1000°C for 1 h under argon atmosphere [45]. They also reported the formation of the Mo_5Si_3 phase with annealing caused by residual molybdenum and silicon elements, but it should be noted that this was a very short-term thermal stability study of only powder.

The quantitative phase analysis studies were also performed by utilizing the Rietveld method on the XRD patterns to determine the volume fractions of the secondary phases compared to all other phases in the composite systems. According to the Rietveld analysis, it is known that the goodness of fit (sig) and weighted profile R-factor (Rwp) values representing the quality of refinement should be less than 2.0 and 0.15, respectively [34]. In all composites except for the 60-40 $\text{WSi}_2\text{-ZrO}_2$, the sig values ranged from 1.3 to 1.9, while the Rwp values ranged from 0.05 to 0.09. For the 60-40 $\text{WSi}_2\text{-ZrO}_2$, the Rwp values were all less than 0.1, but the sig values were between 2.2 and 2.5. In addition, these factors could not be lowered to the recommended values only for the 60-40 $\text{WSi}_2\text{-f.Al}_2\text{O}_3$ composite sample annealed for 24 h due to the noisy background and several peak shifts on its XRD pattern. However, it is important to note that the quality of the Rietveld refinement was highly sufficient in all cases. Figure 40(a-b) show changes in the amount (vol%) of Mo_5Si_3 and W_5Si_3 secondary phases as a function of annealing time, respectively. It is clear that the amount of both 5-3 metal silicide phases increased in all composite systems with increasing annealing time up to 48 h, but at different levels. The amount of Mo_5Si_3 in the 60-40 $\text{MoSi}_2\text{-f.Al}_2\text{O}_3$ composite slightly increased from 0.3 to 3.3 vol% with annealing time. The increase of W_5Si_3 was from 6.9 to 11.4 vol% in the 60-40 $\text{WSi}_2\text{-f.Al}_2\text{O}_3$. The amount of Mo_5Si_3 and W_5Si_3 increased from 5.3 to 7.2, and from 21.8 to 38.8 vol% in the 60-40 $\text{MoSi}_2\text{-c.Al}_2\text{O}_3$ and $\text{WSi}_2\text{-c.Al}_2\text{O}_3$ composites, respectively. As a review, it can be concluded that the amount of the secondary W_5Si_3 phase (11.4-38.8 vol%) was significantly higher than that of the Mo_5Si_3 (3.3-7.3 vol%) in the composites after annealing at 1400°C for 48 h. The secondary 5-3 metal silicide phase formation was found to be significantly lower in the $\text{MoSi}_2\text{-f.Al}_2\text{O}_3$ and $\text{WSi}_2\text{-f.Al}_2\text{O}_3$ composites compared to the ones reinforced by coarse-alumina and zirconia particles as clearly seen in Figure 40.

Figure 40. Changes in the amount (vol%) of (a) Mo_5Si_3 , and (b) W_5Si_3 secondary phases as a function of annealing time.

Table 7. The rates of the formation of secondary 5-3 metal silicide phases (Mo_5Si_3 , W_5Si_3) in the 60-40 composites over two annealing periods.

Composite	From 0 to 24 hours annealing period (vol%/h)	From 24 to 48 hours annealing period (vol%/h)
$\text{MoSi}_2\text{-f.Al}_2\text{O}_3$	0.073	0.053 (<i>decreased</i>)
$\text{MoSi}_2\text{-c.Al}_2\text{O}_3$	0.074	0.007 (<i>decreased</i>)
$\text{MoSi}_2\text{-ZrO}_2$	0.025	0.100 (<i>increased</i>)
$\text{WSi}_2\text{-c.Al}_2\text{O}_3$	0.589	0.121 (<i>decreased</i>)
$\text{WSi}_2\text{-ZrO}_2$	0.193	0.054 (<i>decreased</i>)

In correlation with the XRD data, these results indicate that the interaction between metal disilicide and coarse-grained particles was higher, and also fine-alumina grains potentially restricted oxygen diffusion into the material from residual environmental sources. Since the relative densities of the 60-40 $\text{MoSi}_2\text{-c.Al}_2\text{O}_3$ and $\text{WSi}_2\text{-c.Al}_2\text{O}_3$ (77.7-79.8%) were lower than that of the other composites, the related high-temperature oxidation reactions were more favored, resulting in the formation of Mo_5Si_3 and W_5Si_3 secondary phases with higher levels below the surface oxide layer [10,46,54]. This result demonstrates that secondary phase formation was also affected by density of the composites and degree of porosity. Additionally, the phase transformation kinetics were measured by assuming a linear transformation process, since the formation reaction of secondary 5-3 silicide phases is not only limited to the surface interaction (interface-controlled), but also controlled by thermodynamically feasible oxidation reactions of metal disilicides at high temperatures. Therefore, the increase in the volume fraction of the 5-3 silicide phase was divided by the annealing time for these calculations. By this way, it was determined that rates of the formation of secondary phases (vol% per hour) highly decreased in all composites except for the $\text{MoSi}_2\text{-ZrO}_2$ after annealing for 24 h, as presented in the Table 7, indicating their improved thermal stability over time. However, it is important to point out that high

fractions of secondary W_5Si_3 phase up to 38.8 vol% may cause serious issues in real applications under air atmosphere due to its low oxidation resistance [8,11]. Therefore, $MoSi_2$ -based composites are found to be more thermally stable with the formation of low fractions of Mo_5Si_3 having reasonable high-temperature oxidation resistance, and hence, to be more suitable for advanced sensing applications at high-temperature and harsh-environments.

In addition to the high thermal stability, low grain growth rates are essential for such ceramic composite systems; since mechanical and electrical properties are highly influenced by grain size [55,56]. Therefore, it is crucial to keep the growth rates of metal disilicide grains lower for maintaining the stability and performance of the composites at high temperatures for longer terms. In order to understand the effect of refractory oxide reinforcement on growth rates of the metal silicide grains, the $MoSi_2$ and 60-40 $MoSi_2$ -f. Al_2O_3 samples were initially characterized by SEM. Figure 41 presents the SEM microstructures of the $MoSi_2$ and 60-40 $MoSi_2$ -f. Al_2O_3 samples after sintering and annealing at the same conditions. The grey and bright regions indicate $MoSi_2$ and Mo_5Si_3 grains, respectively. For the $MoSi_2$ sample, the average size of the $MoSi_2$ grains was measured after sintering as 8.3 μm (Figure 41a), which then increased to 11.8 and 12.7 μm with increasing annealing time (Figure 41b-c). Although the individual $MoSi_2$ grains could not be observed for the 60-40 $MoSi_2$ -f. Al_2O_3 after sintering (Figure 37a), average sizes of the $MoSi_2$ grains within this composite were measured as 4.6 and 5.2 μm after annealing at 1400°C for 24 and 48 h, respectively (Figure 41d-e-f). Therefore, it is found that growth rate of $MoSi_2$ grains in the $MoSi_2$ -f. Al_2O_3 composite ($\sim 0.021 \mu m/h$) was significantly lower than that in the $MoSi_2$ sample ($\sim 0.092 \mu m/h$). It is important to note that the grain growth rates were calculated by assuming a linear relation, and thus, by dividing the change in silicide grain size to the total annealing time. The reason of this simplification of the growth process was due to the difficulty of fitting the obtained grain growth data to simple grain growth power laws due to the limited data, and the existence of three grain boundary phases (refractory oxide, 5-3 metal silicide, silica) that potentially have a significant role on

Figure 41. SEM microstructures of the (a-b-c) MoSi_2 , and (d-e-f) 60-40 MoSi_2 -f. Al_2O_3 composite after sintering at 1600°C , and then annealing at 1400°C for 24-48 h.

Figure 41. (continued) SEM microstructures of the (a-b-c) MoSi_2 , and (d-e-f) 60-40 MoSi_2 -f. Al_2O_3 composite after sintering at 1600°C , and then annealing at 1400°C for 24-48 h.

Figure 41. (continued) SEM microstructures of the (a-b-c) MoSi₂, and (d-e-f) 60-40 MoSi₂-f.Al₂O₃ composite after sintering at 1600°C, and then annealing at 1400°C for 24-48 h.

Figure 42. SEM microstructures of the (a-b) 60-40 MoSi₂-c.Al₂O₃, (c-d) 60-40 MoSi₂-ZrO₂, (e-f) 60-40 WSi₂-f.Al₂O₃, (g-h) 60-40 WSi₂-c.Al₂O₃, and (i-j) 60-40 WSi₂-ZrO₂ composites after annealing at 1400°C for 24-48 h.

Figure 42. (continued) SEM microstructures of the (a-b) 60-40 MoSi₂-c.Al₂O₃, (c-d) 60-40 MoSi₂-ZrO₂, (e-f) 60-40 WSi₂-f.Al₂O₃, (g-h) 60-40 WSi₂-c.Al₂O₃, and (i-j) 60-40 WSi₂-ZrO₂ composites after annealing at 1400°C for 24-48 h.

Figure 42. (continued) SEM microstructures of the (a-b) 60-40 MoSi₂-c.Al₂O₃, (c-d) 60-40 MoSi₂-ZrO₂, (e-f) 60-40 WSi₂-f.Al₂O₃, (g-h) 60-40 WSi₂-c.Al₂O₃, and (i-j) 60-40 WSi₂-ZrO₂ composites after annealing at 1400°C for 24-48 h.

Figure 42. (continued) SEM microstructures of the (a-b) 60-40 $\text{MoSi}_2\text{-c.Al}_2\text{O}_3$, (c-d) 60-40 $\text{MoSi}_2\text{-ZrO}_2$, (e-f) 60-40 $\text{WSi}_2\text{-f.Al}_2\text{O}_3$, (g-h) 60-40 $\text{WSi}_2\text{-c.Al}_2\text{O}_3$, and (i-j) 60-40 $\text{WSi}_2\text{-ZrO}_2$ composites after annealing at 1400°C for 24-48 h.

Figure 42. (continued) SEM microstructures of the (a-b) 60-40 MoSi₂-c.Al₂O₃, (c-d) 60-40 MoSi₂-ZrO₂, (e-f) 60-40 WSi₂-f.Al₂O₃, (g-h) 60-40 WSi₂-c.Al₂O₃, and (i-j) 60-40 WSi₂-ZrO₂ composites after annealing at 1400°C for 24-48 h.

the grain growth kinetics, and thus, more complicated microstructure. This aspect will be studied further in the future, which will include the analysis of the grain boundary phases present. But these results clearly demonstrate that the grain growth of MoSi_2 was highly inhibited by using the fine-alumina particle reinforcements. This could be explained with the grain boundary pinning effect of second-phase (reinforcement) particles, since it is known that they increase the energy necessary for the migration of a grain boundary (total grain boundary energy) and thus decrease the grain growth rate [28]. Afterwards, the average size of the MoSi_2 and WSi_2 grains were all measured from the SEM microstructures of the other 60-40 MoSi_2 - and WSi_2 -based composites after sintering (Figure 37) and annealing (Figure 42). However, average grain sizes could not be measured only for sintered MoSi_2 -f. Al_2O_3 , sintered WSi_2 -f. Al_2O_3 and also WSi_2 samples due to difficulty of fine polishing and/or chemical etching for these samples. The changes in the average size of the MoSi_2 and WSi_2 grains are shown in the Figure 43 as a function of annealing time. The grain growth rates for all MoSi_2 -based composites (0.013-0.021 $\mu\text{m/h}$) were found to be substantially lower than that of MoSi_2 sample. The rates of grain growth (0.015-0.023 $\mu\text{m/h}$) were also quite lower for all WSi_2 -based composites. However, it is important to point out that MoSi_2 - and WSi_2 -based composites reinforced by coarse-grained reinforcements (c. Al_2O_3 and ZrO_2) revealed relatively lower grain growth rates in comparison to the MoSi_2 -f. Al_2O_3 and WSi_2 -f. Al_2O_3 composites. This result could be associated with more homogeneous distribution of the coarse-grained reinforcement particles on the grain boundaries and also their high aspect ratio (particle morphology) [57,58]. The more homogeneous distribution can be visually seen from the microstructures of these composites (Figure 37b-c-e-f). In addition, the D index values representing the level of distribution (homogeneity) in the binary composites were measured in our previous study as 0.14 and 0.56 for the 60-40 WSi_2 - ZrO_2 and MoSi_2 -f. Al_2O_3 , respectively [59]. Since a low D index presents more homogeneous distribution, the WSi_2 - ZrO_2 exhibited better distribution, and thus, low rate of grain growth (0.015 $\mu\text{m/h}$) in comparison to the MoSi_2 -f. Al_2O_3 (~0.021 $\mu\text{m/h}$). These results clearly prove the effect of particle distribution or homogeneity on the grain growth kinetics. Based on these studies, it could be concluded

Figure 43. Changes in the average size of the (a) MoSi₂ and (b) WSi₂ grains (grain growth rates) as a function of annealing time.

that the metal silicide-refractory oxide composites displayed significant advantages due to low grain growth rates, which may potentially improve their long-term stability at high-temperatures.

2.3.3 Electrical properties at high-temperatures

The high-temperature electrical conductivity of the MoSi₂- and WSi₂-based composites reinforced by alumina and zirconia particles is shown as a function of temperature in the Figure 44. It is known that these composites are metallic conductors above a critical percolation limit [14], and thus, their electrical conductivity was shown to decrease with increasing temperature as expected. It is also important to note that the electrical conductivity data was achieved only at the temperatures above 400°C for all the 60-40 composites (except for 20-80 MoSi₂-f.Al₂O₃), because of the very low resistance below this temperature which resulted in highly inaccurate measurements using the current digital multimeter. For the given sample dimensions, the upper limit for the electrical conductivity was near 3550 S/cm. Additionally, four-point electrical connections made by Pt wire and ink were lost at 820°-900°C, which inhibited the electrical conductivity measurements above that temperatures. This may be associated with the local reaction between Pt and metal disilicides to form platinum silicide (PtSi) phase having low melting-point on the sample surface [60,61]. Therefore, the exponential fitting was applied to some of the results (60-40 MoSi₂-c.Al₂O₃, WSi₂-f.Al₂O₃, WSi₂-ZrO₂) in order to extrapolate the electrical conductivity data from 820°C to 900°C for a better data comparison (adjusted R-square values: 0.93-0.97). Furthermore, the electrical conductivity data could not be obtained at 20 vol% metal silicide content, except for the 20-80 MoSi₂-f.Al₂O₃ composite. Since the main conduction mechanism within these composites is the formation of three-dimensional continuous percolating network, it is found that the certain percolation threshold could not be exceeded for other 20-80 composites [15,51]. The electrical conductivity of the 20-80 MoSi₂-f.Al₂O₃ was measured as 8.8 and 8.1 S/cm at the temperatures of 900° and 1000°C, respectively (Figure 44a). This level of electrical conductivity, for instance 46.6 S/cm at around 110°C, was significantly higher than that for

Figure 44. The electrical conductivity of the (a) MoSi₂-based and (b) WSi₂-based composites and pure metal disilicides (MoSi₂, WSi₂) as a function of temperature (*Electrical conductivity data is presented on the logarithmic scale*).

a similar 20-80 MoSi₂-Al₂O₃ composite (0.01 S/cm at around 50°C) reported by Kobel et al. [15]. The difference in the percolation concentration of 20-80 composites was found to be highly related to their relative densities and apparent porosities. The relative density of the 20-80 MoSi₂-f.Al₂O₃ composite (98.0%) was substantially greater than that of the other composites (72.9-92.6%). It also displayed a very low apparent porosity (1.2%) compared to the other composites, proving the effect of the degree of porosity on the critical percolation concentration. Therefore, it is clear that densification of the composites should be highly improved to fabricate electroconductive ceramic composites even at very low fractions of conductive phase by decreasing the critical percolation concentration.

Among the 60-40 MoSi₂-based composites, MoSi₂-c.Al₂O₃ exhibited significantly higher electrical conductivity (128 S/cm) than the other compositions (81.9-86 S/cm) at 900°C, as seen in the Figure 44a. The relative density of the MoSi₂-c.Al₂O₃ (77.7%) was lower than that of the MoSi₂-f.Al₂O₃ and MoSi₂-ZrO₂ (87.9-90.9%). It still displayed a higher electrical performance that could be correlated with the more homogeneous distribution of conductive silicide particles within insulating oxide phase, since it is well known that the electrical properties are highly influenced by distribution of particles or homogeneity of microstructure as well as particle size/morphology and density [15,17,49,62]. On the other hand, the 60-40 WSi₂-f.Al₂O₃ showed substantially higher electrical conductivity (126 S/cm) than other WSi₂-based composites (102-106 S/cm) as seen in the Figure 44b, due to its relatively high relative density (88.6%) and low apparent porosity (14.2%). No significant effect of conductive to insulating particle size ratio was observed. Therefore, this result may be also related to the amount of secondary W₅Si₃ phase within the composite system, since its content in the WSi₂-f.Al₂O₃ (6.9 vol%) after sintering was significantly lower than that in the WSi₂-c.Al₂O₃ and WSi₂-ZrO₂ composites (18.5-21.8 vol%) as presented in the Figure 40. However, there is no data reported in the literature regarding to the intrinsic electrical properties of the W₅Si₃ phase. Among all the 60-40 composites, it is determined that the MoSi₂-c.Al₂O₃ and WSi₂-f.Al₂O₃ revealed similar, but the highest electrical conductivities at 900°C. Besides, electrical conductivities

of the pure MoSi_2 and WSi_2 samples are presented as a function of temperature in the Figure 44b. It can be clearly seen that WSi_2 exhibited higher electrical conductivity (310 S/cm) than MoSi_2 (198 S/cm) at 900°C based on the extrapolated data (dotted lines above 780°-800°C) using exponential fitting (adjusted R-square values: 0.93-0.97). Similarly, the significantly high intrinsic electrical conductivity of WSi_2 compared to MoSi_2 was reported on thin films by Gottlieb et al. [14]. This also enhanced the electrical conductivity of the WSi_2 -based composites. As a review of these results, it can be clearly concluded that these composites exhibited promising electrical properties at high-temperatures, which were affected by their relative density and degree of porosity, distribution level of particles (homogeneity), intrinsic conductivity of conductive phase, particle size/morphology and perhaps fraction of secondary 5-3 silicide phase.

2.4 Conclusions

The metal silicide-refractory oxide electroconductive ceramic composites were successfully fabricated by including molybdenum disilicide and tungsten disilicide with fine- and coarse-alumina and zirconia particles, and then their chemical/thermal stability, microstructural evolution, grain growth kinetics and electrical properties at high temperatures were investigated. The phase analysis studies demonstrated that all MoSi_2 - and WSi_2 -based composites are chemically stable at 1600°C, only with formation of secondary 5-3 metal silicide phases. It was found that secondary phase formation is associated with interaction between metal disilicide and refractory oxide particles, as well as, the high-temperature oxidation reactions of metal disilicides with residual oxygen. The increase in the fractions of secondary 5-3 metal silicides was observed for all 60-40 composites with increasing annealing time at 1400°C. The amount of W_5Si_3 phase was significantly higher than that of the Mo_5Si_3 in the composites after annealing for 48 h, but the increased rate highly decreased after 24 h. Therefore, all these composites exhibited enhanced thermal stability at that temperature, particularly after 24 h, without undergoing any decomposition. Additionally, more homogeneous particle distribution was achieved for the MoSi_2 - and WSi_2 -based composites reinforced by coarse-alumina and zirconia. The

SEM and EDS studies demonstrated that the secondary 5-3 metal silicides with a small amount of silica formed mostly around the alumina grains. But the silica phase could not be detected by XRD due to its low amount mostly formed on the surface as a protective layer to further oxidation. Also, it was found that the rate of grain growth could be significantly inhibited by a grain boundary pinning effect. The grain growth rates were lower in the MoSi₂- and WSi₂-based composites reinforced by coarse-grained reinforcements, which explained with their more homogeneous distribution on the grain boundaries and also high aspect ratio. Furthermore, their electrical conductivity decreased with increasing temperature as expected from metal disilicide metallic conductors. At high metal disilicide content, MoSi₂-c.Al₂O₃ and WSi₂-f.Al₂O₃ showed higher electrical conductivity at 900°C. Their electrical properties were found to be highly influenced by density, porosity level, distribution level of particles (homogeneity), intrinsic conductivity of conductive phase, particle size/morphology and fraction of secondary 5-3 silicide phase. In brief, these metal silicide-refractory oxide electroconductive ceramic composites displayed high chemical/thermal stability, low rates of grain growth and high electrical conductivity at high-temperatures (900°-1600°C), which make them very promising materials for advanced sensing applications at high-temperatures and harsh-environments. Further studies are needed to investigate their thermal stability and electrical properties at high-temperatures for longer-terms, and to study the physical properties of 5-3 metal silicide phases for better understanding of the properties/performance of the composites.

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CHAPTER 3: PROCESSING AND PROPERTIES OF NbSi₂ - AND TaSi₂ - OXIDE COMPOSITES

3.1 Introduction

Niobium silicide (NbSi₂) and tantalum silicide (TaSi₂) were previously studied for use in various high temperature structural applications (such as reinforcement for advanced gas turbine and other high-temperature materials) and microelectronic application (such as low-resistance gate and interconnect materials) [1-3]. The high-temperature application of these materials is related to their high melting point (>1930°C), relatively low density, high-temperature oxidation/corrosion resistance and high electrical conductivity [4-6]. Owing to the microelectronics as their major fields of application, electrical transport properties were mostly studied on the thin films of NbSi₂ and TaSi₂ due to the thermodynamic stability of metal disilicides on silicon [7]. In several studies, their thin films were fabricated by utilizing different deposition techniques such as evaporation, cosputtering and chemical vapor deposition, followed by high-temperature heat treatment at different conditions [7-11]. The room-temperature electrical resistivities of the NbSi₂ and TaSi₂ thin films were measured at the ranges of 49.9-203.3 and 35-60 $\mu\Omega\cdot\text{cm}$, respectively, which were highly dependent upon the deposition method, film thickness and annealing temperature [8-10]. Several theoretical studies on the structural stability, mechanical and thermodynamic properties, and experimental high-temperature oxidation studies were also reported for the NbSi₂ and TaSi₂ thin films and monoliths [2,3,5,12,13]. It was demonstrated that the NbSi₂ and TaSi₂ monoliths display relatively lower oxidation resistant than similar disilicides (such as MoSi₂ and WSi₂), since a continuous protective oxide layer like silica (SiO₂) cannot be formed on their surfaces due to the formation of Nb- and Ta-oxides (e.g. NbO₂, Nb₂O₅, Ta₂O₅) [14]. Some other studies reported that the oxidation rate of the TaSi₂ is comparable to that of the MoSi₂, which is known as the most oxidation resistant transition metal silicide at high-temperatures [15,16].

Most of the studies on the NbSi₂ and TaSi₂ were conducted on their various composite forms. The main reasons of focusing on the NbSi₂- and TaSi₂-based composites instead on their monolithic forms were to improve their ductility, fracture toughness (below the ductile-brittle transition temperature), high-temperature strength, oxidation and creep resistance (at high-temperatures) [17-20]. Niobium (Nb) metal is commonly used for reinforcing the niobium silicides (NbSi₂, Nb₅Si₃) to improve their mechanical properties via ductile phase toughening [21,22]. Significant improvements particularly on their mechanical properties were also achieved with the addition of MoSi₂, SiC, Al₂O₃ and WSi₂ reinforcements [4,18,20,23]. However, in the case of TaSi₂-composites, TaSi₂ was mainly utilized as a reinforcement material for enhancing the densification (sinterability), mechanical properties, oxidation resistance and thermal shock behavior of the carbides and borides such as ZrB₂, HfB₂, TaC and HfC [24-27]. Unfortunately, these same compositions were not evaluated for use in high-temperature electronics or sensor interconnect applications. Research has been conducted on other transition metal silicides (MoSi₂, TiSi₂ etc.) and silicide-oxide composites (MoSi₂-Al₂O₃, WSi₂-Al₂O₃ etc.), which showed promising results for electrical applications such as thermocouples and thermistors [15,28-31]. Although NbSi₂ and TaSi₂ are also known as metallic conductors even at elevated temperatures, like most of the transition metal silicides (MoSi₂, WSi₂ etc.) [7,8,11], the high-temperature electrical properties of the bulk NbSi₂- and TaSi₂-based composites have not been investigated for their potential use in advanced sensing applications at high-temperature and harsh-environment conditions. Therefore, this study focuses on the development of NbSi₂- and TaSi₂-oxide electroconductive ceramic composites reinforced by alumina and zirconia particles, and extensive investigation of their sintering/densification, phase development and stability, microstructures, and high-temperature oxidation and electrical properties.

3.2 Experimental

3.2.1 Materials and method

Commercial niobium silicide (NbSi₂, 99.85% metals basis), tantalum silicide (TaSi₂, 99.0% metals basis) and zirconia (ZrO₂, 99+%) as starting powders were purchased

Figure 45. XRD patterns of the commercial (a) niobium disilicide (NbSi_2), and (b) tantalum disilicide (TaSi_2) starting powders.

from Alfa Aesar (Tewksbury, MA). Alumina (Al_2O_3 , 99.8%, SSA: $8.6 \text{ m}^2/\text{g}$) powders purchased from Almatix (Leetsdale, PA) were also used in this study. The Nb_5Si_3 powder (99.5% metals basis, Alfa Aesar) was also used in this study as a reference material system. The close thermal expansion match of Al_2O_3 ($\sim 8.0 \times 10^{-6} \text{ K}^{-1}$) and ZrO_2 ($9.6 \times 10^{-6} \text{ K}^{-1}$) with that of NbSi_2 ($8.4\text{-}11.7 \times 10^{-6} \text{ K}^{-1}$) and TaSi_2 ($\sim 8.9 \times 10^{-6} \text{ K}^{-1}$) in a wide temperature range ($20^\circ\text{-}1070^\circ\text{C}$), and the high-temperature capabilities of these refractory oxides, were major reasons of their selection as reinforcement particles [6]. Phase and microstructural analyses of the starting powders were initially conducted by X-ray diffraction (XRD, Panalytical X'Pert Pro, Westborough, MA) and field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700F, Tokyo, Japan), respectively. For the phase and crystal structure identification, the X'Pert High Score software (Panalytical Inc., Westborough, MA) was used. The ImageJ software [32] was also used to measure the average particle sizes from the SEM microstructures. The XRD patterns of the starting NbSi_2 and TaSi_2 powders are shown in Figure 45. The results clearly displayed that the starting powders are highly pure, since only metal disilicide peaks were identified on their XRD patterns. Both NbSi_2 (#03-065-3551) and TaSi_2 (#01-089-2941) exhibited the hexagonal C40 crystal structure. Additionally, starting Al_2O_3 and ZrO_2 powders exhibited the expected phases with rhombohedral symmetry (#01-078-2427) and monoclinic structure (#00-024-1165), respectively, based on their XRD results (not shown). Figure 46 presents the SEM microstructures of all the starting powders. The NbSi_2 and TaSi_2 powders were found to have random morphology with average particle sizes of 1.4 and $6.4 \text{ }\mu\text{m}$, respectively. Although the NbSi_2 powders (Figure 46a) also consisted of some large particles similar to that of the TaSi_2 (Figure 46b), it is clear that their average particle size was substantially lower than that of the TaSi_2 due to the majority of smaller particles. The Al_2O_3 particles displayed equiaxed morphology with an average size of $0.4 \text{ }\mu\text{m}$ (Fig. 46c), while average size of the ZrO_2 particles having equiaxed and elongated morphology was measured to be $\sim 12.1 \text{ }\mu\text{m}$ (Figure 46d).

Figure 46. SEM microstructures of the commercial (a) NbSi₂, (b) TaSi₂, (c) Al₂O₃, and (d) ZrO₂ starting powders.

Figure 46. (continued) SEM microstructures of the commercial (a) NbSi₂, (b) TaSi₂, (c) Al₂O₃, and (d) ZrO₂ starting powders.

For preparation of the ceramic composites, NbSi₂ and TaSi₂ powders were mixed with refractory oxide reinforcement particles (Al₂O₃ and ZrO₂) by ball-milling in ethanol for 24 h, and then dried at 50°-60°C for 2 h. The NbSi₂-Al₂O₃, TaSi₂-Al₂O₃, NbSi₂-ZrO₂ and TaSi₂-ZrO₂ are composite compositions prepared in this study. The metal silicide-refractory oxide contents were selected as 30-70 and 60-40 volume percentages (vol%) to extensively study these composites at near percolation and above percolation regions, respectively. Therefore, for simplicity, the composites were termed as “30-70” and “60-40” throughout the study. After drying, small (13 mm diameter) and large (26 mm diameter) cylindrical pellets, with ~2-4 mm thickness, were prepared from the as-prepared composite powders using uniaxial pressing (13.8 MPa as applied pressure). The pressed pellets were sintered at 1400°-1600°C using an atmosphere-controlled tube furnace in flowing argon gas at heating and cooling rates of 3°C/min. To study their short- and long-term thermal stability, secondary phase formation, microstructures and high-temperature stability of electrical properties, 60-40 vol% composites previously sintered at 1600°C were further annealed at 1400°C for 24, 48 and 96 h, similarly under argon atmosphere.

3.2.2 Characterization studies

Archimedes method was utilized using ethanol (0.789 g/cm³) for measuring the densities of the sintered composite samples. It is important to note that apparent density and apparent porosity values were used for understanding the densification in different composite systems instead of the relative densities. This was due to the formation of the secondary 5-3 metal silicide phases (Nb₅Si₃ and Ta₅Si₃) during sintering and the significant differences between the theoretical densities of metal disilicides and their 5-3 metal silicide forms, which could be misleading due to the error margins in the theoretical density calculations. After sintering and annealing processes, phase analyses of the composite samples were conducted by X-ray diffraction (XRD, Panalytical X'Pert Pro, Westborough, MA) with CuK_α radiation source. In addition to the XRD analyses, the MAUD software [33] was used to determine the volume percentages of secondary phases within the NbSi₂-Al₂O₃ and NbSi₂-ZrO₂ composite systems via Rietveld method. However, the TaSi₂-based

composites could not be analyzed using the same technique due to lack of a matching Ta_5Si_3 crystallographic information file (CIF) required for the Rietveld analysis. For the microstructural analyses of the composite samples, fine polishing was performed using SiC sanding papers with 600-1200 grits and then applying the diamond paste (0.5 μm) on a polishing cloth (Ted Pella Inc., Redding, CA). Each polishing step was carried out for 5-10 min, followed by ultrasonication in deionized water for 15 min. After the sample preparation, a field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700F, Tokyo, Japan) was used to analyze the cross-sectional microstructures of the as-polished composite samples.

For the oxidation studies, very small rectangular pellets having 0.1-0.3 cm^2 surface area were prepared via cutting and polishing processes, and their dimensions (width $\times$ length $\times$ height) were measured before oxidation tests for their surface area calculations. The high-temperature oxidation studies of these composite samples were conducted using a thermogravimetric analyzer (TGA, Pyris 1, PerkinElmer, Shelton, CT) in flowing air (20 ml/min). The samples were heated from 50°C to 800°C with a heating rate of 10°C/min, and the mass changes (mg/cm^2) were calculated using the recorded mass changes and the calculated specific sample surface areas. The high-temperature electrical measurements were completed using a high-purity four-bore alumina tube and platinum (Pt) wires (99.95% pure). The rectangular bar samples ($\sim 20 \times 4 \times 4$ mm) prepared for the standard electrical measurements (ASTM B193-16) [34] were connected to the test setup, which was then carefully sealed in a high-temperature tube furnace. These measurements were performed up to 900°-1000°C in argon for avoiding the potential materials degradation. The electrical resistance was measured using a digital multimeter (Keithley 2100, Tektronix, Beaverton, OR), and recorded as a function of temperature by LabVIEW (National Instruments, Austin, TX) and Keithley software. Lastly, the specific sample dimensions were used to calculate the electrical conductivity of the composite samples.

3.3 Results and Discussion

3.3.1 Densification as a function of composition and temperature

The NbSi₂- and TaSi₂-based composites with the addition of Al₂O₃ and ZrO₂ particles, all having 30-70 and 60-40 volume percentages, were sintered at three different temperatures ranging from 1400°C to 1600°C. Their apparent densities and porosities were measured to investigate their densification as a function of composition (volume percentage, type of oxide/silicide phase) and increasing sintering temperature. The apparent densities of these composites are listed in Table 8. At the 30-70 volume percentages, the apparent density of the NbSi₂-Al₂O₃ and TaSi₂-Al₂O₃ composites increased with increasing sintering temperature from 1400°C to 1500°C, but then decreased to the lower values at 1600°C. A similar trend was also observed for the NbSi₂-Al₂O₃, TaSi₂-Al₂O₃ and TaSi₂-ZrO₂ composites, which have 60-40 volume percentages. The decreased apparent densities for these composites, particularly from 1500°C to 1600°C, could be attributed to the decreased porosity levels and enhanced densification at high sintering temperature. On the other hand, no significant changes were observed in the apparent densities of all NbSi₂-ZrO₂ and 30-70 TaSi₂-ZrO₂ composites at 1500°-1600°C.

To understand the densification of these composites better, their apparent porosity levels are presented as percentages (%) in Figure 47 as a function of sintering temperature. At 1400°C, the apparent porosity levels were found to be above 22.1% for all the composites except for the 60-40 NbSi₂-Al₂O₃, since it revealed ~16.1% porosity at the same temperature. With increasing sintering temperature from 1400° to 1500°C, significant reductions in the porosity levels ranging from 3.73 to 8.27% were achieved for the NbSi₂-Al₂O₃, NbSi₂-ZrO₂ and TaSi₂-Al₂O₃ composites all having 30-70 volume percentages. However, only a 0.19-0.79% decrease was observed at the same temperature range for the same compositions, but all having the 60-40 volume percentages. The apparent porosity levels were also reduced for all the composites by 2.70-13.5% with increasing sintering temperature from 1500° to 1600°C, but this decrease was drastic (10.3-13.5%) only for the 30-70 NbSi₂-Al₂O₃, 30-70 TaSi₂-Al₂O₃ and 60-40 TaSi₂-Al₂O₃ composites. The lowest

Table 8. Apparent density of the NbSi₂- and TaSi₂-based composites with the addition of Al₂O₃ and ZrO₂ particles, as function of the sintering temperature.

Composite	Apparent density (g/cm ³)		
	1400°C	1500°C	1600°C
30-70 NbSi₂-Al₂O₃	4.41	4.49	4.25
60-40 NbSi₂-Al₂O₃	4.81	5.04	4.98
30-70 NbSi₂-ZrO₂	5.74	5.84	5.83
60-40 NbSi₂-ZrO₂	5.74	5.75	5.75
30-70 TaSi₂-Al₂O₃	5.38	5.53	5.28
60-40 TaSi₂-Al₂O₃	6.85	7.02	6.66
30-70 TaSi₂-ZrO₂	6.78	6.92	6.88
60-40 TaSi₂-ZrO₂	7.64	7.94	7.60

porosity levels were achieved (5.15-7.70%) for the NbSi₂-Al₂O₃ and TaSi₂-Al₂O₃ composites both with 30-70 volume percentages at 1600°C (Figure 47(a-b)). It can also be clearly seen that porosity levels of the silicide-alumina composites were significantly lower than that of the silicide-zirconia composites in all cases. The silicide-zirconia composites displayed porosity levels higher than 25.8% even at 1600°C.

As a review, these results demonstrated that the particle packing and densification kinetics were highly improved by lowering the metal silicide content (60 to 30 vol%) and/or increasing the refractory oxide (40 to 70 vol%) content within these composite systems. It is apparent that the particle packing was substantially enhanced with the addition of 70 vol% alumina particles to the NbSi₂ and TaSi₂, which acted as reinforcement particles in these cases. This could be directly related to the initial agglomeration of the fine

Figure 47. Apparent porosity levels (%) of the (a) NbSi₂-based, and (b) TaSi₂-based composites with the addition of the Al₂O₃ and ZrO₂ particles, as a function of sintering temperature.

alumina particles ($\sim 0.4 \mu\text{m}$) and high metal silicide/alumina particle size ratios ($\text{NbSi}_2/\text{Al}_2\text{O}_3 \approx 3.5$; $\text{TaSi}_2/\text{Al}_2\text{O}_3 \approx 16.0$). It was reported that reinforcement particle size, reinforcement/matrix particle size ratio and volume percentages could highly affect the densification rate of the composite systems during high-temperature sintering [35-37]. Yan et al. reported that the densification rate of the composites could be positively affected by increasing the reinforcement/matrix particle size ratio and decreasing the volume percentage of the reinforcement particles [38]. They also presented that the retarding effect was lower in the case of second phase particle agglomeration at high volume percentage (20 vol%), indicating the adverse effect of the homogeneous particle distribution and increased number of dissimilar grain contacts ($\text{NbSi}_2\text{-Al}_2\text{O}_3$ and $\text{TaSi}_2\text{-Al}_2\text{O}_3$) within the microstructure on the densification. Since the local densification kinetics were also more favored with the existence of agglomerated alumina grains and related single-phase grain boundary regions, the combination of all these parameters significantly enhanced the densification of the $\text{NbSi}_2\text{-Al}_2\text{O}_3$ and $\text{TaSi}_2\text{-Al}_2\text{O}_3$ composites not only at the 30-70 volume percentages, but also at the 60-40. These results were also found to be highly consistent with our previous study on the $\text{MoSi}_2\text{-}$ and $\text{WSi}_2\text{-oxide}$ composites [30]. On the other hand, significantly high porosity levels and low densification for the silicide-zirconia composites at all sintering temperatures could be correlated to lower metal silicide/zirconia particle size ratios ($\text{NbSi}_2/\text{ZrO}_2 \approx 0.1$; $\text{TaSi}_2/\text{ZrO}_2 \approx 0.5$) and insufficient sintering kinetics for the ZrO_2 having the higher melting point. That could be also interrelated with the microcracks that may form within these composite microstructures due to reversible monoclinic-tetragonal phase transformation of zirconia near 1170°C [39], since it was reported by Skandan et al. [40] that a 4.5% strain formed during this martensitic transformation may cause microcracking.

3.3.2 Phase development and stability at high-temperatures

The phase development within the $\text{NbSi}_2\text{-}$ and $\text{TaSi}_2\text{-based}$ composites (60-40 volume percentages) with the addition of 40 vol% alumina and zirconia particles was examined after sintering at 1600°C for 2 h in argon due to the enhanced densification and

Figure 48. XRD patterns of the (a) 60-40 NbSi₂-based, and (b) 60-40 TaSi₂-based composites, with the addition of 40 vol% Al₂O₃ and ZrO₂ particles, sintered at 1600°C for 2 h in argon.

lower porosity levels achieved at that temperature. Figure 48 displays the XRD patterns of the (a) NbSi₂-based and (b) TaSi₂-based composites sintered at 1600°C. For the NbSi₂-Al₂O₃ and NbSi₂-ZrO₂ composites, the XRD peaks detected at 2θ of 25.4°, 40.0° and 46.9° corresponds to the hexagonal NbSi₂ phase, and its major diffraction peaks for the (101), (111) and (112) planes, respectively. The peaks attributed to the Al₂O₃ and ZrO₂ as refractory oxides can be also seen in Figure 48(a), having the corundum and monoclinic crystal structures, respectively. In addition, these XRD results revealed the formation of an intermediate Nb₅Si₃ phase with the hexagonal structure during high-temperature sintering as a result of the diffraction peaks detected at 2θ of 36.4°, 40.4°, 41.5° and 41.9° corresponding to the (210), (211), (300) and (112) planes, respectively. It is also apparent that Nb₅Si₃ peaks are more intense in the NbSi₂-Al₂O₃ than the NbSi₂-ZrO₂ composite after sintering at 1600°C, indicating its higher volume percentage within the NbSi₂-Al₂O₃. Similarly, the XRD patterns of the TaSi₂-Al₂O₃ and TaSi₂-ZrO₂ composites exhibited the existence of an intermediate Ta₅Si₃ phase with the hexagonal structure, along with the hexagonal-structured TaSi₂ and refractory oxides (Al₂O₃, ZrO₂) (Figure 48(b)). The monoclinic structure was also identified for the zirconia phase. The most intense peaks of the TaSi₂ phase were detected at 2θ of 25.4°, 34.9°, 40.1° and 47.0° reflecting the (011), (012), (111) and (112) planes, respectively. The major diffraction peaks of the hexagonal Ta₅Si₃ phase were found to be situated at 2θ of 29.2°, 36.5° and 42.0°, corresponding to the (111), (120) and (112) planes, respectively. In contrast with the NbSi₂-based composites, the intermediate Ta₅Si₃ diffraction peaks are relatively more intense in the TaSi₂-ZrO₂ compared to the TaSi₂-Al₂O₃ composite system after sintering.

It is known that the transition metal disilicides studied for high-temperature applications exhibit two crystal structures, which are C11_b body-centered tetragonal (MoSi₂, WSi₂ etc.) and C40 hexagonal (NbSi₂, CrSi₂, TaSi₂ etc.) [1,2,17]. However, some studies reported that the transition metal silicides having the 5-3 stoichiometry, such as Nb₅Si₃, Ta₅Si₃ and Mo₅Si₃, also possess higher melting points (Nb₅Si₃: 2515°C; Ta₅Si₃: 2550°C), good thermal stability, sufficient mechanical properties and high creep resistance at

elevated temperatures [5,19,22]. Based on the Nb-Si and Ta-Si binary phase diagrams, both the Nb₅Si₃ and Ta₅Si₃ intermediate phases can similarly exist in the two tetragonal equilibrium forms (α -Nb₅Si₃, β -Nb₅Si₃, etc.) and one metastable hexagonal form [21,41-43]. The structure of the intermediate Nb₅Si₃ and Ta₅Si₃ phases formed during sintering at 1600°C was identified as hexagonal in this study. It was demonstrated that these 5-3 metal silicides, having the hexagonal structure, could be observed in the presence of impurities such as carbon, boron, nitrogen and oxygen, which tend to stabilize their hexagonal form instead of the tetragonal [42,44]. Therefore, the formation of Nb₅Si₃ and Ta₅Si₃ phases in the hexagonal form could be an indication of the existence of impurities in small amounts that could not be detected within the NbSi₂- and TaSi₂-based composites by XRD. This could be caused by a small degree of impurities that may potentially exist within the starting silicide and/or oxide powders (e.g. Hf in the commercial ZrO₂), or entrapped oxygen in the pore structures. Similar types of observations regarding the formation of such hexagonal intermediate 5-3 silicide phases both in bulk and thin film samples were reported in several studies [24,25,42,44,45]. In the case of their formation mechanism, metal disilicides (NbSi₂, TaSi₂) could interact with residual oxygen that remained in the starting silicide powders, or was entrapped within the pores during processing of the composites. It is known that NbSi₂ and TaSi₂, like most of the transition metal disilicides, will react with oxygen at high-temperatures to form their 5-3 metal silicide and SiO₂ phases [18,24,30,46].

In addition to the phase development within the NbSi₂- and TaSi₂-based composites during high-temperature sintering, their short- and long-term phase (thermal) stability is very crucial for their potential use in high-temperature sensing applications required for long operation with high thermal stability and measurement accuracy [47-49]. Therefore, the high temperature phase stability studies were also performed on the NbSi₂- and TaSi₂-based composites after further annealing at 1400°C for 24, 48 and 96 h in argon. Their XRD patterns after high-temperature annealing are presented in Figure 49, focusing on the 2 θ region ranging from 20° to 50° due to the major diffraction peaks of the disilicides and 5-3 silicides. For all these composites, the most intense peaks were found to be attributed to

Figure 49. XRD patterns of the (a) NbSi₂-Al₂O₃, (b) NbSi₂-ZrO₂, (c) TaSi₂-Al₂O₃, and (d) TaSi₂-ZrO₂ composites with the addition of 40 vol% alumina and zirconia particles, all further annealed at 1400°C for 24, 48 and 96 h in argon.

Figure 49. (continued) XRD patterns of the (a) NbSi₂-Al₂O₃, (b) NbSi₂-ZrO₂, (c) TaSi₂-Al₂O₃, and (d) TaSi₂-ZrO₂ composites with the addition of 40 vol% alumina and zirconia particles, all further annealed at 1400°C for 24, 48 and 96 h in argon.

metal disilicides (NbSi_2 , TaSi_2) and refractory oxides (Al_2O_3 , ZrO_2). Additionally, the intermediate 5-3 metal silicide phases (Nb_5Si_3 , Ta_5Si_3) existed within the composite systems after annealing up to 96 h, similar to the XRD results after sintering. An increase in the peak intensities of the 5-3 metal silicide phases was also detected for all these composites as a function of annealing time; however, it was found to be more significant within the 60-40 NbSi_2 - ZrO_2 and TaSi_2 - ZrO_2 composites (Figure 49(b-d)) compared to the other composite systems consisting of alumina particles (Figure 49(a-c)). These results clearly demonstrated that the NbSi_2 - and TaSi_2 -based composites did not undergo any compositional (thermal) decomposition at 1400°C within the time period ranging from 24 to 96 h. The detected peak intensity changes may imply relative increments in the volume percentages of the 5-3 silicide phases as a function of annealing time. In addition, more significant intensity changes for the silicide-zirconia composites may be related to more interaction of these metal disilicides with zirconia particles at high-temperatures due to their coarser grain size. Significantly higher porosity levels (27.6-30.6%) existing in the silicide-zirconia composites could also possibly lead to further reaction of the NbSi_2 and TaSi_2 with residual oxygen at high-temperatures resulting in more 5-3 silicide formation with increased annealing time. No study was reported on the thermal stability of the NbSi_2 - and TaSi_2 -oxide composites, and there is only a limited number of papers discussing the solid-state synthesis (e.g. combustion, mechanical alloying) and mechanical characterization of the NbSi_2 - and TaSi_2 -alumina composites [17,20,50].

To understand the change in the amounts of these 5-3 metal silicide phases, 60-40 NbSi_2 -based composites were examined by applying the Rietveld refinement method on the XRD patterns of the composites after both sintering and annealing processes at high temperatures. It is important to note that the TaSi_2 -based composites could not be similarly studied here, due to the lack of the crystallographic information file (CIF) for the Ta_5Si_3 phase in the related databases. As the main parameters of the Rietveld analysis, the goodness-of-fit (sig) and percentage weighted profile R-factor (R_{wp}) were determined as 1.48-2.06 and 1.86-4.47, respectively, indicating the high quality of the Rietveld refinement

Figure 50. Changes in the volume percentage of the Nb₅Si₃ secondary phase within the 60-40 NbSi₂-Al₂O₃ and NbSi₂-ZrO₂ composites as a function of annealing time.

[33]. Figure 50 shows the changes in the amount of the secondary Nb₅Si₃ phase within the 60-40 NbSi₂-Al₂O₃ and 60-40 NbSi₂-ZrO₂ composites as a function of annealing time. The refinement parameters were found to be relatively higher than the required values for the 60-40 NbSi₂-Al₂O₃ annealed at 1400°C for 24 h; therefore, only its quantitative phase analysis data is not presented here. The starting data points represented at “0 hour” annealing time in Figure 50 correspond to the volume percentages of the Nb₅Si₃ phase within these composites only after sintering (with no annealing). The amount of the Nb₅Si₃ phase in the NbSi₂-Al₂O₃ (32.7 vol%) was substantially higher than that in the NbSi₂-ZrO₂ composite (26.4 vol%) after sintering at 1600°C. It is apparent that the amount of the Nb₅Si₃ phase increased with increasing annealing time up to 96 h for all NbSi₂-based

composites. While its volume percentage increased from 32.7 to 36.0 vol% within the 60-40 NbSi₂-Al₂O₃ composite, this increase was found to be from 26.4 to 35.1 vol% for the 60-40 NbSi₂-ZrO₂ composite. Therefore, the level of increase was significantly higher within the NbSi₂-ZrO₂ system, particularly at the annealing period from 0 to 48 h. In addition, it can be clearly seen from Figure 50 that the rate of increase decelerated after 48 h of annealing. However, the Rietveld results displayed close amounts of the Nb₅Si₃ phase for the NbSi₂-Al₂O₃ and NbSi₂-ZrO₂ composites after annealing at 1400°C for 96 h. It should be also noted that the Nb₅Si₃ became the major silicide phase within these composites after 48 h of annealing. As a review, the increase in the amount of the Nb₅Si₃ phase within the NbSi₂-ZrO₂ composite as a function of time was found to be mostly related to its higher porosity level (27.6%) compared to the NbSi₂-Al₂O₃ composite (11.8%), since it possibly increased the oxygen diffusion into the composite from residual sources, and thus, more favored the reaction of the NbSi₂ phase with oxygen at high-temperatures. The slower kinetics for high-temperature oxidation reactions and related formation of the Nb₅Si₃ phase observed after 48 h could be related to the reduced amount of open surface area of the NbSi₂ phase over time due to the initial formation of the Nb₅Si₃ phase and silica layer at grain boundaries and surface [46]. Similar trends may be also assumed for the formation of the Ta₅Si₃ phase within TaSi₂-Al₂O₃ and TaSi₂-ZrO₂ composite systems, since our previous study [30] on the MoSi₂- and WSi₂-oxide composites also demonstrated such trends for the 5-3 metal silicide phase formation as a function of annealing time at high-temperatures.

3.3.3 Microstructural evolution at high-temperatures

The microstructures of the NbSi₂- and TaSi₂-based composites were analyzed after sintering and further annealing processes, to investigate the particle distribution, microstructural evolution and secondary phase formation within these systems. Figure 51 presents the backscattered SEM microstructures of these composites with the addition of 40 vol% refractory oxide after sintering at 1600°C for 2 h in argon at relatively low magnifications. In the NbSi₂-Al₂O₃ microstructure, gray and dark regions refer to the NbSi₂

Figure 51. Low magnification backscattered SEM microstructures of the (a) NbSi₂-Al₂O₃, (b) NbSi₂-ZrO₂, (c) TaSi₂-Al₂O₃, and (d) TaSi₂-ZrO₂ composites with the addition of 40 vol% Al₂O₃ and ZrO₂ particles after sintering at 1600°C for 2 h in argon.

Figure 51. (continued) Low magnification backscattered SEM microstructures of the (a) NbSi₂-Al₂O₃, (b) NbSi₂-ZrO₂, (c) TaSi₂-Al₂O₃, and (d) TaSi₂-ZrO₂ composites with the addition of 40 vol% Al₂O₃ and ZrO₂ particles after sintering at 1600°C for 2 h in argon.

and Al_2O_3 grains, respectively (Figure 51(a)). It was observed that the micron-sized niobium silicide grains were homogeneously distributed between the insulating alumina grains. However, three different phases can be clearly seen within the microstructure of the as-sintered $\text{NbSi}_2\text{-ZrO}_2$ composite, where the bright, gray and dark regions indicate Nb_5Si_3 , ZrO_2 and NbSi_2 grains, respectively (Figure 51(b)). It was found that the intermediate Nb_5Si_3 grains (bright regions) were formed mostly around the NbSi_2 grains (dark regions), which resulted in the formation of different interfaces ($\text{NbSi}_2\text{-Nb}_5\text{Si}_3$ and $\text{Nb}_5\text{Si}_3\text{-ZrO}_2$) and $\text{NbSi}_2\text{-ZrO}_2\text{-Nb}_5\text{Si}_3$ triple phase boundaries. Additionally, it should be noted that the Nb_5Si_3 grains and their formation from the NbSi_2 grain boundaries could positively affect the percolation and electrical properties within the composite. The SEM microstructure of the $\text{TaSi}_2\text{-Al}_2\text{O}_3$ displayed only two phases with a homogeneous distribution at low magnification (Figure 51(c)). Similar results were also observed for the microstructure of the $\text{TaSi}_2\text{-ZrO}_2$ composite (Figure 51(d)). In the TaSi_2 -based composites, the gray and dark regions refer to the TaSi_2 and refractory oxide (Al_2O_3 , ZrO_2) grains, respectively. As a review, all these composites generally exhibited homogeneous distribution of the conductive metal silicide phases within the insulating oxides, which could positively affect the electrical percolation and reduce the critical percolation concentration [28,51]. Besides, except for the $\text{NbSi}_2\text{-ZrO}_2$, intermediate 5-3 metal silicide phases were not detected in the other microstructures by SEM under relatively low magnifications.

Additionally, microstructures of these composites were examined at higher magnifications to better characterize the 5-3 metal silicide formation. Figure 52 shows the high magnification backscattered SEM microstructures of the NbSi_2 - and TaSi_2 -based composites with the addition of 40 vol% refractory oxides after sintering at 1600°C . For the NbSi_2 -based composites, the intermediate Nb_5Si_3 phases formed during high temperature sintering can be observed in the bright regions as presented on the microstructures (Figure 52(a-b)). Similarly, the intermediate Ta_5Si_3 phases were also detected for the TaSi_2 -based composites at high magnifications as seen in Figure 52(c-d). The presence of the 5-3 metal silicide phases was additionally identified by utilizing the energy dispersive spectroscopy

Figure 52. High magnification backscattered SEM microstructures of the (a) NbSi₂-Al₂O₃, (b) NbSi₂-ZrO₂, (c) TaSi₂-Al₂O₃, and (d) TaSi₂-ZrO₂ composites with the addition of 40 vol% Al₂O₃ and ZrO₂ particles after sintering at 1600°C for 2 h in argon.

Figure 52. (continued) High magnification backscattered SEM microstructures of the (a) NbSi₂-Al₂O₃, (b) NbSi₂-ZrO₂, (c) TaSi₂-Al₂O₃, and (d) TaSi₂-ZrO₂ composites with the addition of 40 vol% Al₂O₃ and ZrO₂ particles after sintering at 1600°C for 2 h in argon.

(EDS) on the related regions of the microstructures. The average weight percentages of niobium (Nb) and silicon (Si) elements in the bright microstructural areas of the NbSi₂-based composites were measured as 82.3 and 17.7 wt%, respectively. For the TaSi₂-based composites, the EDS quantification results revealed 91.0 wt% of tantalum (Ta) and 9.0 wt% of Si elements for the related bright regions. These results clearly demonstrated the formation of these intermediate phases in 5-3 stoichiometry, as previously supported with the XRD results. Furthermore, it could be proposed based on the SEM/EDS results that the 5-3 metal silicide phases started to form at the metal disilicide-oxide grain boundaries, and then continued to grow towards the metal disilicide grains. This formation could be attributed to the reaction of the metal disilicides with the entrapped or grain boundary diffused oxygen from environmental sources at high temperatures [18,24,46]. These results hereby demonstrated that the intermediate 5-3 silicide phase formation was predominantly controlled by high-temperature oxidation reactions of the metal disilicides. This also resulted in the reduction of the volume percentages of the metal disilicides; and thus, the increase in the amount of the 5-3 metal silicide phases within these composite systems as a function of increasing temperature (above 1000°C) and hold time. This correlates well with the previously discussed XRD/Rietveld results. The formation of the secondary Nb₅Si₃ phase was similarly presented by Binbin et al. [12] within a microstructure of the dense monolithic NbSi₂ sample, which was prepared by self-propagating high-temperature synthesis followed by hot pressing. Its formation was explained with the loss of silicon from the NbSi₂ phase in that study. The secondary Ta₅Si₃ phase was identified within the HfB₂-TaSi₂ composite by electron diffraction, which was also correlated to the removal of the oxide phases controlled by the high-temperature oxidation reaction of the TaSi₂ [24].

The microstructural evolution and intermediate 5-3 silicide phase formation was further investigated after annealing of the composites at high-temperature up to 96 h. The SEM microstructures of the NbSi₂- and TaSi₂-based composites having 40 vol% oxide additions, which were annealed at 1400°C for 48 and 96 h, are presented in Figure 53. The SEM images are denoted by the (a1-b1-c1-d1), representing their microstructures after

Figure 53. SEM microstructures of the (a1-a2) NbSi₂-Al₂O₃, (b1-b2) NbSi₂-ZrO₂, (c1-c2) TaSi₂-Al₂O₃, and (d1-d2) TaSi₂-ZrO₂ composites with addition of 40 vol% Al₂O₃ and ZrO₂ particles after annealing at 1400°C for 48 and 96 h in argon, respectively. (a1-b1-c1-d1: after annealing for 48 h; a2-b2-c2-d2: after annealing for 96 h).

Figure 53. (continued) SEM microstructures of the (a1-a2) NbSi₂-Al₂O₃, (b1-b2) NbSi₂-ZrO₂, (c1-c2) TaSi₂-Al₂O₃, and (d1-d2) TaSi₂-ZrO₂ composites with addition of 40 vol% Al₂O₃ and ZrO₂ particles after annealing at 1400°C for 48 and 96 h in argon, respectively. (a1-b1-c1-d1: after annealing for 48 h; a2-b2-c2-d2: after annealing for 96 h).

Figure 53. (continued) SEM microstructures of the (a1-a2) NbSi₂-Al₂O₃, (b1-b2) NbSi₂-ZrO₂, (c1-c2) TaSi₂-Al₂O₃, and (d1-d2) TaSi₂-ZrO₂ composites with addition of 40 vol% Al₂O₃ and ZrO₂ particles after annealing at 1400°C for 48 and 96 h in argon, respectively. (a1-b1-c1-d1: after annealing for 48 h; a2-b2-c2-d2: after annealing for 96 h).

Figure 53. (continued) SEM microstructures of the (a1-a2) NbSi₂-Al₂O₃, (b1-b2) NbSi₂-ZrO₂, (c1-c2) TaSi₂-Al₂O₃, and (d1-d2) TaSi₂-ZrO₂ composites with addition of 40 vol% Al₂O₃ and ZrO₂ particles after annealing at 1400°C for 48 and 96 h in argon, respectively. (a1-b1-c1-d1: after annealing for 48 h; a2-b2-c2-d2: after annealing for 96 h).

annealing for 48 h, while the (a2-b2-c2-d2) images refer to the microstructures after annealing for 96 h. The presence of the Nb_5Si_3 phase can be seen within the microstructures of the NbSi_2 -based composites after annealing for 48 and 96 h (a1-a2-b1-b2 in the Figure 53). The significant formation of the Nb_5Si_3 phase was clearly observed within the NbSi_2 - Al_2O_3 composite after annealing for 48 h (Figure 53(a1)), indicating the substantial amount present within the composite systems. As seen in Figure 53(a2), the Nb_5Si_3 phase started to form at the NbSi_2 - Al_2O_3 grain boundaries and around the pores (shown with arrows), and continued to grow as a function of time as the niobium disilicide reacted with residual oxygen sources at high-temperature conditions. Similarly, it was observed that after annealing for 48-96 h, the Ta_5Si_3 phase formed and started to grow from the tantalum disilicide-alumina and tantalum disilicide-zirconia grain boundaries (c1-c2-d1-d2 in the Figure 53). The Ta_5Si_3 layer can be seen between the tantalum disilicide and zirconia grains after annealing for 96 h (Figure 53(d2)), where it formed due to the high-temperature oxidation of the tantalum disilicide phase. Furthermore, the SEM studies displayed the presence of some microcracks within the Nb_5Si_3 and Ta_5Si_3 grains for NbSi_2 - ZrO_2 and TaSi_2 - Al_2O_3 composites after annealing (b1-c2 in the Figure 53). However, the level of microcracking within the Ta_5Si_3 grains was detected to be substantial for the TaSi_2 - ZrO_2 composite, particularly after annealing at 1400°C for 48 h as denoted by the dashed circles in Figure 53(d1). It may be proposed that these cracks were due to the thermal expansion mismatch of the intermediate 5-3 silicide phases with metal disilicides and oxides, and related to the thermal stresses generated during long-term, high-temperature annealing [52,53]. This could be a serious issue for the TaSi_2 - ZrO_2 composites owing to the extent of the thermal stress-induced microcracking. Due to the formation of these intermediate 5-3 metal silicide phases, different interfaces (NbSi_2 - Nb_5Si_3 , Nb_5Si_3 - ZrO_2 , TaSi_2 - Ta_5Si_3 , Ta_5Si_3 - Al_2O_3 etc.) and triple phase boundaries (e.g. TaSi_2 - Al_2O_3 - Ta_5Si_3) can be also seen within these composite microstructures. Such microstructural changes should be carefully taken into consideration for further discussions, since high-temperature properties of these composites can be highly influenced by these grain boundaries.

3.3.4 High-temperature oxidation behavior

Most of the transition metal silicides (e.g. MoSi_2) are known for their excellent oxidation resistance at very high-temperatures (above $\sim 1000^\circ\text{C}$). However, at relatively low temperatures ($\sim 450^\circ\text{C}$ - 900°C) most of the silicides (MoSi_2 , WSi_2 , NbSi_2 etc.) undergo pest oxidation, which is commonly described as an accelerated internal oxidation resulting in a dramatic structural disintegration from the dense solid monolith into a powder form after being exposed to an air atmosphere for a short period of time [54,55]. The presence of defects, microcracks, internal stresses and pores was found to be the major factors affecting the pest oxidation. Since a majority of the studies were focused on the pesting phenomenon within the molybdenum disilicide system, similar oxidation studies for the NbSi_2 and TaSi_2 have received less attention. It was reported that the pest oxidation occurs at 700°C - 750°C and $\sim 800^\circ\text{C}$ - 950°C for the NbSi_2 and TaSi_2 , respectively [12,56,57]. However, it should be noted that no clear information was found in the literature for the temperatures, where the pest oxidation initially starts for these silicides. To overcome these oxidation issues, alloying with different materials (Al, Ti, Cr etc.) for forming a protective oxide layer, and applying oxidation resistant coatings have been extensively investigated as the main approaches for high-temperature structural applications over the years [58-60]. In addition, fabricating these silicide bulk materials with a less number of defects, such as pores and microcracks, is known as another way of controlling their pest oxidation.

To understand the influence of the processing parameters and the addition of the refractory oxide phases on the pest oxidation, the thermogravimetric analyses (TGA) were conducted in ambient air atmosphere at the temperatures reaching 800°C on the as-sintered NbSi_2 - and TaSi_2 -based composites, as well as, the as-sintered metal silicides (NbSi_2 , Nb_5Si_3 , TaSi_2). The composition, volume percentage of oxide phase (40 and 70 vol%) and sintering temperature (1400°C - 1600°C) were extensively studied. Figure 54 shows the mass change per unit surface area (mg/cm^2) of the various NbSi_2 - and TaSi_2 -based composites as a function of oxidation temperature. The temperature axes were all kept in the temperature range of 500°C - 800°C , since an insignificant oxidation ($< 0.18 \text{ mg}/\text{cm}^2$) was detected at the

Figure 54. Oxidation-induced mass change per unit surface area (mg/cm^2) of the various NbSi_2 - and TaSi_2 -based composites in air as a function of oxidation temperature, sintering temperature (*denoted in parenthesis*) and silicide-oxide volume ratio.

Figure 54. (continued) Oxidation-induced mass change per unit surface area (mg/cm^2) of the various NbSi₂- and TaSi₂-based composites in air as a function of oxidation temperature, sintering temperature (*denoted in parenthesis*) and silicide-oxide volume ratio.

temperatures below 500°C for all the composites presented. For all the NbSi₂-Al₂O₃ and NbSi₂-ZrO₂ composites, the mass changes were found to be less than 1.0 mg/cm² at the temperatures below 625°-645°C (Figure 54(a-b)). It demonstrated that the oxidation rates for the NbSi₂-based composites were significantly low below these temperatures, indicating that their pest oxidation slowly started at around 550°-600°C. The mass changes of these NbSi₂-based composites relatively increased up to ~700°C; however, drastic increments were observed at the oxidation temperatures ranging from 700° to 800°C, only except for the 30-70 NbSi₂-Al₂O₃ composite sintered at 1600°C (solid green curve in Figure 54(a)). Furthermore, it is apparent for the NbSi₂-Al₂O₃ composites that the increasing sintering temperature (from 1400°C to 1600°C) and volume percentage of the alumina phase (from 40 to 70 vol%) reduced the overall mass change and pest oxidation at 750°-800°C. This effect was determined to be more significant for the NbSi₂-Al₂O₃ composites sintered at 1600°C, since the overall mass change at 800°C decreased from 12.3 to 1.2 mg/cm² (by 90.2%) with increasing the alumina content from 40 to 70 vol% (Figure 54(a)). No pest oxidation was observed until ~770°C for the 30-70 NbSi₂-Al₂O₃ composite sintered at 1600°C. On the other hand, similar improvements were not achieved for the pest oxidation of the NbSi₂-ZrO₂ composites, as seen in Figure 54(b). Due to the higher pest oxidation temperature of the tantalum silicide system, substantially lower mass changes (≤ 1.15 mg/cm²) were detected for the TaSi₂-based composites throughout the oxidation temperature range (Figure 54(c-d)). The oxidation-induced mass changes of the TaSi₂-Al₂O₃ composites were relatively lower with increasing sintering temperature and alumina content, but only at the sintering temperatures of 1400°C and 1600°C. These composites sintered at 1500°C exhibited similar oxidation behavior, as clearly presented in Figure 54(c). Similar to the 30-70 NbSi₂-Al₂O₃, a significant decrease in the overall mass change from 0.66 to 0.27 mg/cm² (by 59.1%) was observed at 800°C for the TaSi₂-Al₂O₃ composite with increasing the volume percentage of alumina phase (green curves in the Figure 54(c)). These changes were found to be less significant for the TaSi₂-ZrO₂ composites. Also, surprisingly for the individual silicide-zirconia systems, their 60-40

composites that were sintered at 1600°C oxidized relatively more at 750°-800°C than their other composites even sintered at lower temperatures (Figure 54(b-d)).

Additionally, highly pure NbSi₂, Nb₅Si₃ and TaSi₂ pellets were similarly sintered at 1600°C in argon, and their pest oxidation behavior was then compared with the composites sintered at the same temperature. Their mass changes per unit surface area (mg/cm²) are presented in Figure 55, similarly as a function of the oxidation temperature. The pest oxidation of the NbSi₂ and Nb₅Si₃ was observed particularly at the temperatures ranging from 700° to 800°C. However, it was determined that the pest oxidation of the Nb₅Si₃ was more drastic than that of the NbSi₂. The oxidation-induced mass changes for the NbSi₂ and Nb₅Si₃ were measured at 800°C as 8.3 and 17.3 mg/cm², respectively, implying the negative influence of the Nb₅Si₃ phase formation on the pest oxidation of the composites. In addition, in the pest oxidation region, all NbSi₂-ZrO₂ composites and 60-40 NbSi₂-Al₂O₃ displayed lower mass changes than the Nb₅Si₃, but relatively higher than the NbSi₂ (Figure 55(a)). The pest oxidation of the niobium silicide phases was highly eliminated by the 30-70 NbSi₂-Al₂O₃ composite, proving the positive influence of the refractory alumina addition on their oxidation behavior. In comparison to the NbSi₂ and Nb₅Si₃, the oxidation-induced mass change at 800°C was reduced by 85.8 and 93.2%, respectively, with the addition of 70 vol% alumina phase. Similarly, all the TaSi₂-based composites except for the 30-70 TaSi₂-Al₂O₃ oxidized relatively higher than the TaSi₂ at the temperatures ranging from 650°-800°C (Figure 55(b)). There was also a 24.4% reduction in the overall mass change at 800°C for the 30-70 TaSi₂-Al₂O₃ composite compared to the TaSi₂.

As a review of the oxidation studies, increasing sintering temperature and volume percentage of the refractory oxide phase reduced the pest oxidation of the NbSi₂-Al₂O₃ and TaSi₂-Al₂O₃ composites. The lowest oxidation-induced mass changes were achieved by these composites sintered at 1600°C with 70 vol% alumina. The pest oxidation of these composites was also found to be lower than their dense monolithic metal silicides. This could be correlated to the lower porosity levels identified for these composites (5.2-7.7%)

Figure 55. Comparison of the oxidation-induced mass changes (mg/cm²) of the (a) NbSi₂-based composites with NbSi₂ and Nb₅Si₃, and (b) TaSi₂-based composites with TaSi₂, all sintered at 1600°C in argon, as a function of the oxidation temperature.

and reduced oxygen diffusion rates due to the refractory oxide addition. The increase in the sintering temperature reduced the amount of porosity at different levels, and thus, relatively lowered the pest oxidation. However, this effect was more significant in the silicide-alumina composites, particularly at 30-70 volume percentages. Significant changes in the pest oxidation behavior of the silicide-zirconia composites were not similarly observed by adjusting the processing parameters. This could be explained with significantly higher porosity levels within these composites, since they all exhibited above 25.8% porosity at all sintering temperatures. When the porosity levels were above 8.4%, the positive effect of refractory oxide phase addition was also not observed. These results clearly show that the key factor for reducing the pest oxidation rates is low porosity levels and improved densification, since it is apparent that the accelerated oxygen diffusion through the pores and/or across the pore surfaces is the main mechanism of the pest oxidation. The pre-existing microcracks and grain boundaries were additionally described as major oxidation sites within the microstructures causing the pest oxidation of these silicide systems [12,54,56,61]. It is important to note that volume percentages of the intermediate 5-3 metal silicide phases should be also considered due to their different oxidation rates compared to their disilicide forms. Since the Nb_5Si_3 oxidizes faster than NbSi_2 , oxidation rates of the composites could drastically increase over time when the diffusing oxygen reaches the Nb_5Si_3 grains and NbSi_2 - Nb_5Si_3 grain boundaries. The relatively high level of oxidation of the TaSi_2 -based composites (except for the 30-70 TaSi_2 - Al_2O_3) compared to the TaSi_2 may be also correlated to the presence of the intermediate Ta_5Si_3 phase possibly having poorer oxidation resistance. In conclusion, even though the pest oxidation of the metal silicides was highly reduced by fabricating the NbSi_2 - and TaSi_2 -based composites with the addition of 70 vol% alumina phase, further studies need to be performed since surface oxide layers formed (Nb_2O_5 , Ta_2O_5 etc.) did not completely eliminate further oxidation over time [55,57,62]. Strategies for controlled pest formation (pre-oxidation) to produce a more stable and dense protective surface layer should be further investigated to improve the chemical stability at high-temperatures.

3.3.5 High-temperature electrical properties

The electrical properties of these composites were also investigated at high temperatures in this study. It should be noted that the electrical conductivity data is presented in the temperature ranges of 400°-900°C for the metal silicides and the 60-40 composites, and 100°-900°C for the 30-70 composites in this study. The reason is that the very low resistance, and thus high electrical conductivity values above ~2100 S/cm, limited the accurate measurements at lower temperatures. In addition, the Pt-wire/ink electrical connections were lost at around 900°-950°C, which may be related to the local reactions between metal disilicides and platinum resulting in the formation of a low-melting point platinum silicide phase (e.g. PtSi) on the surface of the bulk sample [30,63]. Prior to the electrical measurements of the NbSi₂- and TaSi₂-based composites, the electrical conductivities of the monolithic NbSi₂, Nb₅Si₃ and TaSi₂ samples, that were sintered at 1600°C without addition of any refractory oxide phase, are presented in Figure 56 as a reference data. The electrical conductivity of the composites decreased with increasing temperature with a metallic-type trend for all compositions [11,64]. The results demonstrated that the electrical conductivity of the NbSi₂ decreased from 163.3 to 42.3 S/cm with increasing temperature from 500°C to 900°C, whereas this decrease was from 353.8 to 41.5 S/cm for the TaSi₂ at the same temperature range. The room-temperature bulk resistivities of the NbSi₂ (24.5-50.4 μΩ.cm) and TaSi₂ (38-46 μΩ.cm) were also reported similar to each other by Chow and Steckl [9]. On the other hand, the Nb₅Si₃ displayed a linear trend as a function of temperature, since its electrical conductivity decreased from 233.6 to 152.1 S/cm with increasing temperature from 500°C to 900°C. It can be concluded that the Nb₅Si₃ has substantially higher electrical conductivity than the NbSi₂ and TaSi₂ at the elevated temperatures above ~530°C. Therefore, the continued formation of the intermediate 5-3 metal silicide phases within the disilicide composition may lead to a complex electrical network that evolves with high-temperature oxidation. The conductivity may decrease (or increase) depending upon the change in percolation of the 5-3 metal silicide phases within the microstructure over time.

Figure 56. Electrical conductivity of the dense monolithic NbSi₂, Nb₅Si₃ and TaSi₂ as a reference data, all sintered at 1600°C in argon, as a function of the temperature (Electrical conductivity data is shown on the logarithmic scale).

The electrical conductivity results of the NbSi₂- and TaSi₂-based composites, that were sintered at 1600°C, are presented in Figure 57 as a function of temperature. At the 60-40 volume percentages, NbSi₂-Al₂O₃ and NbSi₂-ZrO₂ composites showed similar electrical conductivities at the temperatures ranging from 450° to 900°C (Figure 57(a)). The electrical conductivities of the 60-40 NbSi₂-Al₂O₃ and NbSi₂-ZrO₂ composites at 900°C were found as 107.3 and 111.3 S/cm, respectively. However, 60-40 TaSi₂-ZrO₂ composite exhibited significantly lower electrical conductivity than all of the other 60-40 composites throughout the same temperature range. At 900°C, the TaSi₂-Al₂O₃ and TaSi₂-ZrO₂ composites with the 60-40 volume percentages revealed 87.3 and 25.9 S/cm, respectively. Furthermore, at the 30-70 volume percentages, the TaSi₂-Al₂O₃ composite showed higher

Figure 57. Electrical conductivity of the NbSi₂- and TaSi₂-based composites having (a) 60-40 and (b) 30-70 metal silicide-refractory oxide volume percentages, all sintered at 1600°C in argon, as a function of the temperature (*Electrical conductivity data is shown on the logarithmic scale*).

electrical conductivity than the NbSi₂-Al₂O₃ at the temperature range of 100°-900°C, as clearly seen in Figure 57(b). The electrical conductivities of the 30-70 NbSi₂-Al₂O₃ and TaSi₂-Al₂O₃ composites were measured at 900°C as 5.3 and 16.3 S/cm, respectively. It is important to note that the electrical conductivities of the 30-70 NbSi₂-ZrO₂ and TaSi₂-ZrO₂ composites are not presented here, since their electrical conductivity data could not be recorded at the temperatures above 450°-500°C due to their high brittleness and related sample cracking during measurements at elevated temperatures.

As a review, it was demonstrated that the 60-40 NbSi₂-Al₂O₃ and NbSi₂-ZrO₂ composites revealed significantly higher electrical conductivities (107.3-111.3 S/cm) than the monolithic NbSi₂ (42.3 S/cm) at 900°C. This result clearly indicated the positive influence of the intrinsic electrical conductivity of the intermediate Nb₅Si₃ phase (152.1 S/cm at 900°C) on the electrical properties of these composites, which included 26.4-32.7 vol% Nb₅Si₃ phase based on the Rietveld data. Although the 60-40 NbSi₂-ZrO₂ composite had higher level of porosity (27.6%), it still displayed a slightly higher electrical conductivity than the 60-40 NbSi₂-Al₂O₃ at high temperatures. For the TaSi₂-based composites with 60-40 volume percentages, TaSi₂-Al₂O₃ exhibited substantially higher electrical conductivity (87.3 S/cm) than the TaSi₂-ZrO₂ (25.9 S/cm) and monolithic TaSi₂ (41.5 S/cm) at 900°C. It was found that the high porosity level (30.6%) within the 60-40 TaSi₂-ZrO₂ composite adversely affected its electrical properties at high-temperatures. It should be noted that these results may also be influenced by the unknown intrinsic electrical conductivity of the intermediate Ta₅Si₃ phase and microstructural homogeneity. The distribution of the silicide phases will drastically affect the three-dimensional electrical network that controls electron movement through the composite [28,51]. Due to the low porosity levels (5.2-7.7%), the electrical percolation was achieved even at 30-70 metal silicide-oxide volume percentages. The electrical conductivities of the 30-70 NbSi₂-Al₂O₃ and TaSi₂-Al₂O₃ were found to be relatively lower than that of the monolithic metal silicides at high-temperatures. The higher electrical conductivity achieved by the 30-70 TaSi₂-Al₂O₃ composite could be an indication of a higher level of percolation formed

within this composite system. Therefore, these NbSi₂- and TaSi₂-based composites displayed promising high-temperature electrical properties at low and high metal silicide volume percentages. As discussed, the physical properties of the composites at high temperatures were found to be highly influenced by porosity levels, volume percentages of the intermediate 5-3 metal silicide phases (Nb₅Si₃, Ta₅Si₃) and microstructural homogeneity or percolation.

3.4 Conclusions

The NbSi₂- and TaSi₂-based electroconductive ceramic composites were fabricated with the addition of 40 and 70 vol% refractory oxides (Al₂O₃, ZrO₂). The particle packing and densification of the composites were enhanced by lowering the metal silicide and/or increasing the oxide phase, as well as, increasing the sintering temperature. Significant improvements were particularly achieved for the silicide-alumina composites due to the higher silicide/alumina particle size ratios and local densification kinetics favored by the single-phase grain boundary regions such as silicide-silicide and oxide-oxide. The insufficient sintering kinetics and phase transformation-induced microcracking adversely affected the densification of the silicide-zirconia composites. The formation of the intermediate Nb₅Si₃ and Ta₅Si₃ phases during high-temperature sintering and annealing processes was found to be related to the interaction of starting metal disilicides with residual oxygen that remained in the starting silicide powders, and was entrapped within the pores or diffused from environmental sources. It was proposed that these 5-3 silicide phases were initially formed at the metal disilicide-oxide grain boundaries, and predominantly controlled by their high-temperature oxidation reactions. Furthermore, the presence of microcracks was detected particularly within the silicide-zirconia composites after long-term (48-96 h) high-temperature annealing, which was attributed to the thermal expansion mismatch of the 5-3 silicide phases with that of the metal disilicides and oxides and thermal stresses generated at high-temperatures. The increasing sintering temperature and volume percentage of the oxide phase highly reduced the pest oxidation, particularly for the silicide-alumina composites, which exhibited even lower mass changes than their

monolithic metal silicides. It was determined that the oxygen diffusion through the pores, grain boundaries and microcracks resulted in an increase of the internal oxidation. Due to the metallic conducting behavior of these transition metal silicides, the electrical conductivities of these composites decreased with increasing temperature. In addition, the high-temperature electrical conductivities of these composites at 900°C ranged from 5.3 to 111.3 S/cm depending on the silicide-oxide volume percentages, which were highly affected by porosity levels, volume percentages of the conductive silicide phases and microstructural homogeneity (percolation). In conclusion, particularly the NbSi₂-Al₂O₃ and TaSi₂-Al₂O₃ ceramic composites exhibited very promising results for their use in high temperature advanced electronic and sensing applications owing to their phase and microstructural stability, reduced oxidation rates and high electrical conductivities at elevated temperatures. However, further studies are needed to investigate the influence of the intermediate 5-3 metal silicide phases on the properties of the composites, and to further improve their high-temperature oxidation resistance by enhancing the densification and/or the quality of the protective surface oxide layer.

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CHAPTER 4: PROCESSING AND PROPERTIES OF CHROMIUM SILICIDE-BASED COMPOSITES

4.1 Introduction

The various transition metal silicides show both metallic and covalent bonding within their structures, resulting in a variety of physical properties [1,2]; thus, they exhibit different electrical properties ranging from semiconducting to metallic, which makes them interesting materials for electronic applications. The chromium-silicon (Cr-Si) material system displays great potential for high-temperature electrical applications, such as thermoelectrics and interconnects, due to the promising electrical properties, high melting points ($>1410^{\circ}\text{C}$), and structural and thermal stability of the binary chromium silicide compounds [3,4]. The binary phases of the Cr-Si system are listed as CrSi_2 , Cr_3Si , Cr_5Si_3 and CrSi ; previous research studies primarily focused on the former three silicides.

Among these binary compounds, chromium disilicide (CrSi_2) is the most extensively studied phase for high-temperature thermoelectric applications. Like some of the other disilicides (e.g. MnSi_2), this phase demonstrates chemical/thermal stability, high melting temperature (1490°C), semiconducting nature, large power factor and low toxicity [4-6]. It is known as a p-type degenerate semiconductor with a narrow band gap of ~ 0.30 eV and a relatively high Seebeck coefficient (S) of $\sim 90 \mu\text{V/K}$ [4,7,8]. Although its high S and low electrical resistivity are advantageous for thermoelectric applications, it was intensively reported that the thermal conductivity of the CrSi_2 should be reduced to increase its thermoelectric figure-of-merit (ZT) and performance [6,9,10]. Therefore, many attempts have been made using different approaches such as grain size reduction, stoichiometry adjustment and doping over the years. In addition, several studies presented that the CrSi_2 exhibits a high oxidation resistance in oxygen-rich atmospheres at temperatures up to $725^{\circ}\text{-}1000^{\circ}\text{C}$ with a very low mass gain owing to the formation of chromium oxide (Cr_2O_3) and amorphous silica (SiO_2) phases as a protective surface layer

[8,11,12]. Its sufficient mechanical properties and high creep resistance at elevated temperatures were also noted as advantages for their potential use in thermoelectrics, as well as, high temperature structural applications in aggressive environments.

The Cr_3Si and Cr_5Si_3 compounds are classified as metallic conductors, with relatively higher melting temperatures (1680°C - 1770°C) than chromium monosilicide and disilicide [3,13,14]. These chromium silicides have been mainly described as promising candidates for the high temperature structural applications, such as aircraft engines and aerospace gas turbines, due to their higher melting points, high stiffness, excellent high-temperature oxidation and corrosion resistance [15-18]. However, their low fracture toughness and ductility at room- and moderately high-temperatures were identified as major issues that needed to be addressed before their use in such industrial applications. Therefore, several methods such as secondary ductile phase addition (e.g. chromium), solid solution alloying and impurity reduction were applied only to the Cr_3Si system [17,19]. It was also determined that the Cr_3Si compound exhibits an excellent oxidation resistance at temperatures up to 1000°C with a very low specific mass change $\leq 0.5 \text{ mg/cm}^2$ even after 100 h exposure to air [16,20]. Unfortunately, high-temperature oxidation behavior of the Cr_5Si_3 compound has not been reported yet, since the limited studies for this compound typically focus on the synthesis, mechanical and electrical properties of the single crystal and thin film forms [2,18,21]. The electrical properties of the Cr_3Si and Cr_5Si_3 compounds were only reported using the thin films by Mazzega et al. [2]. They studied their electrical properties at temperatures up to 827°C ; they reported the electrical resistivities for the Cr_3Si and Cr_5Si_3 thin films to be ~ 95.0 and $\sim 170.0 \text{ } \mu\Omega\cdot\text{cm}$, respectively. However, no study reported the electrical properties of the bulk forms of these two chromium silicides. This is surprising, since these compositions display substantially high electrical conductivity values at elevated temperatures, and thus, great potential for the high-temperature electrical applications, such as interconnects and advanced sensors. The Cr_3Si and Cr_5Si_3 phases were reportedly synthesized by a variety of methods from chromium (Cr) and silicon (Si) metals or powders using arc melting, double-cathode glow discharge

and electron beam evaporation techniques [2,16,22,23]. Unlike the CrSi_2 compound, the Cr_3Si and Cr_5Si_3 powders are not commercially available to the authors' knowledge.

In summary, different chromium silicide compounds present a unique combination of properties and electrical characteristics, which make them highly useful for a broad range of high-temperature electrical applications ranging from thermoelectric devices to advanced physical sensors. However, there are very limited studies conducted on their electrical properties, oxidation behavior and stability at high-temperatures, particularly for the Cr_3Si , Cr_5Si_3 and CrSi compounds, since the main attention has been given to the CrSi_2 phase and related thermoelectric applications. Therefore, in this study, various composite materials were fabricated by solid-state sintering of chromium silicide and chromium oxide powders at high temperature. The main purpose was to achieve highly stable, oxidation resistant and electrically conductive composites, which are composed of conductive chromium silicide phases and high-temperature refractory phases (e.g. chromia, silica), for their particular use in high-temperature applications. The phase development and stability, microstructure, oxidation behavior and electrical properties of the composites were extensively investigated at elevated temperatures.

4.2 Experimental

4.2.1 Materials and method

Commercial chromium silicide (CrSi_2 , 99+%) and chromium (III) oxide (Cr_2O_3 , 98+%) powders were selected as precursor materials, which were purchased from Alfa Aesar (Tewksbury, MA). The starting powders were initially characterized by x-ray diffraction (XRD, Panalytical X'Pert Pro, Westborough, MA). Figure 58 displays the XRD pattern of the chromium silicide powder. X'Pert High Score software (Panalytical Inc., Westborough, MA) was used for phase and crystal structure identification. It was determined that starting chromium silicide powder consisted of two different silicide phases, which are hexagonal-structured CrSi_2 (#98-062-6776, P6_222) and cubic CrSi (#98-001-6837, P2_13). In addition, the XRD result (not shown) of the starting chromium oxide

Figure 58. XRD pattern of the commercial chromium silicide starting powder.

powder displayed the expected Cr₂O₃ phase with a rhombohedral structure (#01-084-0312, R-3c).

The composite powder mixtures were prepared by ball-milling the appropriate amounts of the chromium silicide and oxide starting powders in ethanol (200 proof) for 24 h, followed by a drying step at around 60°C for 4 h. The amounts of the powders were all determined based on volume percentage (vol%), and the volume percentages of the chromium silicide phase ranged from 40 to 90 vol% within the composites. For simplicity, the composites were described by abbreviations including the first letters and initial volume percentages of the powders throughout the paper, as presented in Table 9. For example, a (40-60) vol% chromium silicide-chromium oxide (CC) composite was labeled as “CC-4060”. The as-prepared powder mixtures were uniaxially pressed (~ 13.8 MPa) into

Table 9. Compositions and denotations of the chromium silicide-based composites.

Amount of starting chromium silicide powder (vol%)	Amount of starting chromium oxide powder (vol%)	Composite sample denotation
40	60	CC-4060
50	50	CC-5050
55	45	CC-5545
60	40	CC-6040
65	35	CC-6535
70	30	CC-7030
80	20	CC-8020
90	10	CC-9010

cylindrical pellets with 13-26 mm diameter and 2-4 mm thickness by using a stainless-steel die. The pellets were then placed in an alumina crucible and sintered at 1370°C for 2 h in a tube furnace under flowing argon gas (50 sccm). The heating and cooling rates were kept constant at 3°C/min for all sintering experiments. Also, several CrSi₂ pellets were sintered under similar conditions as baseline samples for comparison. After sintering, selected composite samples were additionally annealed at 1350°C for 24-96 h to further study the phase stability, microstructural changes, oxidation behavior and electrical properties at elevated temperatures.

4.2.2 Characterization

The phase analyses of the composite samples were performed after sintering and annealing by x-ray diffraction (Panalytical X'Pert Pro, Westborough, MA) with a CuK_α radiation source. Prior to the microstructural analyses, the composite samples were

prepared by fine polishing with silicon carbide (SiC) polishing sheets (600-1200 grits) and lastly diamond paste (0.5 μm). After each polishing step, the as-polished sample surfaces were cleaned by 10 min of ultrasonication in deionized water and ethanol, respectively. The cross-sectional microstructure and elemental analyses were conducted using a field-emission scanning electron microscopy (FE-SEM, Hitachi S-4700F, Tokyo, Japan). For the high-temperature oxidation studies, very small square or rectangular pellets with a surface area ranging from 0.09 to 0.20 cm^2 were prepared by cutting and fine polishing with a 600 grit SiC polishing sheet, followed by sample cleaning in ethanol by ultrasonication. The dimensions of the as-prepared composite samples were measured before oxidation experiments to calculate their surface areas, which are required to determine the oxidation-induced specific mass changes. The non-isothermal oxidation tests of the chromium silicide-based composite samples were performed in air atmosphere at temperatures from 50°C to 870°C using a thermogravimetric analyzer (TGA, Pyris 1, PerkinElmer, Shelton, CT) with a heating rate of 10°C/min. In addition, the isothermal oxidation studies were conducted at 850°C in air, but the samples were heated to that temperature in an argon atmosphere. The volumetric flow rates of the air and argon were kept constant at 20 ml/min during the oxidation tests. For the standard electrical measurements (ASTM B193-16) [24], rectangular bar samples with dimensions of $\sim 20 \times 4 \times 4$ mm were prepared, and then attached to the test setup made from a high-purity four-bore alumina tube and platinum (Pt) wires (99.95% pure, 0.28 mm diameter, Surepure Chemetals, Florham Park, NJ). The test setup was then sealed in a high-temperature tube furnace to perform the high-temperature electrical measurements up to 870°-1000°C in argon atmosphere. Additionally, a B-type thermocouple was inserted into the furnace to record the testing temperature during the experiments. The electrical resistance of the samples was measured as a function of temperature using a digital multimeter (Keithley 2100, Tektronix, Beaverton, OR) directly connected to the LabVIEW (National Instruments, Austin, TX) and Keithley software. Their electrical conductivities were lastly calculated using the recorded resistance data and specific sample dimensions.

4.3 Results and Discussion

4.3.1 Phase development via solid-state reactions

The phase development within the chromium silicide-based composites was investigated after sintering of the various particulate mixtures at 1370°C leading to the solid-state reactions between starting chromium silicide and chromium oxide phases. Figure 59(a-b) present the XRD patterns of the as-sintered chromium silicide-based composites, which are all entitled by volume percentages of the starting powders (e.g. CC-4060, CC-5545) as described in the experimental section. The XRD result of the CC-4060 composite revealed that $\text{Cr}_{0.91}\text{Si}_{0.09}$ and silica (SiO_2) phases were formed as a result of the solid-state reactions between 40 vol% chromium silicides (CrSi , CrSi_2) and 60 vol% chromium oxide (Cr_2O_3). The diffraction peaks of the cubic-structured $\text{Cr}_{0.91}\text{Si}_{0.09}$ phase (#98-010-8354, space group: $\text{Im}\bar{3}\text{m}$) were detected at 2θ of 44.5°, 64.7° and 81.9° corresponding to the (011), (002) and (112) planes, respectively. It should be noted that the $\text{Cr}_{0.91}\text{Si}_{0.09}$ is not a common silicide phase, since it was reported only by studies on the chromium-silicon phase relations [13] and the high-temperature corrosion of nickel alloy including chromium [25]. Additionally, it was found that the diffraction peaks at the 2θ of 22.0°, 31.5° and 36.1° displayed the formation of the SiO_2 phase in the low-cristobalite (or α -cristobalite) form with a tetragonal structure and space group of P4_12_12 , which is known as the low temperature phase of the cristobalite structure [26]. For the CC-5050 composite, the XRD peaks detected at 2θ of 39.4°, 44.3° and 48.8° corresponded to the cubic Cr_3Si phase (#98-062-6771, space group: $\text{Pm}\bar{3}\text{n}$), and its major diffraction peaks for the (002), (012) and (112) planes, respectively. The low-cristobalite SiO_2 phase was also observed within the CC-5050 composite after sintering. Therefore, it is apparent that the chromium silicide phase completely changed from $\text{Cr}_{0.91}\text{Si}_{0.09}$ to Cr_3Si with increasing volume percentage of starting chromium silicide by 10 vol% (from 40 to 50 vol%), as expected due to the increased silicon (Si) amount reacting with the Cr_2O_3 . The XRD pattern of the CC-5545 composite revealed a similar result with the CC-5050 composite, since the major diffractions peaks of Cr_3Si and low-cristobalite SiO_2 phases were observed. However, the presence of Cr_5Si_3 and CrSi_2 phases was additionally detected for the CC-5545 composite

Figure 59. XRD patterns of the (a) CC-4060, CC-5050, CC-5545 and CC-6040, and (b) CC-6535, CC-7030, CC-8020 and CC-9010 chromium silicides-based composites, which were all sintered at 1370°C for 2 h in argon.

with the additional 5 vol% increase in starting chromium silicide powder. The XRD peaks detected at 2θ of 43.7° , 44.2° and 45.3° were attributed to the tetragonal-structured Cr_5Si_3 (#98-062-6793, space group: $I4/mcm$), and its (022), (240) and (141) planes, respectively. The CC-6040 composite exhibited a more complex structure, where four different chromium silicide phases (Cr_3Si , Cr_5Si_3 , CrSi , CrSi_2) were detected along with the low-cristobalite SiO_2 and initial phases. The presence of starting chromium silicide phases (cubic- CrSi , hexagonal- CrSi_2) and chromium oxide (Cr_2O_3) within the CC-6040 composite implied a partial solid-state reaction during sintering resulting in the formation of new metal silicide phases (Cr_3Si , Cr_5Si_3) and unreacted phases. The increased peak intensities of the Cr_5Si_3 compared to that of the CC-5545 composite imply that there is a concentration increase of this phase in the CC-6040 composite (Figure 59a). The XRD results of the CC-6040 and CC-6535 composites were found to be quite similar, since they both displayed structures consisting of four different silicide phases (Cr_5Si_3 , Cr_3Si , CrSi , CrSi_2) and the low-cristobalite SiO_2 phase. However, no remaining Cr_2O_3 phase was observed for the CC-6535 composite after sintering. For the CC-7030 composite, Cr_5Si_3 and low-cristobalite SiO_2 phases were detected along with the unreacted CrSi and CrSi_2 phases. It is clear that no Cr_3Si phase was formed within the composites when starting with a metal silicide content above 65 vol%. On the other hand, for the CC-8020 and CC-9010 composites, solid-state reactions resulted only in the formation of low-cristobalite silica minor phase due to the small amount of Cr_2O_3 to be reacted with the starting silicides. The major phases within these composites were similarly identified as CrSi and CrSi_2 after sintering (Figure 59b). In addition, a small amount of unreacted Cr_2O_3 was detected in the CC-9010 composite.

As a review of the XRD results, high-temperature solid-state reactions between the initial Cr_2O_3 and CrSi_2 (with the presence of CrSi phase) mixed phases resulted in the formation of different chromium silicides (Cr_3Si , Cr_5Si_3 , $\text{Cr}_{0.91}\text{Si}_{0.09}$) and the low-cristobalite phase depending on the volume percentages of the starting metal silicide and oxide powders. For all initial compositions, the Cr_2O_3 phase completely disappeared after

thermal processing. In the CC-4060 composite with a 40 vol% initial silicide content, the major silicide phase was found to be $\text{Cr}_{0.91}\text{Si}_{0.09}$. For the composites with the initial silicide contents ranging from 50 to 65 vol%, Cr_3Si and Cr_5Si_3 phases were formed. The homogeneity ranges (*nonstoichiometry range* or *difference between maximum and minimum concentration of Si in a Cr-silicide phase*) for the Cr_3Si and Cr_5Si_3 phases were reported based on the atomic percentage of silicon (Si) as 22.5-26.4 and 36.0-41.0 at.% Si, respectively [3,13]. This indicated that the starting silicon content within the CC-5050 was in the homogeneity range of Cr_3Si phase, since initial chromium silicides reacted with Cr_2O_3 to form Cr_3Si and SiO_2 . However, the increased volume percentage of the starting metal silicide from 50 to 65 vol% resulted in a sufficient increase in the at% of Si within the composite, which caused a shift towards the right side of the Cr-Si phase diagram from the homogeneity range of Cr_3Si (22.5-26.4 at.% Si). Since the Cr_3Si and Cr_5Si_3 phases coexisted within the CC-5545, CC-6040 and CC-6535 composites, the amount of reacted silicon within these composites ranged from 26.4 to 36.0 at.%. There was no formation of Cr_3Si and Cr_5Si_3 phases when the starting silicide content was above 70 vol%, as expected based on the Cr-Si phase diagram and the homogeneity ranges of these two equilibrium phases (≥ 50 at.% Si) [3]. These results clearly demonstrated that the type of chromium silicide phases and their amounts within the composites could be controlled via high-temperature solid-state reaction by adjusting the volume percentages of starting chromium silicide and chromium oxide powders. It should be noted that this knowledge is very beneficial for producing composite materials composed of different chromium silicides, silica and chromium oxide in a controlled manner, which could provide a variety of physical properties depending on the major silicide phases formed via solid-state reactions.

4.3.2 Composite microstructures after solid-state reactions

The microstructural development within the chromium silicide-based composites was examined after the solid-state reactions occurred during high-temperature sintering at 1370°C. The SEM microstructures of the CC-4060, CC-5050, CC-5545 and CC-6040 composites are shown in Figure 60. The homogeneous distribution of the $\text{Cr}_{0.91}\text{Si}_{0.09}$ phase

Figure 60. SEM microstructures of the (a1-a2) CC-4060, (b1) CC-5050, (c1-c2) CC-5545 and (d1-d2) CC-6040 chromium silicides-based composites after sintering at 1370°C for 2 h in argon.

Figure 60. (continued) SEM microstructures of the (a1-a2) CC-4060, (b1) CC-5050, (c1-c2) CC-5545 and (d1-d2) CC-6040 chromium silicides-based composites after sintering at 1370°C for 2 h in argon.

Figure 60. (continued) SEM microstructures of the (a1-a2) CC-4060, (b1) CC-5050, (c1-c2) CC-5545 and (d1-d2) CC-6040 chromium silicides-based composites after sintering at 1370°C for 2 h in argon.

Figure 60. (continued) SEM microstructures of the (a1-a2) CC-4060, (b1) CC-5050, (c1-c2) CC-5545 and (d1-d2) CC-6040 chromium silicides-based composites after sintering at 1370°C for 2 h in argon.

(bright regions) within the low-cristobalite SiO₂ grains (dark regions) was clearly observed for the CC-4060 composite, as displayed in Figure 60(a1-a2). Similarly, CC-5050, CC-5545 and CC-6040 composites all revealed highly homogeneous microstructures, where the bright and dark regions refer to chromium silicide phases and low-cristobalite SiO₂, respectively (Figure 60(b1-c1-d1)). The Cr₃Si and SiO₂ phases were detected for the CC-5050 composite (Figure 60(b1)), which was found to be consistent with the previously discussed XRD data. The composition of the chromium silicide phase was also identified as Cr₃Si (86.0 wt% Cr + 14.0 wt% Si) based on the quantitative EDS analysis (not shown). Although the CC-5545 composite seemed to be a two-phase system based on its low magnification SEM image (Figure 60(c1)), it is apparent that chromium silicide grains were composed of two different phases as detected at a higher magnification. As also supported with the EDS analyses, the brighter, gray and dark regions corresponded to Cr₃Si, Cr₅Si₃

and SiO₂ grains, respectively (Figure 60(c2)). These results are in good correlation with the XRD data of the CC-5545 composite; however, unreacted CrSi₂ phase, which was detected by XRD, was not observed in the SEM microstructures, indicating its very low concentration remained after sintering. Two major phases (Cr₅Si₃, SiO₂) can be clearly seen within the microstructures of the CC-6040 composite after sintering as shown in Figure 60(d1-d2). Although the XRD analysis also demonstrated the presence of Cr₃Si, CrSi₂, CrSi and Cr₂O₃ as minor phases, they could not be observed in their microstructures probably due to their small amounts and lack of color contrast between different chromium silicide grains. In addition, Figure 61 presents the SEM microstructures of the CC-6535, CC-7030, CC-8020 and CC-9010 composites after sintering at 1370°C. The homogeneous distribution of the chromium silicide phases within the grain boundary silica phase can be similarly seen for all these composites. However, the reduced amount of the silica phase was observed particularly within the microstructures of the composites (CC-8020, CC-9010) including the high amount of starting metal silicide content (≥ 80 vol%) due to their solid-state reaction only with low chromia content (Figure 61(c1-d1)). Although the XRD data demonstrated the presence of Cr₅Si₃, Cr₃Si, CrSi, CrSi₂ and SiO₂, only two phases were observed within the microstructures of the CC-6535 composite (Figure 61(a1-a2)). For the CC-7030 composite, the SEM microstructure displayed three different phases (CrSi, Cr₅Si₃, SiO₂) as shown in Figure 61(b1). This was found to be consistent with the XRD data; however, unreacted CrSi₂ phase was not detected by SEM due to its small concentration that remained after sintering. The SEM microstructures of the CC-9010 composite clearly revealed three different phases (CrSi, CrSi₂, SiO₂), as supported with the XRD and EDS analyses (Figure 61(d1-d2)). These results indicated that a small portion of starting chromium silicides (CrSi, CrSi₂) partially reacted with 10-20 vol% Cr₂O₃ phase only to form silica in low-cristobalite structure as a grain boundary phase.

As a review of the composite microstructures achieved after solid-state reaction, it can be concluded that different chromium silicide phases were homogeneously distributed within the grain boundary silica phase for all the composite systems. This could be highly

Figure 61. SEM microstructures of the (a1-a2) CC-6535, (b1) CC-7030, (c1) CC-8020 and (d1-d2) CC-9010 chromium silicides-based composites after sintering at 1370°C for 2 h in argon.

Figure 61. (continued) SEM microstructures of the (a1-a2) CC-6535, (b1) CC-7030, (c1) CC-8020 and (d1-d2) CC-9010 chromium silicides-based composites after sintering at 1370°C for 2 h in argon.

Figure 61. (continued) SEM microstructures of the (a1-a2) CC-6535, (b1) CC-7030, (c1) CC-8020 and (d1-d2) CC-9010 chromium silicides-based composites after sintering at 1370°C for 2 h in argon.

advantageous for achieving a better electrical network (percolation) and consistent electrical properties within the electroconductive composite systems composed of both conductive and insulating materials [27,28]. It was demonstrated that CC-4060 and CC-5050 composites are two-phase systems consisting of a single chromium silicide phase ($\text{Cr}_{0.91}\text{Si}_{0.09}$, Cr_3Si) and a silica grain boundary phase. However, other composite systems displayed more complex microstructures owing to the presence of at least two different chromium silicide phases (e.g. Cr_5Si_3 , CrSi) along with the silica and some unreacted phases. Therefore, the formation of different grain boundary structures within these composites (e.g. CrSi-CrSi_2 , $\text{Cr}_5\text{Si}_3\text{-CrSi}$, $\text{Cr}_3\text{Si-Cr}_5\text{Si}_3$) could significantly influence their physical properties. It is also clear that all chromium silicide-based composites had a certain amount of porosity within their microstructures after sintering. In addition, grain boundaries of the chromium silicide grains were found to be highly smooth (not angular), particularly at the regions where the chromium silicide grains were in contact with the silica phase. The presence of highly rounded silicide grains can be clearly seen. This result implied the presence of an additional amorphous (glassy) silica phase at the grain boundaries, which highly wetted the chromium silicide grains and provided the formation of rounded grains by lowering the silicide-silica interfacial energy. Similar observation was reported for the rounded zirconia grains due to the presence of glassy silica phase at grain boundaries [29]. This could be also attributed to the formation of the silica phase in cristobalite form, its metastable nature and related phase transitions. It is known that the cristobalite structure undergoes phase transformations during both cooling and heating at around 275°C (*low-cristobalite* $\leftrightarrow$ *high-cristobalite* or α -*cristobalite* $\leftrightarrow$ β -*cristobalite*) [26,30,31]. This tetragonal-cubic transition was reported to be rapid and reversible, but it could create up to $\sim 2.8\%$ change in volume (contraction or expansion), which may affect the microstructures.

4.3.3 High-temperature non-isothermal oxidation of the composites

The thermogravimetric analyses (TGA) were performed in ambient air at the temperatures ranging from 50°C to 870°C on the as-sintered chromium silicide-based

composites, as well as, the as-sintered starting chromium silicide (mixture of CrSi_2 and CrSi). Figure 62(a-c) present their specific mass changes per unit surface areas (mg/cm^2) as a function of oxidation temperature. The oxidation-induced mass change for the CC-4060 composite, which is a mixture of $\text{Cr}_{0.91}\text{Si}_{0.09}$ and SiO_2 , was less than $0.10 \text{ mg}/\text{cm}^2$ up to $\sim 450^\circ\text{C}$, but starting from this point, it relatively increased to the level of $0.63 \text{ mg}/\text{cm}^2$ with increasing temperature to 870°C . This implied that the $\text{Cr}_{0.91}\text{Si}_{0.09}$ phase could oxidize at relatively higher rate at temperatures above 450°C , since the specific mass change at $\sim 855^\circ\text{C}$ was found to be six times higher than that at 450°C (Figure 62(a)). The CC-5050, CC-5545 and CC-6040 composites displayed a similar type of oxidation behavior, since their specific mass changes were measured to be less than $0.24 \text{ mg}/\text{cm}^2$ at the temperatures below 700°C (Figure 62(a-b)). However, a notable increase ($+0.25$ - $0.34 \text{ mg}/\text{cm}^2$) was observed in their oxidation at the temperatures ranging from 700°C to 870°C . The oxidation-induced mass changes at 870°C for the CC-5050, CC-5545 and CC-6040 composites were 0.47 , 0.58 and $0.40 \text{ mg}/\text{cm}^2$, respectively, indicating their relatively lower oxidation kinetics compared to the CC-4060 composite. Similarly, a negligible oxidation with mass changes less than $0.18 \text{ mg}/\text{cm}^2$ was detected for the CC-6535 and CC-7030 composites at the temperatures below 700°C as shown in Figure 62(b). Their specific mass changes increased at higher temperatures; however, the level of increase was two times higher in the CC-7030 composite ($+0.38 \text{ mg}/\text{cm}^2$) compared to the CC-6535 composite ($+0.19 \text{ mg}/\text{cm}^2$). The oxidation-induced mass changes at 870°C for the CC-6535 and CC-7030 composites were 0.35 and $0.56 \text{ mg}/\text{cm}^2$, respectively. The non-isothermal oxidation behavior of the CC-8020 and CC-9010 composites was different compared to the above-mentioned composites, but quite similar to the as-sintered chromium silicide reference sample (mixture of $\text{CrSi}_2 + \text{CrSi}$ as denoted) as presented in Figure 62(c). The specific mass changes were similarly found to be negligible ($< +0.1 \text{ mg}/\text{cm}^2$) at the temperatures up to around 550°C . However, differently, a slight reduction in the mass change was observed in these composites at the temperatures ranging from 550°C to around 650°C - 750°C , probably due to the evaporation of a small amount of a volatile surface oxide phase (e.g. CrO_3) formed at the lower temperatures. At higher temperatures, the specific mass changes

Figure 62. Mass change per unit surface area as a function of oxidation temperature for the (a) CC-4060, CC-5050, CC-5545, (b) CC-6040, CC-6535, CC-7030, and (c) CC-8020, CC-9010, reference $\text{CrSi}_2 + \text{CrSi}$ sample during non-isothermal oxidation from 50°C to 870°C in air.

Figure 62. (continued) Mass change per unit surface area as a function of oxidation temperature for the (a) CC-4060, CC-5050, CC-5545, (b) CC-6040, CC-6535, CC-7030, and (c) CC-8020, CC-9010, reference CrSi₂ + CrSi sample during non-isothermal oxidation from 50°C to 870°C in air.

increased in the CC-8020 and CC-9010 composites, as well as, in the as-sintered CrSi₂ + CrSi reference bulk sample. The oxidation-induced mass changes at 870°C for the CC-8020 and CC-9010 composites were 0.32 and 0.22 mg/cm², respectively. The as-sintered CrSi₂ + CrSi sample exhibited relatively lower oxidation rates (< 0.095 mg/cm²) at high temperatures compared to all chromium silicide-based composite systems.

Based on the non-isothermal oxidation studies, the chromium silicide-based composites, which are composed of different silicide phases (Cr₃Si, Cr₅Si₃, CrSi, CrSi₂, Cr_{0.91}Si_{0.09}) did not show any pest oxidation (*structural disintegration due to cracking or extreme spallation*) behavior at the temperatures ranging from 50°C to 870°C; therefore, no accelerated internal oxidation and related structural disintegration was observed. The CC-4060 composite was composed of Cr_{0.91}Si_{0.09} and SiO₂ phases, which displayed a negligible

oxidation below 450°C and 0.63 mg/cm² specific mass change at 870°C. Its oxidation was determined to be relatively higher than the other composites at high temperatures, which was an indication of the lower oxidation resistance of the Cr_{0.91}Si_{0.09} phase compared to the other chromium silicide phases. The major silicide phases were Cr₃Si and Cr₅Si₃ for the CC-5050, CC-5545 and CC-6040 composites, which revealed specific mass changes ranging from 0.40 to 0.58 mg/cm² at 870°C. These results demonstrated that the presence of the Cr₅Si₃ phase within the CC-5545 adversely affected its oxidation resistance, since it oxidized relatively higher than the CC-5050 composite including only Cr₃Si as a silicide phase. It was reported that the sputter-deposited Cr₃Si film exhibited substantially high oxidation resistance at 700°C and 800°C with very low mass changes (~0.15-0.32 mg/cm²) after cyclic oxidation in air for 100 h [16]. Its oxidation behavior was due to the formation of a protective surface layer composed of Cr₂O₃ and amorphous SiO₂ phases, and its good adhesion on the Cr₃Si phase. The chromium silicide-based composites consisting of Cr₃Si as a major phase also showed negligible mass gain at temperatures below 500°-650°C. This was found to be in good correlation with the previous studies [15,32]. Shah and Anton [33] reported that the Cr₃Si displayed an initial weight loss saturating around 3.12 mg/cm² after cyclic oxidation tests performed at 1200°C in air. The Cr₂O₃, SiO₂ and CrSi₂ phases were identified as the oxidation products in this study. The oxidation resistance of the Cr₃Si phase was hereby reported to be sufficiently high up to around 1150°-1200°C, which makes it a good candidate material for a broad range of high temperature structural and electrical applications [20,34]. However, due to the faster oxidation rate of chromium than silicon, it was described that protective silica layer could not be formed on the Cr₃Si surface at the temperatures of 1200°-1500°C, which needs to be further studied (e.g. alloying with molybdenum) [23]. Additionally, it should be pointed out that no study has been conducted yet on the oxidation of the Cr_{0.91}Si_{0.09} and Cr₅Si₃ silicide phases. The relatively lower oxidation of the CC-6040 and CC-6535 composites compared to the other composites composed of similar silicide phases could be attributed to the presence of unreacted silicide (CrSi, CrSi₂) and Cr₂O₃ phases. The composites with only CrSi and CrSi₂ major phases (CC-8020, CC-9010) exhibited significantly lower mass changes, and thus,

lower oxidation at high temperatures. The non-isothermal oxidation studies were similarly conducted on the CrSi_2 sample from room temperature to 1000°C in a 50 ml/min flowing air with a heating rate of $10^\circ\text{C}/\text{min}$ by Stathokostopoulos et al. [4]. The results showed that specific mass gain for the CrSi_2 was around $0.03 \text{ mg}/\text{cm}^2$, and then increased to $\sim 0.08 \text{ mg}/\text{cm}^2$ with increasing temperature up to 1000°C . The excellent oxidation resistance of the CrSi_2 phase was mainly attributed to the formation of a protective surface layer consisting of Cr_2O_3 and amorphous SiO_2 [5,8,11]. These results were determined to be in good correlation with the oxidation behavior of the as-sintered $\text{CrSi} + \text{CrSi}_2$ baseline samples studied. The relatively higher oxidation of the CC-8020 and CC-9010 composites compared to the as-sintered reference sample could be correlated to the reduced amount of CrSi_2 and relatively poor oxidation resistance of the CrSi phase. However, it should be noted that the oxidation behavior of the CrSi phase has not been investigated to date. Additionally, a slight specific mass loss was detected at the temperatures between 550°C and 750°C for the CC-8020 and CC-9010 composites, as well as, the as-sintered reference sample. A similar type of oxidation behavior was also reported for the CrSi_2 material at a similar temperature range, but was not explained [5]. This could be correlated to the different oxidation behavior of the CrSi_2 and CrSi phases at the temperatures below 700°C - 750°C and possible formation of volatile chromium oxide species (e.g. CrO_3) in small amounts [22].

4.3.4 High-temperature electrical properties of the composites

The high-temperature electrical conductivities of the chromium silicide-based composites were measured at the temperatures up to 1000°C in argon, and their electrical properties are presented as a function of temperature in Figure 63. The electrical data was recorded at the temperatures of $\sim 200^\circ\text{C}$ - 1000°C , since very low resistance values for the tested sample dimensions caused relatively inaccurate measurements at lower temperatures. The electrical connections made by platinum were lost at $\sim 896^\circ\text{C}$ - 998°C depending on the composite samples; therefore, exponential decay fitting (1st-3rd degree, R-square: 0.98-0.99) was applied to extrapolate the electrical data up to 1000°C (dotted lines) for a better

Figure 63. Electrical conductivity as a function of the temperature for the (a) CC-4060, CC-5050, CC-5545 and CC-6040, and (b) CC-6535, CC-7030, CC-8020 and CC-9010 chromium silicide-based composites, which were all sintered at 1370°C in argon (Electrical conductivity data is shown on the logarithmic scale).

comparison. It is apparent from Figure 63(a-b) that the electrical conductivity of all the chromium silicide-based composites decreased with increasing temperature. These results demonstrated that all composites exhibited a metallic-type electrical behavior due to the presence of different chromium silicide phases. As presented in Figure 63a, the electrical conductivities of the CC-4060 and CC-5050 composites were found at 1000°C as 45.7 and 42.1 S/cm, respectively. These results may imply that the $\text{Cr}_{0.91}\text{Si}_{0.09}$ and Cr_3Si silicides have a similar intrinsic electrical conductivity at high temperatures ($> 550^\circ\text{C}$), since these two composites were two-phase systems composed of a single chromium silicide phase along with silica. At 1000°C, the electrical conductivities of the CC-5545 and CC-6040 composites were 213.7 and 122.1 S/cm, respectively. It is clear that these composites displayed substantially higher electrical conductivity values compared to the CC-4060 and CC-5050 composites, which could be related to the increased fraction of the Cr_3Si phase and presence of the Cr_5Si_3 phase. Mazzega et al. [2] reported that the pure Cr_3Si and Cr_5Si_3 films possessed the electrical conductivities of ~ 10500 and ~ 5900 S/cm at around 827°C , respectively. The electrical conductivity of the CC-6040 composite was found to be lower than that of the CC-5545 composite at the temperatures above $\sim 420^\circ\text{C}$, even though the major silicide phases were identified as Cr_3Si and Cr_5Si_3 within both composites. This could be attributed to the presence of the remaining CrSi and CrSi_2 phases within the CC-6040 composite, since their electrical conductivities were shown to be significantly lower compared to the Cr_3Si and Cr_5Si_3 [4]. Based on the previous studies, electrical conductivities at $\sim 500^\circ\text{C}$ for the CrSi , CrSi_2 , Cr_5Si_3 and Cr_3Si compounds are around 500, 725, 6700 and 14300 S/cm, respectively [2,4,5]. As shown in Figure 63b, the electrical conductivity of the CC-6535 composite was 118.4 S/cm at 1000°C, which was found to be very close to that of the CC-6040 composite (122.1 S/cm) due to the same silicide phases (Cr_3Si , Cr_5Si_3 , CrSi , CrSi_2) existing within these composites. The electrical conductivities of the CC-7030, CC-8020 and CC-9010 composites at 1000°C were 98.1, 129.6 and 86.3 S/cm, respectively. These results point out that the higher concentration of the CrSi_2 phase within the CC-7030 and CC-9010 composites lowered their electrical conductivity, particularly compared to the CC-6040, CC-6535 and CC-8020 composites.

The metallic-type of electrical conduction behavior is expected for the chromium silicide-based composites including Cr_3Si , Cr_5Si_3 and CrSi as major silicide phases, since Cr_3Si and Cr_5Si_3 compounds are known to display a temperature-dependent electrical resistivity like a metal [2,14]. It was reported that the electrical conductivity of the CrSi decreased with increasing temperature ($\sim 50^\circ\text{--}400^\circ\text{C}$) [4]; however, it should be noted that its electrical properties and behavior have not been reported for high temperatures. The electrical data of the CC-8020 and CC-9010 composites with a CrSi major silicide phase (Figure 63b) demonstrated that the CrSi could have a metallic conductivity similar to the Cr_3Si and Cr_5Si_3 . Several studies also demonstrated that the electrical conductivity of the CrSi_2 , which is known as a p-type degenerate semiconducting material, initially decreased with increasing temperature to $\sim 300^\circ\text{--}430^\circ\text{C}$, and then started to increase as a function of temperature [5,8,35,36]. This behavior of the CrSi_2 was explained with its degenerated semiconducting nature and related transition from extrinsic to intrinsic conduction regime at that temperature range. However, this type of electrical behavior was not detected in any chromium silicide-based composites throughout the temperature range, even though some composites (e.g. CC-8020, CC-9010) contained the CrSi_2 phase within their structure. This could be highly related to the small amount that remained as a minor phase after solid-state reaction. Additionally, the CC-5545 composite composed of Cr_3Si , Cr_5Si_3 as major conductive silicide phases displayed higher electrical conductivity values than the other composites at the temperatures above $\sim 550^\circ\text{C}$, which is in consistent with the higher electrical conductivities of these phases compared to the other chromium silicides [4]. The relatively low electrical conductivities of the CC-4060 and CC-5050 composites could be correlated to the low volume percentage of the silicide phases and high content of the insulating grain boundary silica phase formed via solid-state reaction.

As schematically reviewed in the Figure 64 with a spline diagram, the electrical conductivities of the chromium silicide-based composites ranged from 42.1 to 213.7 S/cm at 1000°C depending on the major silicide phases (Cr_3Si , Cr_5Si_3 , CrSi , CrSi_2 , $\text{Cr}_{0.91}\text{Si}_{0.09}$) and their amounts. Thus, it should be noted that their electrical properties can be controlled

Figure 64. Schematic review (spline diagram) of changes in the electrical conductivities of the chromium silicide-based composites at 1000°C as a function of the initial chromium silicide/oxide ratios.

by adjusting the initial chromium silicide/oxide volume ratio. As a review of the studies conducted on the chromium silicide-based composites fabricated via solid-state reactions, their compositions (major/minor phases) and high temperature oxidation/electrical properties are additionally summarized in Table 10. All composites exhibited high oxidation resistance at the temperatures up to 870°C, since their oxidation-induced specific mass changes were 0.09-0.16 mg/cm² and 0.22-0.63 mg/cm² at 500°C and 870°C, respectively. They also showed metallic-type conductivity throughout the temperature range, and their electrical conductivities ranged from 64.1 to 409.5 S/cm at 500°C, and from 42.1 to 213.7 S/cm at 1000°C, depending on the chromium silicide phases present and their volume percentages.

Table 10. Summary of the composite compositions, and high-temperature oxidation and electrical properties of the chromium silicide-based composites.

Composite samples	Major/minor phases present	Oxidation-induced mass change/gain (mg/cm ²)		Electrical conductivity (S/cm)	
		500°C	870°C	500°C	1000°C
CC-4060	Cr _{0.91} Si _{0.09} , SiO ₂	+ 0.13	+ 0.63	74.9	45.7
CC-5050	Cr ₃ Si, SiO ₂	+ 0.12	+ 0.47	64.1	42.1
CC-5545	Cr ₃ Si, Cr ₅ Si ₃ , CrSi ₂ , SiO ₂	+ 0.16	+ 0.58	351.9	213.7
CC-6040	Cr ₃ Si, Cr ₅ Si ₃ , CrSi, CrSi ₂ , SiO ₂ , Cr ₂ O ₃	+ 0.11	+ 0.40	208.0	122.1
CC-6535	Cr ₅ Si ₃ , Cr ₃ Si, CrSi ₂ , CrSi, SiO ₂	+ 0.11	+ 0.35	177.2	118.4
CC-7030	CrSi, Cr ₅ Si ₃ , CrSi ₂ , SiO ₂	+ 0.11	+ 0.56	189.1	98.1
CC-8020	CrSi, CrSi ₂ , SiO ₂	+ 0.09	+ 0.32	409.5	129.6
CC-9010	CrSi, CrSi ₂ , SiO ₂ , Cr ₂ O ₃	+ 0.09	+ 0.22	216.0	86.3

4.3.5 High-temperature stability of the selected Cr₃Si- and Cr₅Si₃-based composites

It was presented that the major chromium silicide phases were Cr₃Si and Cr₅Si₃ within the CC-5050, CC-5545 and CC-6040 composites after solid-state reactions. Due to the higher melting temperatures of the Cr₃Si and Cr₅Si₃ compounds (1680°-1770°C) in the Cr-Si binary system, these three composites were further annealed at 1350°C for 24-96 h in argon to better understand their thermal stability and microstructural evolution, as well as, the stability of their high-temperature oxidation and electrical properties.

4.3.5.1 Thermal stability and microstructural evolution

The XRD patterns of the CC-5050, CC-5545 and CC-6040 composites, which were further annealed at 1350°C for 24, 48 and 96 h, are shown in Figure 65. The XRD data of these composites after sintering was also included to compare the possible phase changes, and thus, they are described with “0 h” implying non-annealed composites as reference samples. No phase changes were observed for the CC-5050 composite, since only Cr₃Si and low-cristobalite SiO₂ phases were detected after annealing for 24-96 h (Figure 65a). However, it is apparent that the SiO₂ peak intensities increased as a function of annealing time, particularly after 24 h of annealing compared to the as-sintered sample (0 h). For the as-sintered CC-5545 composite, the phases detected were Cr₃Si, Cr₅Si₃, CrSi₂ and SiO₂ as previously discussed. Similarly, no thermal decomposition was identified for the CC-5545 composite system after annealing at 1350°C up to 96 h, as presented in Figure 65b. Unlike the CC-5050 composite system, the peak intensities of the SiO₂ phase remained almost the same for the CC-5545 composite. However, it should be noted that the presence of the remaining CrSi₂ phase was observed only within the as-sintered and 24 h annealed CC-5545 samples, but not after 48 and 96 h of annealing. After 24 h annealing, there was also an increase in the peak intensities of the Cr₅Si₃ phase, but a decrease in the peak intensities of the Cr₃Si phase. Therefore, these results indicate that further solid-state reactions took place between the chromium silicides (e.g. Cr₃Si) and the remaining CrSi₂ phase to form more Cr₅Si₃ phase within the CC-5545 composite during high-temperature annealing. For the CC-6040 composite, there was a more complex structure due to the presence of multiple silicides (Cr₃Si, Cr₅Si₃, CrSi, CrSi₂) and oxides (SiO₂, Cr₂O₃) after sintering. All these phases were also identified after annealing for 24 h (Figure 65c). However, there was a significant increase in the peak intensities of the SiO₂, Cr₃Si, Cr₅Si₃, and a decrease in that of the remaining phases (CrSi, CrSi₂, Cr₂O₃). After 96 h of annealing, a similar structure to the annealed CC-5545 composite was achieved, since the phases detected were Cr₃Si, Cr₅Si₃ and SiO₂. It should be noted that the Cr₅Si₃ phases were found to be more intense within the CC-6040 composite, indicating the higher volume percentage of the Cr₅Si₃ after high-temperature annealing. As a review of these annealing studies, it can be

Figure 65. XRD patterns of the (a) CC-5050, (b) CC-5545, and (c) CC-6040 composites after sintering (denoted as “0 h” annealing), and after further annealing at 1350°C for 24, 48 and 96 h in argon.

Figure 65. (continued) XRD patterns of the (a) CC-5050, (b) CC-5545, and (c) CC-6040 composites after sintering (denoted as “0 h” annealing), and after further annealing at 1350°C for 24, 48 and 96 h in argon.

concluded that the CC-5050 composite, which consisted of the Cr_3Si and SiO_2 phases, displayed higher thermal stability compared to the CC-5545 and CC-6040 composite. The lower thermal stability of the CC-5545 and CC-6040 composites could be attributed to the presence of the remaining initial phases (CrSi , CrSi_2 , Cr_2O_3) within their structure after sintering, which resulted in further solid-state reactions taking place during annealing at 1350°C for 24–96 h. In addition, peak intensities of the SiO_2 phase increased as a function of annealing time, which may also be related to the metastable nature of the cristobalite structure and related phase transition (low-cristobalite $\leftrightarrow$ high-cristobalite) [26,30]. After 96 h of annealing, the CC-5050 composite revealed a two-phase system ($\text{Cr}_3\text{Si} + \text{SiO}_2$), while a similar three-phase system ($\text{Cr}_3\text{Si} + \text{Cr}_5\text{Si}_3 + \text{SiO}_2$) was achieved for the CC-5545 and CC-6040 composites.

The microstructural changes within these composites were also examined as a function of the annealing time. Figure 66 presents the SEM microstructures of the CC-5050, CC-5545 and CC-6040 composites after annealing at 1350°C for 24, 48 and 96 h. It is apparent that the similar microstructures were observed after annealing. The highly homogeneous distribution of the chromium silicide phases (bright regions: Cr_3Si , Cr_5Si_3) within the silica grain boundary phase (dark regions) can be seen from Figure 66(a1-c3). The presence of the pores within the microstructures was observed after annealing. To better understand the changes in the degree of porosity, the apparent porosity levels were additionally measured by Archimedes method. The results displayed that there was ~ 0.7-3.5% decrease in porosity within the CC-5050 and CC-5545 composites as a function of annealing time. However, the degree of porosity increased by 6.6% in the CC-6040 composite after annealing, which is directly related to the extent of the continued solid-state reaction during the initial 48 h of annealing period. Furthermore, the chromium silicide grains became smoother and more round with increasing annealing time, since the presence of nearly round chromium silicide grains were clearly observed within the composite microstructures, particularly after 48 and 96 h of annealing at 1350°C (Figure 66(a2,a3,b3,c2,c3)). These observations were found to be more apparent when the silicide grains were in contact with the silica phase, which may indicate the occurrence of a solid-phase grain boundary wetting by the amorphous glass phase. It should be noted that the phenomenon of grain boundary wetting is well-known by the presence of a liquid phase, but wetting of grains by a solid phase was also reported for ceramic composites (e.g. $\text{ZrO}_2\text{-SiO}_2$) [29] and binary alloy systems (e.g. Al-Mg, Al-Zn) [37,38]. However, further studies are needed to better understand this wetting mechanism within these intermetallic composites. In addition, the formation of a highly-dense surface layer with an average thickness of 31.8 μm ($\pm 2.2 \mu\text{m}$) was observed within the microstructure of the CC-5545 composite after 48 h of annealing at 1350°C, as shown in Figure 67. The EDS analysis revealed that the composition of the surface layer is silica based on the quantitative elemental data (47.0 wt% Si + 53.0 wt% O). As a review, the above-discussed phase and microstructural changes during high-temperature annealing could highly influence the high

Figure 66. SEM microstructures of the (a1-a2-a3) CC-5050, (b1-b2-b3) CC-5545, and (c1-c2-c3) CC-6040 composites after further annealing at 1350°C for 24, 48 and 96 h in argon (a1-b1-c1: *after annealing for 24 h*; a2-b2-c2: *after annealing for 48 h*; a3-b3-c3: *after annealing for 96 h*).

Figure 66. (continued) SEM microstructures of the (a1-a2-a3) CC-5050, (b1-b2-b3) CC-5545, and (c1-c2-c3) CC-6040 composites after further annealing at 1350°C for 24, 48 and 96 h in argon (a1-b1-c1: *after annealing for 24 h*; a2-b2-c2: *after annealing for 48 h*; a3-b3-c3: *after annealing for 96 h*).

Figure 66. (continued) SEM microstructures of the (a1-a2-a3) CC-5050, (b1-b2-b3) CC-5545, and (c1-c2-c3) CC-6040 composites after further annealing at 1350°C for 24, 48 and 96 h in argon (a1-b1-c1: *after annealing for 24 h*; a2-b2-c2: *after annealing for 48 h*; a3-b3-c3: *after annealing for 96 h*).

Figure 66. (continued) SEM microstructures of the (a1-a2-a3) CC-5050, (b1-b2-b3) CC-5545, and (c1-c2-c3) CC-6040 composites after further annealing at 1350°C for 24, 48 and 96 h in argon (a1-b1-c1: *after annealing for 24 h*; a2-b2-c2: *after annealing for 48 h*; a3-b3-c3: *after annealing for 96 h*).

Figure 66. (continued) SEM microstructures of the (a1-a2-a3) CC-5050, (b1-b2-b3) CC-5545, and (c1-c2-c3) CC-6040 composites after further annealing at 1350°C for 24, 48 and 96 h in argon (a1-b1-c1: *after annealing for 24 h*; a2-b2-c2: *after annealing for 48 h*; a3-b3-c3: *after annealing for 96 h*).

temperature physical properties of these chromium silicide-based composites, and therefore, they may need to be sintered longer or pre-heat treated before use in real applications to complete the solid-state reactions (if any unreacted phases exist) and achieve a more stable structure.

4.3.5.2 High-temperature oxidation and electrical properties after annealing

The non-isothermal and isothermal oxidation tests were additionally performed in an air atmosphere using the as-sintered and as-annealed CC-5050, CC-5545 and CC-6040 composites. Figure 68 displays the specific mass changes per unit surface areas (mg/cm^2) as a function of time during isothermal oxidation of the as-sintered composites at 850°C. The CC-5545 composite oxidized substantially higher compared to other composites, since the mass changes after 12 h exposure to air were 0.78, 1.98 and 0.75 mg/cm^2 for CC-5050,

Figure 67. SEM microstructure of the highly dense silica surface layer formed within the CC-5545 composite after annealing at 1350°C for 48 h in argon.

CC-5545 and CC-6040 composites, respectively. The CC-5050 and CC-6040 composites revealed a similar isothermal oxidation behavior at 850°C. However, the isothermal oxidation of these composites could be divided into two regions as (i) 0-2 h and (ii) 2-12 h due to the different rates of oxidation observed (Figure 68). The specific mass gain drastically increased in the initial 2 h of oxidation, but then their oxidation was slower following a more linear trend from 2 to 12 h of oxidation. These results demonstrated that there was a formation of a protective surface oxide layer in the initial stage, which lowered the oxidation rates afterwards. Similar trends were also presented for the isothermal oxidation of the sputter-deposited nanocrystalline Cr_3Si film at 700°C and 800°C [16]. Due to relatively lower oxidation rates at 700°C-800°C, a linear trend was observed in that study after exposed to air for ~30-40 h. After 12 h of oxidation, the mass changes were ~0.07 and ~0.16 mg/cm^2 at 700°C and 800°C, respectively. The surface layer formed on the CC-5050, CC-5545 and CC-6040 composites is assumed to be composed of Cr_2O_3 and SiO_2 ,

Figure 68. Isothermal oxidation of the CC-5050, CC-5545 and CC-6040 composites in air at 850°C for 12 h.

where it was previously reported as the major surface oxide species in correlation with the oxidation mechanisms of the chromium silicide systems (particularly Cr_3Si) [16,32,33].

To understand the stability of their high-temperature oxidation behavior, non-isothermal oxidation of these chromium silicide-based composites was examined after annealing at 1350°C for 24-96 h. Figure 69(a-c) present the specific mass changes within the as-annealed CC-5050, CC-5545 and CC-6040 composites as a function of oxidation temperature. For comparison, the oxidation data of the as-sintered composites is also shown. The mass changes decreased for the as-annealed CC-5050 and CC-5545 composites (Figure 69(a-b)). For the CC-5050 composite system, the specific mass gain at 870°C reduced from 0.47 to ~0.24 mg/cm² after annealing for 24-48 h, but then there was

Figure 69. Mass change per unit surface area as a function of oxidation temperature for the as-sintered and as-annealed (a) CC-5050, (b) CC-5545, and (c) CC-6040 composites during non-isothermal oxidation from 50°C to 870°C in air.

Figure 69. (continued) Mass change per unit surface area as a function of oxidation temperature for the as-sintered and as-annealed (a) CC-5050, (b) CC-5545, and (c) CC-6040 composites during non-isothermal oxidation from 50°C to 870°C in air.

an increase to 0.38 mg/cm² after 96 h of annealing. The non-isothermal oxidation of the CC-5545 composite was substantially reduced after annealing, where the specific mass gain at 870°C decreased from 0.58 to ~0.18 mg/cm², as presented in Figure 69b. There was a drastic increase in the oxidation rate of the as-sintered CC-5545 composite above ~650°C, but this behavior was not observed after high-temperature annealing. No significant changes were observed in the non-isothermal oxidation behavior of the CC-6040 composite after annealing (Figure 69c). The specific mass changes were all in the range of 0.38-0.40 mg/cm² for the CC-6040 composite system. The reduced oxidation rates for the CC-5050 and CC-5545 composites could be correlated to the formation of a dense protective silica layer on their surfaces, as observed by SEM analysis (Figure 67), and the reduced porosity levels (by ~0.7-3.5%) after annealing. It is known that the oxidation rates of the transition metal silicides are highly affected by the type of surface layer formed,

degree of porosity and microcracks [32,39,40]. It can be concluded that all these Cr_3Si - and Cr_5Si_3 -based composites exhibited sufficiently high oxidation resistance in air during both non-isothermal and isothermal conditions.

The electrical conductivities of the CC-5050, CC-5545 and CC-6040 composites after annealing for 24-96 h are presented as a function of temperature in Figure 70. Similarly, the electrical data of the as-sintered composites is also displayed here to observe the changes after high-temperature annealing. As shown in Figure 70a, the electrical conductivities of the as-annealed CC-5050 composite samples were substantially higher than that of its as-sintered sample throughout the temperature range. At 1000°C , the electrical conductivities of the CC-5050 samples after annealing for 24, 48 and 96 h were 214.2, 232.7 and 355.2 S/cm, respectively. The electrical conductivity drastically increased from 42.1 to 355.2 S/cm after 96 h of annealing at 1350°C . For the CC-5545 composite, similar trends were observed after annealing for 24 and 96 h, where the electrical conductivity increased from 213.7 to 261.0, and then to 540.1 S/cm, respectively (Figure 70b). However, there was a slight decrease in its electrical conductivity at the temperatures above $\sim 600^\circ\text{C}$ only after 48 h of annealing (green curve). The electrical conductivities of the CC-6040 composite samples were also found to increase as a function of annealing time as displayed in Figure 70c. The CC-6040 composite samples revealed quite similar electrical conductivity data at all temperatures (350°C - 1000°C) after annealing for 24 and 48 h (red-green curves), with conductivities of 138.0 and 144.5 S/cm at 1000°C , respectively. Therefore, a slight increase was identified compared to the as-sintered CC-6040 sample. However, the level of increase was significantly higher after 96 h of annealing, since the electrical conductivity increased to 244.2 S/cm at 1000°C .

As a review, the high-temperature electrical conductivities of the CC-5050, CC-5545 and CC-6040 composites were highly influenced by annealing processes at 1350°C for 24-96 h. After 96 h of annealing, their electrical conductivities drastically increased (+ 122.1-326.4 S/cm). This increase was found to be much higher for CC-5545 and CC-5050

Figure 70. Electrical conductivity as a function of temperature for the as-sintered and as-annealed (a) CC-5050, (b) CC-5545, and (c) CC-6040 composites (*Electrical conductivity data is shown on the logarithmic scale*).

Figure 70. (continued) Electrical conductivity as a function of temperature for the as-sintered and as-annealed (a) CC-5050, (b) CC-5545, and (c) CC-6040 composites (Electrical conductivity data is shown on the logarithmic scale).

composites compared to the CC-6040. The positive influence of the annealing on their high-temperature electrical properties could be correlated to the above-mentioned phase and microstructural changes observed after high-temperature annealing. The presence of the remaining initial phases (e.g. CrSi, CrSi₂) within the structures of the CC-5545 and CC-6040 composites after sintering resulted in further solid-state reactions and the formation of three-phase system (Cr₃Si + Cr₅Si₃ + SiO₂) after annealing. Therefore, the removal of the remaining phases via solid-state reactions and increased amount of the Cr₃Si and Cr₅Si₃ phases enhanced their electrical conductivities. The CrSi and CrSi₂ phases are known to exhibit lower electrical conductivities compared to the Cr₃Si and Cr₅Si₃ [2,4,5]. Although these two composites had the same three-phase structure after 96 h of annealing, the CC-5545 composite exhibited substantially higher electrical conductivity than the CC-6040. This could be related to the major Cr₃Si and minor Cr₅Si₃ phases within the CC-5545 composite, and higher intrinsic electrical conductivity of the Cr₃Si. The Cr₅Si₃ XRD peaks

became more intense for the CC-6040 composite indicating the higher content, which possibly reduced its overall electrical conductivity compared to the Cr₃Si-dominant CC-5545 composite. On the other hand, the increase in the electrical conductivity of the CC-5050 composite after annealing could be attributed to the slight changes in the volume percentages of the Cr₃Si and SiO₂ phases, but no major phase changes were observed within this composite system. Therefore, it should be noted that the percolation and electrical transport could also be positively influenced by the microstructural changes and formation of more rounded grains via solid-phase grain boundary wetting by a metastable and/or amorphous silica phase. It is known that the electrical percolation of the mixtures of conductive and insulating materials are highly influenced by several factors including grain size and morphology, microstructural homogeneity, particle interactions and wetting behavior [28,41,42]. The importance of wetting behavior (connectivity of two phases) on the electrical conductivity and critical percolation threshold is commonly discussed for conductive polymer composites (e.g. wetting of a polymer by a filler material) [43,44], but a similar relation may be of importance for these intermetallic composites.

4.4 Conclusions

The chromium silicide-based electroconductive composites were fabricated by solid-state reactions between chromium silicide and oxide compounds, and their phase stability, microstructural evolution, oxidation behavior and electrical properties were studied at high temperatures. By adjusting the starting silicide/oxide volume ratio, different chromium silicide phases (e.g. Cr_{0.91}Si_{0.09}, Cr₃Si, Cr₅Si₃) were formed along with a metastable and/or amorphous grain boundary silica phase. The distribution of the silicide phases within the silica was determined to be homogeneous for all the composite systems. No pest oxidation (structural disintegration) were observed during both non-isothermal and isothermal conditions. Their excellent oxidation resistance was attributed to the formation of a protective surface layer composed of chromium oxide and amorphous silica. All of the composites exhibited a metallic-type conduction behavior, and their electrical conductivities ranged from 42.1 to 213.7 S/cm at 1000°C depending on the major silicide

phases present and their amount. In addition, further phase and microstructural changes were identified after high-temperature annealing, which mostly enhanced their oxidation resistance and electrical conductivities at high-temperatures. Further studies are needed to better understand the effects of the silica grain boundary phase and the high-temperature heat treatment on their phase stability, microstructures (e.g. solid-phase grain boundary wetting), oxidation behavior and electrical properties.

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CHAPTER 5: DETERMINATION OF A HOMOGENEITY FACTOR FOR COMPOSITE MATERIALS

5.1 Introduction

Composites are a prominent class of material systems that consist of a combination of at least two constituent materials typically with distinctively different property characteristics. Over the past half century, composite materials with advanced material properties were achieved by using various matrix and reinforcement (or additive) materials. Work continues on the development of these unique materials in many industrial fields including electronics, aerospace, and automotive [1-3]. It is well known that the distribution of the additive phase within a matrix material has a major effect on the constitutive properties of composite material (e.g. electrical, mechanical, thermal), and this distribution is dependent upon the concentration, particle size and morphology of the additive phase [1-5]. Various quantitative microscopy methods have been developed in different fields such as ecology and materials science to characterize the microstructure of composites, but methods to describe the spatial distribution of the phases within the matrix have been limited. A simple method and index to quantify the degree of distribution, dispersion and/or mixedness of the composite microstructures would be beneficial to correlate processing and microstructure to the final properties of the materials. Quantitative analysis of the degree of distribution is crucial for understanding and controlling the process parameters for improving the microstructural homogeneity and composite properties. It is known that qualitative methods such as visual observation of composite microstructures do not provide objective and numeric results as needed [1,6]. For the quantification of the additive distribution within a matrix material, characteristics such as relative particle size [7,8], local concentration [2,9], number of particles [3,10,11,12], and distance between neighboring particles [4,5,13-15] have been selected as measures for the distribution in various methods. The method based on the relative particle size (RPS) is the

simplest technique used to quantify the level of clustering and/or agglomeration by calculating the particle size ratio of matrix to the additive material [1,8]. Therefore, the RPS method is mostly used for metal matrix composites (MMCs) prepared by dry mixing and sintering/hot-pressing due to high level of clustering.

As discussed above, the most common methods to quantify the degree of distribution or homogeneity are based upon microstructural parameters such as local concentration, number of particles, and distance between neighboring particles. These parameters are usually further analyzed by mathematical equations and distribution models including various statistical measures of distribution and variability such as standard deviation, coefficient of variation, and variance. The homogeneity of a multi-phased material is typically defined through these statistical analyses by a *degree of distribution* or *homogeneity index*, and often correlated with local concentration of the additive material and concentration ratio [2,9]. The degree of distribution was shown to be dependent on the local concentration of the dispersed phase by Ondracek & Renz (1989) [9]. They utilized the coefficient of variation, where the standard deviation is divided by the mean, to statistically quantify the degree of distribution; this paper used this coefficient to determine the homogeneity within metal-polymer composite structures. Kalyon *et al.* (2002) [2] developed a similar method using concentration variations, which are characterized by a wide-angle X-ray diffraction (WAXD)-based quantitative phase analysis route. The degree of mixedness was quantitatively assessed in that study by a mixing index developed using the statistical variance in order to provide a relationship between electrical properties of the composites and mixing homogeneity. The quadrat method is known as the most commonly used technique for quantification of the distribution due to its simplicity among all methods developed. In the quadrat method, a micrograph to be studied is simply divided into quadrats, and then the number of particles in each quadrat is measured. Using the quadrat method, a *Skewness index* (β) is calculated as the degree of asymmetry of a statistical distribution around its mean based on the number of particles, the standard deviation of the particle population, and the number of quadrats studied [12,16]. Therefore, high β values

are accepted as an indication of poor distribution, and this index is only used to compare the reinforcement distribution within different specimens. This technique is mostly used for MMCs and nanocomposites with highly clustered particle distributions and high level of agglomeration due to the principle of the quadrat method [3,10-12,14-16].

In addition to the parameters of local concentration and number of particles that are utilized by the methods discussed above, distance between neighboring particles is also considered as an important microstructural parameter to quantify the degree of distribution. The mean free-path and nearest-neighbor distance techniques, which are both based on the average distance between neighboring particles or features, have been frequently used. Although they have similar principles, distances between particle surfaces (interfaces), and distances between centroids of the nearest neighboring particles are measured for mean free-path and nearest-neighbor distance methods, respectively [15,17]. In the mean free-path method proposed by Luo & Koo (2008) [4] for the quantification of nanoparticle dispersions, the free-path spacing between fillers were measured by dividing a representative micrograph into multiple grid lines. Since the distribution of the free-path distance exhibits a lognormal distribution model, a dispersion parameter was calculated as the probability of this distribution. A modified version of this method was developed by considering the combination of the percentage of distribution (free-path spacing) and agglomeration size in order to analyze the dispersion of nanoparticles in composite materials [5]. The mean free-path was also calculated by using the volume fraction of particles, sum of the perimeter length and total test area in several studies on MMCs [15,17]. The nearest-neighbor distance method proposed by Clark & Evans (1954) [13] measured the distance from each individual to its nearest-neighbor, and then they correlated the population by the mean distance, which is expected for a random distribution, for quantitative measurement of distribution. Furthermore, several other methods on the basis of the amount of work (dispersive work), relative entropy, radial distribution function, and Voronoi tessellation are alternatively developed, and particularly used for characterization

of nanoparticle/inclusion dispersion and particle clustering in composite structures [1,18-21].

All of the methods reviewed above were developed for the quantitative characterization of particle distribution and clustering/agglomeration in different composite materials by considering different microstructural parameters. However, it is known that most methods have several shortcomings which limits their accuracy, scalability and practical use in different types of composite structures; the prime limits include the selection of the number of quadrats, quadrat size/shape, and the relation of these factors to the relative size and distribution of the agglomerated particles. The quantitative measure of the distribution should consider these limiting factors, while also being simple and applicable to different types of composite microstructures. In this paper, an image analysis method and a new index is presented for quantifying the distribution (homogeneity) efficiently in binary composite materials. The proposed method is based on the free-path spacing between the particles, which considers the method developed by Luo & Koo (2008) [4] in principle, but the present study distinctly takes the coefficient of variation into account as a measure of the degree of distribution instead of an equation based on the lognormal distribution model.

5.2 Materials and methods

5.2.1 Homogeneity analysis method

The proposed method is a microstructural image analysis technique for the quantification of the phase or granular distribution (homogeneity) in composite materials based upon the free-path spacing, which can be also defined as the distance between two neighboring particles on a micrograph as a basic measure of the distribution. Therefore, multiple straight lines (total $2N$ lines) are drawn both horizontally (N lines) and vertically (N lines) on a cross-sectional microstructure of a composite, which only consists of the particles of its one constituent after making the microstructure image binary by using the ImageJ software [22], as schematically illustrated in the Figure 71. The free-path spacing

Figure 71. Schematic illustration of the proposed image analysis method for quantifying the degree of distribution (homogeneity) in composite materials on a representative microstructure. (Black circles represent the particles on the image).

$(X_1, X_2, \dots, X_n)$ data between all the neighboring particles are recorded as profile plots as a function of distance, and then measured by processing the data in the Microsoft Excel. The free-path spacing values can be used as pixels or microns after setting the scale. The arithmetic mean of the free-path spacing values on each line $(\overline{X_{h1}}, \overline{X_{h2}}, \dots, \overline{X_{hN}}; \overline{X_{v1}}, \overline{X_{v2}}, \dots, \overline{X_{vN}})$ are separately calculated as:

$$\overline{X_{h1}} = \frac{1}{n} \sum_{i=1}^n X_i ; \overline{X_{v1}} = \frac{1}{n} \sum_{i=1}^n X_i ; \dots \dots \dots (1)$$

where n is defined as the total number of free-path spacing on a specific line drawn, and h and v are abbreviations of horizontal and vertical lines, respectively. Afterwards, the arithmetic mean ($\bar{X}$) and the standard deviation (s) of the all free-path spacing values obtained for total $2N$ lines are calculated by using the equation (2) and (3), respectively.

$$\bar{X} = \frac{(\overline{X_{h1}} + \overline{X_{h2}} + \dots \dots + \overline{X_{hN}}) + (\overline{X_{v1}} + \overline{X_{v2}} + \dots \dots + \overline{X_{vN}})}{2N} (2)$$

$$s = \sqrt{\frac{[\sum_{i=1}^N (\overline{X_{hi}} - \bar{X})^2] + [\sum_{i=1}^N (\overline{X_{vi}} - \bar{X})^2]}{2N - 1}} (3)$$

The degree of distribution or homogeneity can be identified as maximum, if all the arithmetic mean values of the free-path spacing are the same on each line analyzed, and also the same with the mean ($\bar{X}$) value. But in the case of an inhomogeneity or inhomogeneous distribution of particles, these mean values ($\overline{X_{h1}}, \overline{X_{h2}}, etc.$) differ from each other, and also from the mean ($\bar{X}$) of all free-path spacing values obtained for the total $2N$ lines. Since the mean free-path spacing values are different for each line analyzed, and the standard deviation value is also depending on $\bar{X}$ value in that case, the coefficient of variation (C_v) was selected to be used for assessing the relative variability of the mean free-path spacing at a total $2N$ lines. Thus, the C_v can be efficiently used to determine the degree of variation (distribution) for one variable having different mean values among multiple lines. Therefore, C_v is accepted as the distribution index (D index) in the proposed homogeneity analysis method, and presented as:

$$D \text{ index} = C_v = \left(\frac{s}{\bar{X}} \right) (4)$$

The D index exhibits a zero value ($C_v = 0$) for a perfectly homogeneous composite material and its representative microstructure, since all free-path spacing values between particles (additive or reinforcement particles) and their arithmetic mean values on each line are the same. If the particles are agglomerated or clustered in a composite material at a certain

level, then the D index diverges from zero, and thus tends to increase up to 1 and/or above 1. If the D index is found to be above 1.0 at some regions with low number of analyzed lines (e.g. $N \leq 10$), this means that the standard deviation is higher than the mean value, which clearly indicates that the agglomeration level of particles is extremely high. Thus, the proposed method can also provide important information regarding the high level of agglomeration of the individual particles. As a review, when the D index equals 0, then this indicates a maximum homogeneity and degree of distribution; a higher D index presents a minimum homogeneity and poorer distribution. Therefore, the proposed method based on the free-path spacing and its outcome, the D index, can be efficiently used to quantify the degree of distribution and to compare the distribution levels of different composite samples.

5.2.2 Description of the data and experimental method

To test the accuracy and potential limitations of the proposed homogeneity analysis method, six binary images representing the reference composite microstructures were created. The calculations based on the free-path spacing were performed on each image to determine the D index values as a function of the number of lines analyzed for comparison. In addition to the reference images, actual microstructures of ceramic-matrix composites were also analyzed. Metal silicide-refractory oxide composites were fabricated using molybdenum disilicide (MoSi_2 , 99.5%), tungsten disilicide (WSi_2 , 99.5%), aluminum oxide (Al_2O_3 , 8.6 m^2/g), zirconium oxide (ZrO_2 , 99+%), and yttrium oxide (Y_2O_3 , 99.99%) powders, all purchased from a commercial vendor (*Alfa Aesar*). The three composite compositions that will be discussed in this work were (60-40) vol% MoSi_2 - Al_2O_3 , (60-40) vol% WSi_2 - Y_2O_3 , and (60-40) vol% WSi_2 - ZrO_2 . These composites were synthesized by ball-milling in ethanol for 24 h, followed by drying at room temperature in a fume hood. The synthesized composite powders were uniaxially pressed into pellets (1 cm diameter, 2 mm thickness) by using a stainless steel die. Afterwards, these pellets were placed in an alumina crucible and sintered in a tube furnace in flowing argon gas (50 sccm) to a temperature of 1600°C. This was followed by the cutting of the sintered samples with a

diamond saw, and fine polishing with SiC grit papers and also diamond paste. The microstructural analysis of the cross-sectional areas of the metal silicide-refractory oxide composites were performed by scanning electron microscope (SEM, Hitachi S-4700F, Japan). To prepare these micrographs for quantitative image analysis, the micrographs were converted into binary images consisting of only metal silicide grains by using ImageJ [22]. The proposed image analysis method and related calculations were similarly applied to these composite microstructures in order to determine the degree of distribution (homogeneity) of transition metal silicides (D index values) within the refractory oxide matrix materials quantitatively. In addition, the quadrat method, which is known as the most commonly used technique described in literature for homogeneity analysis, was applied to the same composite microstructures for comparison of the D index values obtained by the proposed analysis method.

5.3 Results and Discussion

5.3.1 Homogeneity analysis of generated binary images

In this study, six binary patterns (P1-P6) were generated in order to act as representative composite microstructures presenting the distribution of reinforcement particles within a matrix. These generated microstructures were used to demonstrate the accuracy, and also show the potential limitations of the proposed homogeneity analysis method. Figure 72 displays these generated composite microstructures, all including 19×19 units, a hundred identical reinforcement particles, and thus, the same reinforcement volume fraction as a standard measurement. These patterns represent different degrees of distribution of reinforcement particles, from a perfectly homogeneous microstructure (P1) to an extremely agglomerated or poorly homogeneous microstructure (P6).

In order to investigate how well the proposed method quantifies the degree of distribution and homogeneity, 20 horizontal and 20 vertical lines were projected on each pattern, and then the arithmetic mean of the free-path spacing values on each line ($\overline{X_{h1}}, \overline{X_{v1}}$ etc.) were measured to calculate the D index values based on the coefficient of variation.

Figure 72. Images of six 19x19 reference patterns (P1-P6) which act as representative composite microstructures with different degrees of distribution of identical reinforcement particles. (Black squares represent the particles on the binary images).

Figure 73 presents the calculated D index values for six reference patterns from P1 to P6 as a function of total number of lines analyzed ($2N$). It is clear that the D index value is zero for the P1 pattern representing a perfectly homogeneous microstructure, since all free-path spacing values, and their arithmetic means on all 40 lines, are the same indicating that there is no variance. In the Figure 73, the curve composed of D index values for the P1 (blue triangles) is beneath the P6 curve (orange triangles) due to the same D index values measured. In the case of the P2 pattern, the measured D index values range from 0.257 to 0.226 with increasing total number of lines analyzed from 5 to 40. It is important to note that the total number of lines analyzed should be high enough to cover all the free-path spacing between particles and thus to achieve more accurate results. Therefore, the D index value for the P2 pattern representing a microstructure with high level of homogeneity is considered as 0.226, which slightly diverges from zero due to the existence of small

Figure 73. D index values calculated for six reference patterns (microstructures) from P1 to P6 as a function of total number of lines analyzed (2N) by using the proposed method. (Blue triangles of the P1 are under the orange triangles of the P6).

agglomerates only at the left and right edges of the pattern (Figure 72). Since the majority of the particles are well distributed and the variance is low, the P2 pattern presents a highly homogeneous microstructure as expected. In addition, it is obvious that the number of these small agglomerates, and the free-path spacing values, increase from P2 to P3, which results in an increase of the variance and D index for the P3 pattern. The results present D index values for the P3 pattern range between 0.408 and 0.386 with an increasing total number of lines analyzed from 8 to 40, which is reasonable for the pattern representing a moderate level of homogeneity (distribution). In addition to the P1, P2 and P3 patterns, P4 and P5 patterns were also studied by the proposed method for representing low and very low levels

of homogeneity, respectively. The D index values measured for P4 and P5 patterns based on total 40 lines are 0.592 and 0.671, respectively. It is clear that the D index values for P4 and P5 highly diverge from zero, and tend to get close to a value of one, indicating a low level of homogeneity and poor distribution. These results are directly related to the high level of particle agglomeration on these reference patterns and representative composite microstructures. Although the agglomeration level is very high, and this is similar for P4 and P5, the proposed method is found to be able to differentiate their degree of distribution and homogeneity levels efficiently from free-path spacing and C_v values. In addition, it is observed that the D index values are above 1.0 at some points for P5, which may be an indication of a high level of agglomeration. It can also be seen from Figure 73 that the D index values for P1, P2 and P3 patterns are all very stable after roughly 8 lines analyzed, while the values for P4 and P5 are mostly stable above 23 lines. This result indicates that more lines should be carefully analyzed in the case of a high level of agglomeration and low levels of homogeneity, in order to obtain a more accurate analysis by covering all agglomerated regions of a microstructure. Lastly, for the P6 pattern representing the extreme level of agglomeration, the D index is measured as zero, which is similar to the P1 pattern, since all free-path spacing values are same. In that case, it is important to note that the D index is measured inaccurately, because it is not possible to measure most of the free-path spacing values between individual particles due to such a high level of agglomeration, which can be stated as the main limitation of the proposed method. As a review of all the reference patterns, it is demonstrated that the D index values increase from 0.0 to 0.671 depending on the degree of distribution or homogeneity level, from maximum (perfect) to very low homogeneity. Therefore, the degrees of distribution or homogeneity levels for composites are classified based on the D index values for the proposed method as i) perfect (maximum) homogeneity ($D=0.00$), ii) high level of homogeneity ($0.00 < D \leq 0.25$), iii) moderate level of homogeneity ($0.25 < D \leq 0.40$), iv) low level of homogeneity ($0.40 < D \leq 0.60$), and v) very low level of homogeneity ($D > 0.60$), which is also schematically illustrated in Figure 74. These boundary values (0.25, 0.40 and 0.60) for classifying the levels of homogeneity were determined based on the level of increase in free-path spacing

Figure 74. Classification of the homogeneity (degree of distribution) levels for composites based on D index ranges in the proposed method.

values, level of decrease in reference number of particles measured (agglomeration level), and corresponding D index values obtained for the five reference patterns (P1-P5).

The quantification of the degree of distribution and homogeneity can be efficiently performed for the proposed microstructure using the D index simply by increasing the total number of lines for horizontal and vertical axes, since the distance between two individual particles (free-path spacing) is of prime importance in for calculating homogeneity. By simply tracking this variable, the use of any quadrats becomes unnecessary, and thus, eliminates any effects produced by quadrat size selection on the distribution data, as expressed by Clark & Evans (1954) [13]. Therefore, the proposed method has a significant advantage compared to the popular quadrat method, which produces the β index as its major outcome from the number of particles. The selection of the optimum quadrat size and total number of quadrats is reported as the major downside of the quadrat method, since the distribution results are highly dependent on them, and thus not objective [6,12,17]. For example, many particle-free regions can be analyzed with a very small selected quadrat

size, which may incorrectly result in clustering [15]. In addition, the RPS method does not provide direct information regarding the arrangement and distribution of particles, because it is only a measure of particle clustering, so a higher RPS is accepted as an indication of higher clustering [1]. In the proposed method, the microstructure should be carefully selected as a representative of the composite sample. If we assume that there are only four large individual particles on P6 pattern (Figure 72), then the D index would be measured as zero, and this value would not be representative of the microstructure for the composite sample due to a very high image magnification. Therefore, it is very crucial to select a composite microstructure at the correct magnification that can cover enough particles and represent the composite sample for the proposed method, and likewise, for the previously developed methods such as quadrat, mean free-path, and nearest-neighbor distance. The main limitation of the proposed method can be defined when inaccurate D index values are obtained as a result of homogeneously distributed agglomerates existing at the same size level (which usually occurs at high agglomeration levels). It is known that the quadrat method may also give incorrect β values in that case. For the mean free-path method, it is reported by Karnezis *et al.* (1998) [15] that the perimeter length of the cluster could be falsely measured if a cluster of particles is analyzed as one particle. Therefore, incorrect distribution data may be obtained by the mean free-path method in the case of agglomeration. The similar problem is identified for the nearest-neighbor distance method in the same study, since the related distance may be measured inaccurately when a particle diameter falsely refers to a high level of agglomeration. In addition, it was demonstrated by Cetin & Kalkanli (2009) [19] on their study for quantitative characterization of particle clustering, that the practical use of their cumulative radial distribution function is limited particularly in discontinuously reinforced composites which include well-separated clusters of reinforcement particles that may falsely change the measured data. In the study performed by Tyson *et al.* (2011) [5], it was reported that the free-path spacing and particle size values can be utilized to assess the dispersion and agglomeration quantities, respectively. However, the selection of the lognormal distribution function was found as one of the shortcomings for that modified free-path spacing technique, because inaccurate

Figure 75. Original cross-sectional SEM images of the metal silicide-refractory oxide composites and their converted binary images showing individual metal silicide grains as black regions: **a)** (60-40) vol% $\text{WSi}_2\text{-ZrO}_2$, **b)** (60-40) vol% $\text{WSi}_2\text{-Y}_2\text{O}_3$, and **c)** (60-40) vol% $\text{MoSi}_2\text{-Al}_2\text{O}_3$.

data may be obtained if the selected function is not suitable for that state of partial dispersion. As a review, it was demonstrated by using the reference patterns that the proposed homogeneity analysis method works with high accuracy to quantify the degree of distribution in composite materials by considering the coefficient of variation as a measure

of the distribution and also eliminating the problematic quadrat effect. But similar to other previously developed methods, it was presented that the existence of well-distributed large agglomerates limits its use for some composite microstructures due to lack of the free-path spacing values to be measured.

5.3.2 Homogeneity analysis of actual composite microstructures

In addition to the analysis of six reference patterns, the proposed homogeneity analysis method was applied to actual ceramic-matrix composite microstructures. Figure 75 presents the original cross-sectional SEM microstructures of the metal silicide-refractory oxide composites and also their converted binary images showing individual metal silicide grains as black regions. The selected composite compositions are (60-40) vol% $\text{WSi}_2\text{-ZrO}_2$, (60-40) vol% $\text{WSi}_2\text{-Y}_2\text{O}_3$, and (60-40) vol% $\text{MoSi}_2\text{-Al}_2\text{O}_3$, which all represent different degrees of distribution of metal silicide grains within a refractory oxide matrix. In order to quantify the degree of distribution and homogeneity of these composites using the D index, the free-path spacing and their arithmetic mean values were similarly measured on a total of 40 lines drawn both in the horizontal and vertical direction. The free-path spacing and all calculated values are measured in microns, not pixels after setting the conversion.

Figure 76 shows the calculated D index values for three different metal silicide-refractory oxide composites' SEM microstructures as a function of total number of lines analyzed (2N). The measured D index values for the (60-40) vol% $\text{WSi}_2\text{-ZrO}_2$ composite range from 0.189 to 0.142 with increasing total number of lines analyzed from 2 to 40. For high accuracy, its D index is accepted as 0.142 based on the results obtained with 40 lines, since the arithmetic mean ($\bar{X}$) and standard deviation (s) of the all free-path spacing values are found as 1.043 and 0.148 μm , respectively (Table 11). These results show that the D index of (60-40) vol% $\text{WSi}_2\text{-ZrO}_2$ composite slightly diverges from zero, and thus the distribution of the WSi_2 grains within ZrO_2 ceramic matrix is highly homogeneous. It is important to note that there may be a low level of error for the calculated D index values due to the existence of pores in small quantities within the microstructure to be analyzed, as

Figure 76. The D index values calculated for three different metal silicide-refractory oxide composite SEM microstructures as a function of total number of lines analyzed (2N) by using the proposed method.

seen in the original SEM images of the composites (Figure 75). For the (60-40) vol% WSi₂-Y₂O₃ composite, the arithmetic mean and standard deviation of the all free-path spacing values obtained on 40 lines was measured as 4.817 and 1.651 μm , respectively. Therefore, the D index value for WSi₂-Y₂O₃ composite was found as 0.343, which represents a moderate level of homogeneity and distribution of WSi₂ grains within Y₂O₃ ceramic matrix due to agglomeration at certain regions. In comparison of WSi₂-ZrO₂ and WSi₂-Y₂O₃ composites, it is clear that the D index increases from 0.142 to 0.343 due to particle agglomeration and related change in the free-path spacing values. It can also be seen that the D index values for these two composites are highly stable after 8 lines were

Table 11. Review of the results obtained for three different metal silicide-refractory oxide composites after 40 lines analyzed by using the proposed method.

Composites	$\bar{X}$	s	D index (Cv)
(60-40) vol% WSi ₂ -ZrO ₂	1.043 μm	0.148 μm	0.142
(60-40) vol% WSi ₂ -Y ₂ O ₃	4.817 μm	1.651 μm	0.343
(60-40) vol% MoSi ₂ -Al ₂ O ₃	7.935 μm	4.423 μm	0.557

* $\bar{X}$: arithmetic mean of the all free-path spacing values

* s: standard deviation of the all free-path spacing values

analyzed, which proves that accurate results for these kinds of microstructures can be simply achieved by analyzing several lines on both axes (Figure 76). In addition, it was found that the D index values for the (60-40) vol% MoSi₂-Al₂O₃ composite range from 0.444 to 0.557 with increasing total number of lines. However, its D index is considered as 0.557 based on the results obtained with 40 lines as presented in Table 11. Since the standard deviation (4.423 μm) is relatively high compared to its arithmetic mean (7.935 μm) due to high variations in the free-path spacing values, the MoSi₂-Al₂O₃ composite exhibits a low level of homogeneity. These results are directly related with particle agglomeration and also poor distribution of MoSi₂ grains within Al₂O₃ matrix. Therefore, it can be clearly seen that D index values are not stable until 28 lines are analyzed (Figure 76).

Lastly, the quadrat method was applied to the same binary images of the SEM microstructures of the metal silicide-refractory oxide composites for comparison of the D index values with the Skewness index (β) values, since it is known as the most commonly used and simple method in literature for quantification of the particle distribution. In order to calculate β index values, the binary images were divided into a number of square quadrats, and then, number of particles in each quadrat were determined by using ImageJ

Table 12. Review of the Skewness index (β) values as a function of the number of quadrats, and their comparison with the D index values for the metal silicide-refractory oxide composites.

Composites	β index			D index
	4-quadrats	16-quadrats	64-quadrats	
(60-40) vol% WSi ₂ -ZrO ₂	-0.772	0.211	0.168	0.142
(60-40) vol% WSi ₂ -Y ₂ O ₃	-0.779	0.318	0.518	0.343
(60-40) vol% MoSi ₂ -Al ₂ O ₃	1.954	0.828	0.839	0.557

software [12,3,22]. The β index values were calculated by using three different cell systems: (i) 4-quadrats, (ii) 16-quadrats, and (iii) 64-quadrats, since the main limitation of the quadrat method is known as the selection of the number of quadrats. Table 12 presents the review of the calculated β index values as a function of the number of quadrats, and also D index values for a better comparison of different index values. It was found that the β index values changed depending on the number of quadrats selected, and it even became negative in the 4-quadrats system. The β index values obtained for three different composites ranged between 0.168 and 0.839 in the 16- and 64-quadrats system. However, the β index obtained for the WSi₂-Y₂O₃ composite increased from 0.318 to 0.518 with increasing number of quadrats, which indicates that it is not clear which data is more accurate, and thus the selection of the number of quadrats is very difficult. In comparison, it is clear that the D index and the Skewness index (β) both increase from WSi₂-ZrO₂ to MoSi₂-Al₂O₃ composite, but at different intervals. Therefore, both index values can be used to understand which composite sample is more homogeneous than others. However, the D index provides a relatively stable description of the degree of distribution and also level of particle agglomeration for an individual composite based on the proximity of the D index to zero and/or one, since it is measured by using the ratio of standard deviation to the arithmetic mean. Instead, the β index utilizes the difference between the number of particles in each cell and mean number of particles per cell, and thus, quite a large

distribution of β index values (38.9, 52.7 etc.) can be obtained depending on the number of quadrats and representative microstructures [12]. Therefore, it is important to note that the β index can be generally used for comparison.

As a review, it was presented that the D index values measured for metal silicide-refractory oxide composite microstructures increase from 0.142 to 0.557 depending on the free-path spacing, coefficient of variation, and degree of distribution. It was found that the (60-40) vol% $\text{WSi}_2\text{-ZrO}_2$ composite displayed a high homogeneity, while the (60-40) vol% $\text{WSi}_2\text{-Y}_2\text{O}_3$ and (60-40) vol% $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites exhibited moderate and low level of homogeneity, respectively. It was demonstrated that the measured D index values and related degrees of distribution are quite reasonable based on the visual observation of the microstructures and their converted binary images. Furthermore, it was shown that accurate results for the composite microstructures having high or moderate level of homogeneity can be obtained by analyzing several lines (≤ 10), while there is a need to analyze more lines (≥ 28) for microstructures presenting low or very low level of homogeneity. These results clearly indicate that the proposed homogeneity analysis method works very accurately on different kinds of binary composite microstructures by considering the coefficient of variation and related D index value as a measure of the degree of distribution.

5.4 Conclusions

An image analysis method based on measuring free-path spacing was presented for the quantification of the degree of distribution or homogeneity in composite materials. It was presented that the proposed method is a useful tool for quantifying the degree of distribution with high accuracy by considering the coefficient of variation and related distribution (D) index as measures of the distribution, and also by eliminating the problematic quadrat effect. Since a high value of D index indicates a poor distribution, the homogeneity levels for composites are classified from perfect (maximum) to very low level based on increasing D index values. However, it was found that analysis of more lines may be needed in the case of a high level of agglomeration and low levels of homogeneity in

order to achieve more accurate data by covering all regions within a binary composite microstructure. In the case that homogeneously distributed, similar-sized agglomerates or clusters exist, then the proposed method may provide incorrect D index values due to lack of the free-path spacing values to be measured, which limits its use only for these specific kinds of composite microstructures. But in general, it was clearly shown that the proposed method can be efficiently applied to different types of binary composite microstructures for characterizing the degree of distribution. The presentation of this index will help in the correlation of microstructures and properties, and thus, assist in presenting a direction for controlling processing parameters for improved homogeneity and the associated physical properties of the composites. Continued studies are needed for improving its accuracy and practical use, and also transferring it to a computing environment for faster quantitative image analysis on more complex composite microstructures. Further advancement in this area can be quickly achieved through the collaboration of the materials science community with maturing computational areas such as mathematical morphology, computer/machine vision, and biometrics.

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CHAPTER 6: FABRICATION AND THERMOELECTRIC PROPERTIES OF EMBEDDED CERAMIC COMPOSITE THERMOCOUPLES

6.1 Introduction

Thermocouples are extensively used to measure the temperature of kilns, gas turbines, diesel engines and many other industrial processes and scientific applications due to their ability to cover a wide range of temperatures and their relative low cost [1]. However, the state of the art high temperature thermocouples based on noble metals are not stable for the applications demanding multiple atmospheres, as well as, extreme harsh environments for long duration [2]. Recently, thick- and thin-film thermocouples are preferred over conventional thermocouples due to their advantages of excellent spatial resolution, low cost, and capability of direct deposition on any surface without adhesives and surface preparation [3]. Budhani et al. [4] reviewed the problems and prospects of noble metal thin-film thermocouples for the application of blades and vanes of a high-temperature gas turbine jet engines. One of the issues with the most commonly used platinum-rhodium (Pt//Rh) alloy thin-film thermocouples is their poor oxidation resistance above 800°C [4]. Ceramic-based oxides, carbides and silicides are suggested as alternative materials for thermocouples used in high-temperature and harsh-environment applications due to their unique features of oxidation resistance, corrosion resistance, high melting points and relative thermodynamic stability on both oxidizing and reducing environments [5]. Chen et al. [6] developed thin film Pt-In₂O₃ and In₂O₃-In₂O₃:SnO₂ thermocouples for monitoring the surface temperature of components used in hot sections of gas turbine engines. The Pt//In₂O₃ thermocouple showed an average Seebeck coefficient of 224 $\mu\text{V}/^\circ\text{C}$ and thermoelectric voltage of 238 mV at 1273°C, whereas In₂O₃//In₂O₃:SnO₂ [95:05] wt% thermocouple displayed an average Seebeck coefficient of 162 $\mu\text{V}/^\circ\text{C}$ and thermoelectric voltage of 179 mV at 1273°C in air. These thermocouples exhibited higher stability and reproducibility compared to conventional Pt//Rh thermocouples from room temperature to 1300°C in air. However, the authors did not study the performance of these thermocouples

at lower partial pressures of oxygen (pO_2) where In_2O_3 and SnO_2 typically reduce. Wrbanek et al. [7] demonstrated TiC- and TaC-based thermocouples at very low pressure, but their performance degraded above $1000^\circ C$. They also reported the performance of the $CrSi_2//Pt$ and $TaC//Pt$ thermocouples in air up to 600° and $400^\circ C$, respectively. However, thermoelectric data is found to be very limited on non-metallic thin-film and thick-film thermocouples above $1000^\circ C$ [8].

Transition metal silicides ($MoSi_2$, WSi_2 etc.) are known for their excellent high-temperature oxidation resistance due to the formation of a passive oxide layer on their surface [9]. They may also form solid solutions with other oxides and exhibit stability on both high and low pO_2 . Metal silicides such as $MoSi_2$ and WSi_2 , and their composites, are widely used in heating applications including high-performance gas igniters and diesel glow plugs. The $MoSi_2-Al_2O_3$ composite-based igniter is known for its capability of heating to $1450^\circ C$ in less than ten seconds in both oxidizing and reducing atmospheres [9]. Thin-films of $MoSi_2$ also show excellent corrosion and erosion resistance at temperatures below $1500^\circ C$ due to formation of the Mo_5Si_3 and Mo_3Si passivation layers [10,11]. In the present work, $MoSi_2-Al_2O_3//WSi_2-Al_2O_3$, $MoSi_2-Al_2O_3//Pt$, $WSi_2-Al_2O_3//Pt$ and $MoSi_2//WSi_2$ thick-film ceramic composite thermocouples were fabricated by screen printing and lamination techniques using particulate mixtures of $MoSi_2-Al_2O_3$ and $WSi_2-Al_2O_3$, and Pt. The Al_2O_3 was added to the metal silicides in order to limit the grain growth/sintering mechanisms and oxidation reactions potentially during the extended use at the temperatures above $500^\circ C$. A set of thermocouples were fabricated by screen printing the silicide-oxide composite mixtures and platinum on alumina substrates, and by incorporating that design within the alumina microstructure via tape lamination processing. The phase development, microstructure and high-temperature thermoelectric performance of the sintered thermocouples were investigated. After optimization of the silicide-oxide composite composition, 22.9 cm long ceramic composite thermocouples with $400\text{ }\mu m$ thickness were fabricated, and the thermoelectric performance was subsequently evaluated up to $1350^\circ C$ in argon.

6.2 Materials and Method

Commercial MoSi_2 (99.5%) and WSi_2 (99.5%) powders (Alfa Aesar, Tewksbury, MA), and Al_2O_3 powder (99.8%, 8.6 m^2/g SSA; Almatiss, Leetsdale, PA) were used as starting materials for preparation of the particulate composite mixtures in this study. The initial X-ray diffraction (XRD, X'Pert Pro Panalytical, Westborough, MA) results of the starting powders (not shown) showed that the starting MoSi_2 powder consists of MoSi_2 (tetragonal, #98-064-4400) Mo_5Si_3 (tetragonal, #98-064-4413) and Mo (cubic, #01-089-5023) phases. Similar to the MoSi_2 starting powder, it was also found that WSi_2 (tetragonal, #98-065-2553), W_5Si_3 (tetragonal, #98-007-3331) and W (cubic) phases exist within the WSi_2 starting powder. Furthermore, the XRD result of the alumina powder (not shown) revealed that it had the corundum structure with the rhombohedral symmetry (#01-078-2427).

6.2.1 Formulation of ink and screen printing on alumina substrates

The thick-film thermocouple elements were deposited on alumina substrates by a screen printing technique. The details of the compositions of thermocouple elements are presented on the Table 13. The $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite powders with volume percentages of MoSi_2 and WSi_2 ranging from 50 to 90 vol% were synthesized by roll-milling. For simplicity, only the volume percentages were used to identify the composite compositions such as [50-50] and [90-10], since all amounts for the composites were determined based on volume percentages. The appropriate amounts of metal silicide (MoSi_2 , WSi_2) powders (Alfa Aesar, Tewksbury, MA) were mixed with fine alumina (Al_2O_3) powder (99.8%, SSA: 8.6 m^2/g , Alfa Aesar) and ball-milled in ethanol for 24 hours in a high-density polyethylene (HDPE) jar using 5 mm diameter yttria-stabilized zirconia milling media (Tosoh Corporation, Japan). The well-mixed powders were dried at 80°C in a vacuum oven and subsequently screened through a sieve having 44 μm size openings (325 mesh). Metal silicide-alumina composite inks required for the screen printing were prepared by mixing as-prepared silicide-oxide composite powders with an organic vehicle

Table 13. Configurations and compositions of the various metal silicide-oxide//Pt, metal silicide//metal silicide and metal silicide-oxide//metal silicide-oxide thermocouples studied (volume percentages are represented by []).

Thermocouple	Leg 1	Leg 2
[50-50] MoSi ₂ -Al ₂ O ₃ //Pt	[50-50] MoSi ₂ -Al ₂ O ₃	Pt
[60-40] MoSi ₂ -Al ₂ O ₃ //Pt	[60-40] MoSi ₂ -Al ₂ O ₃	Pt
[90-10] MoSi ₂ -Al ₂ O ₃ //Pt	[90-10] MoSi ₂ -Al ₂ O ₃	Pt
[50-50] WSi ₂ -Al ₂ O ₃ //Pt	[50-50] WSi ₂ -Al ₂ O ₃	Pt
[60-40] WSi ₂ -Al ₂ O ₃ //Pt	[60-40] WSi ₂ -Al ₂ O ₃	Pt
[75-25] WSi ₂ -Al ₂ O ₃ //Pt	[75-25] WSi ₂ -Al ₂ O ₃	Pt
[90-10] WSi ₂ -Al ₂ O ₃ //Pt	[90-10] WSi ₂ -Al ₂ O ₃	Pt
[50-50] MoSi ₂ -Al ₂ O ₃ //[50-50] WSi ₂ -Al ₂ O ₃	[50-50] MoSi ₂ -Al ₂ O ₃	[50-50] WSi ₂ -Al ₂ O ₃
[60-40] MoSi ₂ -Al ₂ O ₃ //[60-40] WSi ₂ -Al ₂ O ₃	[60-40] MoSi ₂ -Al ₂ O ₃	[60-40] WSi ₂ -Al ₂ O ₃
[75-25] MoSi ₂ -Al ₂ O ₃ //[75-25] WSi ₂ -Al ₂ O ₃	[75-25] MoSi ₂ -Al ₂ O ₃	[75-25] WSi ₂ -Al ₂ O ₃
[90-10] MoSi ₂ -Al ₂ O ₃ //[90-10] WSi ₂ -Al ₂ O ₃	[90-10] MoSi ₂ -Al ₂ O ₃	[90-10] WSi ₂ -Al ₂ O ₃
MoSi ₂ //WSi ₂	MoSi ₂	WSi ₂

(63-2 vehicle, Johnson Matthey, USA) followed by ultra-sonication. The ratio of composite powders to organic vehicle was fixed as 70:30 by wt% in all ink formulations.

The alumina substrates required for the thermocouples were fabricated by a tape casting process. The alumina tapes were prepared by using deflocculated alumina powders (SG20, SSA: 2.6 m²/g) mixed with the polyvinyl butyral binder, poly-alkaline glycol and benzyl butyl phthalate plasticizers/modifiers (Tape Casting Warehouse, Morrisville, PA). The slurries were casted into thin sheets with thickness of ~200 μm. The casted tapes were

cut into 175 mm x 175 mm thin sheets, vacuum packed and laminated at 90°C under 10 MPa pressure to form ~800 µm thick tape laminates. The as-prepared alumina tapes were laser cut into 30 mm x 15 mm substrates. The thermocouples were screen printed on alumina substrates with dimensions of 30 mm x 15 mm x 0.8 mm using an Aremco's Accu-Coat™ screen printer using a nylon screen (250 mesh). Initially, the left leg of the thermocouple was printed with the MoSi₂-Al₂O₃ composite ink followed by a heat treatment for 5 min at 50°C in an oven to dry the ink. The screen printing and drying processes were repeated four times to achieve a 400 µm thick thermocouple leg. After screen printing and drying of the left leg of the thermocouple, the right leg was similarly printed with the WSi₂-Al₂O₃ composite ink or Pt ink. The screen printing of two legs of the thermocouples was completed separately only due to the ease of processing the multiple repeat sensor samples. All these thermocouples were lastly sintered at 1500°C for 2 h under argon atmosphere. Figure 77 shows an optical photograph of a MoSi₂-Al₂O₃//WSi₂-Al₂O₃ thermocouple screen printed on an alumina substrate and sintered at 1500°C for 2 h in argon. The // symbol represented in the paper denotes a couple being formed with the compositions preceding and following the symbol. Figure 77 also displays the SEM micrographs of the post-annealed ceramic composite thermocouple legs made by [75-25] MoSi₂-Al₂O₃ and [75-25] WSi₂-Al₂O₃. After optimization of the metal silicide-oxide composition, both 5.1 and 22.9 cm long thermocouples were fabricated and subsequently embedded into the as-prepared alumina preforms.

6.2.2 Structural and thermoelectric characterization of thermocouples

An X'Pert Pro Panalytical X-ray diffractometer (Westborough, MA) with CuK_α radiation source was used to investigate the phase development of the sintered thick-film thermocouples. Data was collected from 16° to 110° angles (2θ) with a step size of 0.02 increments at a rate of 1°/min. An X'Pert High Score software was used to identify the phases, lattice parameters and crystal structure. The microstructures of the sintered thermocouples were examined by a scanning electron microscopy (SEM, JEOL 7600F, Peabody, MA; FE-SEM, Hitachi S-4700F, Tokyo, Japan). In addition to the XRD analyses,

Figure 77. Optical photograph and SEM micrographs of the [75-25] $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{WSi}_2\text{-Al}_2\text{O}_3$ composite thermocouple screen printed on an alumina substrate and then sintered at 1500°C for 2 h.

quantitative phase analysis studies via Rietveld method were performed by using the MAUD software [12] to determine the volume percentages of secondary phases formed after sintering. X-ray photoelectron spectroscopy (XPS) measurements were also carried out using a Physical Electronics, PHI 5000 Versa Probe spectrometer with a monochromatic AlK_α source operated at 300 W and a base pressure of 5×10^{-8} Torr. The XPS analysis was performed to understand the changes in the valence state and binding energy of the constituent elements present in the samples. Furthermore, thermoelectric properties of the ceramic composite thermocouples were measured using an atmospheric controlled high-temperature furnace, where K- and S-type thermocouples were used to monitor the cold and hot junction temperatures, and a National Instruments thermocouple reader was digitally connected to the computer through a LabVIEW software. The electrical contacts to thermocouples were made using platinum (Pt) paste and Pt wires at the cold junction held at the same temperature back to the digital multimeter.

6.3 Results and Discussion

6.3.1 Phase development in the composite thermocouples

XPS analyses were carried out to obtain information regarding chemical bonding and chemical state of the elements presented in the silicide-oxide composites. Figure 78a shows the XPS wide range survey spectra of all the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites with volume

Figure 78. (a) XPS wide range survey spectra and (b) high-resolution XPS spectra (Mo3d, Si2p, Al2p, O1s) of the various MoSi₂-Al₂O₃ composites after sintering at 1500°C for 2 h.

percentages of MoSi_2 varying from 50 to 90 vol% that were sintered at 1500°C for 2 h. The similar spectra and peaks corresponding to Mo, Si, Al, and O elements can be clearly seen for all the composites. In addition, high-resolution XPS spectra for the Mo3d , Si2p , Al2p and O1s collected from the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite samples are presented in the Figure 78b. The Mo3d spectra consists of two doublet peaks arising from $\text{Mo3d}_{5/2}$ and $\text{Mo3d}_{3/2}$ at the binding energies of 227.9 and 231.1 eV, respectively, corresponding to Mo^4 [13]. It is clearly evident that both $\text{Mo3d}_{5/2}$ and $\text{Mo3d}_{3/2}$ peaks shifted towards lower binding energies with increasing MoSi_2 content in the composite. The peak observed at 98.7 eV, that is characteristic for the Si2p high-resolution spectra, refers to the MoSi_2 phase [14]. Another high-intensity peak observed at 102.6 eV corresponds to SiO_2 phase, which indicated that the MoSi_2 was oxidized to form the SiO_2 and Mo_5Si_3 secondary phases based on its thermodynamically feasible oxidation reaction. In addition, the peaks appeared at 99.9 eV in the Si2p spectra were found to be a supportive data for the formation of Mo_5Si_3 phase in significant amounts particularly at the [75-25] and [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites. For the Al2p spectra, the peaks observed at 75.0 eV presents the existence of Al_2O_3 phase in the composites after sintering [15]. It is important to note that several peak shifts observed in the high-resolution XPS spectra may be related to the changes in Fermi energy levels caused by variations in defect concentrations and changes in electron charge density [16]. The peaks observed at 532.2 eV in the O1s spectra indicate that SiO_2 may be in its amorphous state. In addition to the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites, XPS survey spectra of the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites sintered at 1500°C for 2 h are shown in the Figure 79a. In the XPS spectra, the peaks corresponding to W, Al, Si and O were detected as expected for all the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite samples. Also, the high-resolution XPS spectra for the W4f , Si2p , Al2p and O1s peaks collected for these composites are presented in the Figure 79b. In the W4f spectra, two doublet peaks at the binding energies of 31.1 eV ($\text{W4f}_{7/2}$) and 33.5 eV ($\text{W4f}_{5/2}$) and a peak at 29.16 eV imply the presence of the WSi_2 phase. However, another single peak appeared at 35.4 eV, which represents WO_3 phase that might form on the surface in a very small amount due to high-temperature oxidation of the WSi_2 phase [17]. It is also found that Si2p spectrum of the [50-50] $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite displayed two peaks

Figure 79. (a) XPS wide range survey spectra and (b) high-resolution XPS spectra (W4f, Si2p, Al2p, O1s) of the various $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after sintering at 1500°C for 2 h.

at 97.9 and 101.5 eV, which represent WSi_2 and W_5Si_3 phases, respectively [18]. The peak shifts to lower binding energy levels were clearly observed with increasing metal silicide content from 50 to 90 vol%. The peak detected at 73.3 eV in the $\text{Al}2\text{p}$ spectra shows the presence of the Al_2O_3 phase. In addition, similar to the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites, peaks detected at 530.4 eV in the $\text{O}1\text{s}$ spectra reveal the presence of SiO_2 phase and its potential amorphous state [19]. The peak shifts to lower binding energy levels were also clear in $\text{Si}2\text{p}$, $\text{Al}2\text{p}$ and $\text{O}1\text{s}$ spectra with increasing WSi_2 content from 50 to 90 vol%. As a review of the XPS results, it was demonstrated that $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites having different volume percentages of metal silicide (50 to 90 vol%) consist of MoSi_2 and Al_2O_3 initial phases with Mo_5Si_3 and SiO_2 secondary phases formed during sintering. For all the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites, presence of WSi_2 , W_5Si_3 , Al_2O_3 and SiO_2 phases was similarly determined. However, the XPS results for the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite samples also revealed that there may be a formation of WO_3 phase in a small amount on the sample surface due to the high-temperature oxidation of WSi_2 . The formation of the 5-3 metal silicides (Mo_5Si_3 , W_5Si_3) and SiO_2 as secondary phases could be related to the high-temperature oxidation of starting metal silicide phases and metal silicide-oxide interactions at high-temperatures [20-22].

The phase analysis studies were additionally performed by XRD to understand the phase development and secondary phase formation in the composite systems during sintering better. Therefore, two representative samples with the lowest and highest metal silicide content, which are [50-50] and [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites, were selected for this study. Figure 80a shows the XRD patterns of these $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites after sintering at 1500°C for 2 h. MoSi_2 , Mo_5Si_3 and Al_2O_3 phases were detected for these composites, since they revealed similar XRD patterns after sintering. The crystal structure of MoSi_2 is a body-centered tetragonal with a space group of $\text{I}4/\text{mmm}$ and $\text{C}11_b$ type characterized by ABAB-type stacking along the c-axis, while Mo_5Si_3 has a tetragonal crystal structure with a space group of $\text{I-}42\text{m}$ [14]. However, the silica phase could not be detected by XRD due to its very small amount on the surface and possibly its amorphous

Figure 80. (a) XRD patterns of the [50-50] and [90-10] MoSi₂-Al₂O₃ composites after sintering at 1500°C for 2 h; (b-c) Rietveld refinement results of the [50-50] and [90-10] MoSi₂-Al₂O₃ composites, respectively [solid red lines = fitting curves; black dots = experimental XRD data].

state based on the XPS data. The presence of Mo_5Si_3 as a secondary phase may not be disadvantageous, since it has a higher melting point, improved creep resistance and relatively low oxidation resistance [9,23]. Lin and Speyer also studied surface oxidation mechanisms of MoSi_2 in the high-temperature combustion environments, and their studies revealed that material stability could be reestablished after a transient period under oxidizing and reducing environments due to the formation of a stable Mo_5Si_3 layer [24]. It is important to point out that alumina addition as an oxidation-resistant refractory oxide could substantially lower the oxygen diffusion into the composite systems. Therefore, it may significantly lower the amount of Mo_5Si_3 secondary phase in the composite systems, particularly at [50-50] and [60-40] volume percentages due to a significant amount of alumina phase (≥ 40 vol%). To determine the volume percentages of Mo_5Si_3 secondary phase and the changes in its amount as a function of increasing metal silicide content, quantitative phase analysis studies were additionally performed by utilizing the Rietveld method on the XRD patterns of the [50-50] and [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites. Figure 80(b-c) present the Rietveld refinement results of the [50-50] and [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites, where solid red lines and black dots represent fitting curves and experimental XRD data, respectively. It is important to note that the quality of the Rietveld refinement was sufficient enough, since the goodness of fit (sig) and weighted profile R-factor (R_{wp}) values were 2.7-3.0 and 5.1-5.8, respectively. The amounts of Mo_5Si_3 phase for the [50-50] and [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite samples were determined as 4.6 and 20.2 vol%, respectively. This result demonstrated that there was a 15.6 vol% increase in the volume percentage of Mo_5Si_3 secondary phase with increasing metal silicide content in the composite from 50 to 90 vol%. It was similarly reported in our previous study on the bulk $\text{MoSi}_2\text{-}$ and $\text{WSi}_2\text{-oxide}$ composites that amount of the Mo_5Si_3 and W_5Si_3 secondary phases substantially increased as a function of the refractory oxide material (fine/coarse Al_2O_3 , ZrO_2) and the annealing time at 1400°C [25]. The XPS and XRD data in the current work shows that the $\text{MoSi}_2\text{-}$ and $\text{WSi}_2\text{-based}$ thick-film composites also undergo a similar transformation to the 5-3 metal silicide phase as shown for the bulk samples; further work

Figure 81. SEM micrographs of the (a) [50-50], (b) [60-40], (c) [75-25] and (d) [90-10] MoSi₂-Al₂O₃ composites after sintering at 1500°C for 2 h.

is currently being completed to better understand the effect of sample density, oxygen partial pressure, and metal silicide-alumina grain boundaries on the transformation kinetics.

6.3.2 Microstructures of the composite thermocouples

Figure 81(a-d) displays the SEM micrographs of the MoSi₂-Al₂O₃ composites after sintering at 1500°C for 2 h. The bright and dark regions within all microstructures correspond to the MoSi₂ and Al₂O₃ particles, respectively. It is clear that distribution of MoSi₂ and Al₂O₃ grains are relatively homogeneous within the composites. These results also demonstrated that the degree of percolation and MoSi₂ grain size increased by increasing MoSi₂ volume percentage from 50 to 90 vol%. Another feature observed in the microstructures of [60-40] and [75-25] MoSi₂-Al₂O₃ composites was agglomeration of the MoSi₂ grains in some regions. This may be due to the difference in wetting behavior and

Figure 82. SEM micrographs of the (a) [50-50], (b) [60-40], (c) [75-25] and (d) [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after sintering at 1500°C for 2 h.

surface free energies of Al_2O_3 and MoSi_2 influencing the driving forces for sintering and grain growth. Further kinetic studies are currently being completed to understand the mechanisms of grain growth within the metal silicide-oxide composites. The SEM micrographs of the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites sintered at 1500°C are presented in the Figure 82(a-d). The bright and dark regions within these microstructures refer to the WSi_2 and Al_2O_3 particles, respectively. The microstructures were found to be highly similar to that of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites based on the homogeneity and grain sizes. The well-developed percolation paths of the conductive WSi_2 phase can be clearly seen for all $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites. However, it is important to note that 5-3 metal silicide (Mo_5Si_3 , W_5Si_3) secondary phases formed during sintering were not observable in the composite microstructures.

Figure 83 presents optical photographs and SEM micrographs of the [75-25] MoSi₂-Al₂O₃/Pt thermocouple screen printed on an alumina substrate and sintered at 1500°C for 2 h in argon. The microstructures of the alumina substrate, left leg (MoSi₂-Al₂O₃), right leg (Pt) and thermocouple junction can be seen in detail. The average size of the MoSi₂ grains were measured as 3-5 μm, and they were found to be well-connected in such a way that the percolation path of MoSi₂ grains on the left leg of the thermocouple was continuous without any cracks or voids. However, Pt right leg, as well as, the thermocouple junction revealed a porous structure. Also, as-sintered alumina substrate showed a few large grains within a fine grain matrix. No cracks or voids were observed on the alumina substrate after sintering. In addition, the Pt right leg revealed a very fine grain microstructure having slightly more porosity than the MoSi₂-Al₂O₃ composite (left leg). As a review, all thermocouple lines made of MoSi₂-Al₂O₃ and WSi₂-Al₂O₃ composites in the present study showed a good adhesion on the alumina substrate. No evidence of degradation, blisters or coalesce was observed on the composite and platinum thermocouple lines even after high-temperature sintering in argon. It is well known for fabrication of the ceramic composites that occurrence of interfacial microcracks due to thermal expansion and sintering mismatch between substrate and composite films is an important issue that needs to be addressed [9,25,26]. However, there was no evidence of interfacial microcracking in the presented composite microstructures. It must be noted that there is a close match between the coefficients of thermal expansion (CTEs) of metal silicides (MoSi₂, WSi₂) and alumina. Kobel et al. [27] studied thermal expansion behavior of the MoSi₂-Al₂O₃ composites with varying volume percentages of the MoSi₂ in a wide temperature range. They reported that CTEs of the pure Al₂O₃ and MoSi₂ only differ by 4%, and CTE of the [75-25] MoSi₂-Al₂O₃ composite matches with that of the pure Al₂O₃ from room temperature to 900°C. Therefore, it can be pointed out that the possibility of interfacial cracking within the MoSi₂-Al₂O₃ and WSi₂-Al₂O₃ composites is expected to be very low after repeated thermal cycling. Lu et al. [28] also investigated the MoSi₂-based composites reinforced by alumina fibers and platelets, and they similarly reported that both types of reinforcement did not create any interfacial cracks between the fillers and matrix,

Figure 83. Optical photograph and SEM micrographs (alumina substrate, left leg, right leg, junction) of the [75-25] MoSi₂-Al₂O₃//Pt thermocouple screen printed on an alumina substrate and then sintered at 1500°C for 2 h.

which is highly beneficial for these silicide-oxide composite thermocouples screen printed on the alumina substrates.

6.3.3 Thermoelectric characterization of the composite thermocouples

The Seebeck coefficient is a material property that dictates the thermally-derived voltage generated within a material. This property may be measured for a material by evaluating the slope of thermoelectric voltage (E)-temperature difference (ΔT) graph. Thermocouple sensors are based upon the junction of two electrically dissimilar materials having dissimilar Seebeck coefficients (S_A and S_B). The generated thermoelectric voltage is defined by the difference in their Seebeck coefficients ($S_{AB} = S_A - S_B$), and this can be written as [29]:

$$S_{AB} = \lim_{\Delta T \rightarrow 0} \frac{\Delta V_{AB}}{\Delta T} \quad (1)$$

where ΔV_{AB} is the electric potential across the interface of two dissimilar conductors within a thermal gradient, ΔT . In the present study, intrinsic Seebeck coefficients of the MoSi₂-Al₂O₃ (S_{MA}) and WSi₂-Al₂O₃ (S_{WA}) composites were estimated from the effective Seebeck coefficients of the MoSi₂-Al₂O₃//Pt (S_{MAPt}) and WSi₂-Al₂O₃//Pt (S_{WAPt}) thermocouples tested up to 1000°C in argon. According to the equation (1), difference in the effective Seebeck coefficients of the thermocouples with configurations of the MoSi₂-Al₂O₃//Pt and WSi₂-Al₂O₃//Pt can be written as:

$$S_{MAPt} = S_{MA} - S_{Pt} \quad (2)$$

$$S_{WAPt} = S_{WA} - S_{Pt} \quad (3)$$

where S_{MAPt} is the difference in the intrinsic Seebeck coefficients of the MoSi₂-Al₂O₃ (S_{MA}) and Pt (S_{Pt}) legs of the thermocouple; and S_{WAPt} is the difference in the intrinsic Seebeck coefficients of the WSi₂-Al₂O₃//Pt (S_{WA}) and Pt (S_{Pt}) legs of the thermocouple. By using the equations (2-3), the effective Seebeck coefficient of a composite thermocouple with a configuration of the MoSi₂-Al₂O₃//WSi₂-Al₂O₃ (S_{MAWA}) could be estimated as:

$$S_{MAWA} = S_{MA} - S_{WA} \quad (4)$$

where ΔS_{MAWA} denotes the estimated effective Seebeck coefficient of the MoSi₂-Al₂O₃//WSi₂-Al₂O₃ thermocouple by using the data obtained from the thermocouples made of MoSi₂-Al₂O₃//Pt and WSi₂-Al₂O₃//Pt.

To evaluate this experimentally, standard thermocouples with configurations of [50-50], [60-40], [75-25] and [90-10] MoSi₂-Al₂O₃//Pt, and [50-50], [60-40], [75-25] and [90-10] WSi₂-Al₂O₃//Pt were fabricated, and their thermoelectric responses were recorded as a function of temperature difference. It was reported that a Pt//Pd wire thermocouple (Pt-67 reference standard maintained by NIST) exhibited a Seebeck coefficient of 18.2 $\mu\text{V/K}$ at 900°C [30]. In the present study, thermocouples were tested by recording the voltage drop across the device with an acquisition system (DAQ, National Instruments) associated with a computer-based LabView software. The

estimated Seebeck coefficients of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites were determined by using the intrinsic Seebeck coefficient of Pt and effective Seebeck coefficients of $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ and $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples in the equations (2-3). Figure 84(a-d) presents the thermoelectric voltage and effective Seebeck coefficients of the various $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ and $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples as a function of temperature difference. The error margin in the thermoelectric characterization of [75-25] $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouple was very high; therefore, the related data is not presented and not included in further Seebeck coefficient calculations. The thermoelectric voltages of the [50-50], [60-40], and [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples were measured at 1000°C as 15.4, 21.9 and 36.2 mV, respectively. In addition, thermoelectric voltages of [50-50], [60-40], [75-25] and [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples measured at 1000°C were 12.8, 11.5, 14.8 and 30.5 mV, respectively. The thermoelectric voltage increased with increasing temperature, as well as, increasing metal silicide content (from 50 to 90 vol%) in the $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ and $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples. However, [50-50] $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ showed relatively higher thermoelectric voltage than [60-40] $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ only at the temperature gradients above 570°C, which could be related to the differences in percolation, volume percentage of secondary W_5Si_3 phase and its overall effect on thermoelectric output with respect to platinum. At lower temperature differences up to ~200°C, the thermoelectric voltages of all the $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ and $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples were found to be relatively low (<3 mV) (Figure 84a-c). It is also clear that the $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples exhibited higher thermoelectric voltages than the $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples at [50-50] and [60-40] volume percentages. In addition, at [90-10] volume percentage, they displayed relatively similar thermoelectric performance (>12 mV) at the temperature gradient above 600°C. As presented in the Figure 84c, [50-50] and [60-40] $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples also exhibited a very similar thermoelectric performance. However, a significant increase in the thermoelectric voltage was achieved by the [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouple.

Figure 84. (a-c) Thermoelectric voltages (E) and (b-d) effective Seebeck coefficients (S) measured for the various MoSi₂-Al₂O₃/Pt and WSi₂-Al₂O₃/Pt thermocouples as a function of temperature difference.

Figure 84. (continued) (a-c) Thermoelectric voltages (E) and (b-d) effective Seebeck coefficients (S) measured for the various $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ and $\text{WSi}_2\text{-Al}_2\text{O}_3\text{/Pt}$ thermocouples as a function of temperature difference.

To determine the effective Seebeck coefficients of these thermocouples, thermoelectric responses were fit to a second-order or a third-order polynomial using a least square method. Based on the theory [31], thermoelectric voltage (E) and Seebeck coefficient (S) can be expressed as:

$$\text{2}^{\text{nd}} \text{ order:} \quad E = A\Delta T + B\Delta T^2 + C \quad S = A + 2B\Delta T \quad (5)$$

$$\text{3}^{\text{rd}} \text{ order:} \quad E = A\Delta T + B\Delta T^2 + D\Delta T^3 + C \quad S = A + 2B\Delta T + 3D\Delta T^2 \quad (6)$$

where A, B, C and D are fitting coefficients, and ΔT is temperature gradient. In order to calculate the Seebeck coefficient in $\mu\text{V/K}$, the units of fitting coefficients were converted prior to these calculations. The effective Seebeck coefficients of the $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ and $\text{WSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ thermocouples are presented in the Figure 84(b-d) as a function of temperature difference (ΔT). Their thermoelectric properties and related fitting coefficients are additionally reviewed in the Table 14 and Table 15. At 500°C , the effective Seebeck coefficients (S_{500}) of [50-50], [60-40] and [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ thermocouples were measured as 12.1, 21.4 and $36.1 \mu\text{V/K}$, respectively; while [50-50], [60-40], [75-25] and [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ exhibited effective Seebeck coefficients of 12.0, 11.0, 12.4 and $28.2 \mu\text{V/K}$, respectively. The effective Seebeck coefficients of all thermocouples increased with increasing temperature difference up to 1000°C . The [50-50] and [60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ thermocouples exhibited similar behavior up to 200°C ; however, [60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ revealed higher effective Seebeck coefficients than [50-50] above that temperature. In the case of $\text{WSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ thermocouples, relatively higher Seebeck coefficients were observed for the [75-25] composition at the temperatures above 600°C , compared to the [50-50] and [60-40] thermocouples. Similar to their thermoelectric voltage data, [50-50] $\text{WSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ thermocouple showed relatively higher Seebeck coefficient than [60-40] only at higher temperature gradients. However, a substantial increase in the Seebeck coefficient was observed at the 90 vol% metal silicide content both for $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ and $\text{WSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ thermocouples (Figure 84b-d). These drastic increases in the effective Seebeck coefficients may be attributed to the interaction of charge carriers with non-equilibrium portion of the phonon distribution and spatial redistribution of the charge

Table 14. Summary of the fitting parameters (A, B and D) and R^2 values calculated, and then, used in thermoelectric calculations.

Thermocouple composition	A ($\mu\text{V/K}$)	B ($\mu\text{V/K}^2$)	D ($\mu\text{V/K}^3$)	R^2
[50-50] $\text{MoSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$	-9.93	0.0220	-	1.0
[60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$	0.96	0.0204	-	1.0
[90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$	8.09	0.0280	-	1.0
[50-50] $\text{WSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$	-7.36	0.0194	-	1.0
[60-40] $\text{WSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$	-4.55	0.0155	-	1.0
[75-25] $\text{WSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$	-9.65	0.0220	-	1.0
[90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$	-0.25	0.0284	-	1.0
[50-50] $\text{MoSi}_2\text{-Al}_2\text{O}_3//$ [50-50] $\text{WSi}_2\text{-Al}_2\text{O}_3$	3.93	0.0085	3.4×10^{-6}	0.999
[60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3//$ [60-40] $\text{WSi}_2\text{-Al}_2\text{O}_3$	-25.33	0.0657	-3.0×10^{-5}	0.999
[75-25] $\text{MoSi}_2\text{-Al}_2\text{O}_3//$ [75-25] $\text{WSi}_2\text{-Al}_2\text{O}_3$	6.38	0.0195	-1.2×10^{-5}	0.999
[90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3//$ [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$	14.17	0.0033	-	0.999
$\text{MoSi}_2//\text{WSi}_2$	25.03	0.0003	-	0.999

carriers in the composite matrix that promotes the average energy of the charge carrier [6]. In addition, it can be seen that [50-50] $\text{MoSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$ and [50-50] $\text{WSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$ thermocouples revealed a similar trend for their effective Seebeck coefficients, whereas $\text{MoSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$ thermocouples always exhibited higher Seebeck coefficients than the $\text{WSi}_2\text{-Al}_2\text{O}_3//\text{Pt}$ thermocouples with [60-40] and [90-10] compositions in a wide temperature range.

Table 15. Summary of the measured thermoelectric voltage (E_{1000}) and effective Seebeck coefficients (S_{500} , S_{1000}) of all thermocouples at 500°C and 1000°C.

Thermocouple composition	E_{1000} (mV)	S_{500} (μ V/K)	S_{1000} (μ V/K)
[50-50] MoSi ₂ -Al ₂ O ₃ // Pt	15.43	12.07	34.07
[60-40] MoSi ₂ -Al ₂ O ₃ // Pt	21.97	21.36	41.76
[90-10] MoSi ₂ -Al ₂ O ₃ // Pt	36.18	36.09	64.09
[50-50] WSi ₂ -Al ₂ O ₃ // Pt	12.84	12.04	31.44
[60-40] WSi ₂ -Al ₂ O ₃ // Pt	11.45	10.95	26.45
[75-25] WSi ₂ -Al ₂ O ₃ // Pt	14.81	12.35	34.35
[90-10] WSi ₂ -Al ₂ O ₃ // Pt	30.47	28.15	56.55
[50-50] MoSi ₂ -Al ₂ O ₃ // [50-50] WSi ₂ -Al ₂ O ₃	15.21	15.04	31.29
[60-40] MoSi ₂ -Al ₂ O ₃ // [60-40] WSi ₂ -Al ₂ O ₃	16.03	18.09	16.97
[75-25] MoSi ₂ -Al ₂ O ₃ // [75-25] WSi ₂ -Al ₂ O ₃	14.11	17.11	10.28
[90-10] MoSi ₂ -Al ₂ O ₃ // [90-10] WSi ₂ -Al ₂ O ₃	17.49	17.52	20.87
MoSi ₂ // WSi ₂	25.67	25.35	25.67

The experimental results of the MoSi₂-Al₂O₃//Pt and WSi₂-Al₂O₃//Pt thermocouples were initially used in this study to determine the estimated intrinsic Seebeck coefficients of the MoSi₂-Al₂O₃ and WSi₂-Al₂O₃ composites. Afterwards, these estimated values were utilized to calculate the estimated Seebeck coefficients of the various MoSi₂-Al₂O₃//WSi₂-Al₂O₃ composite thermocouples, which were then compared with the measured effective Seebeck coefficients of equivalent MoSi₂-Al₂O₃//WSi₂-Al₂O₃ composite thermocouples.

Figure 85. Estimated Seebeck coefficients (S) of the various $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites as a function of temperature difference (S_{Pt} is also presented).

Figure 85 presents the estimated intrinsic Seebeck coefficients of various $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites that were calculated by using the measured effective Seebeck coefficients of metal silicide-oxide//Pt thermocouples and reference intrinsic Seebeck coefficients of Pt [32] within the equations (2-3). At 500°C, the intrinsic Seebeck coefficients of the [50-50], [60-40] and [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites were calculated as -1.70, 7.59 and 22.3 $\mu\text{V/K}$, respectively. The intrinsic Seebeck coefficients of [50-50], [60-40], [75-25] and [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites were also determined at 500°C as -1.73, -2.82, -1.42 and 14.4 $\mu\text{V/K}$, respectively. Interestingly, the [60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3$, [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites revealed mostly positive estimated Seebeck coefficients, all other composites displayed negative estimated Seebeck

coefficients. In addition, the intrinsic Seebeck coefficients of the [50-50] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and [50-50], [60-40] and [75-25] $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites decreased with increasing temperature gradient, since their intrinsic Seebeck coefficients were all higher as negative values (-13.8 to -4.11 $\mu\text{V/K}$) at the temperatures below 400°C. These composites displayed very low intrinsic Seebeck coefficients at the temperatures above that temperature. Also, [50-50] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and [75-25] $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites showed almost identical intrinsic Seebeck coefficients at all temperatures (Figure 85). However, the intrinsic Seebeck coefficients of [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ significantly increased with increasing temperature gradient, particularly above 200°C. These results indicated that the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites could have higher intrinsic Seebeck coefficients at [90-10] composition based on the estimation using the data obtained by metal silicide-oxide//Pt thermocouples.

As previously described, $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{//WSi}_2\text{-Al}_2\text{O}_3$ composite thermocouples were fabricated by screen printing on tape-casted alumina substrates and sintered at 1500°C. Their thermoelectric performance was analyzed under argon atmosphere and compared with the estimated values. Pure $\text{MoSi}_2\text{//WSi}_2$ thermocouples were also fabricated to investigate the effect of alumina content on their thermoelectric performance. The thermoelectric voltages and effective Seebeck coefficients of these thermocouples are presented in the Figure 86(a-b) as a function of temperature difference (ΔT). These results are additionally summarized in the Table 15 for a better review of their thermoelectric performance. The thermoelectric voltage of all $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{//WSi}_2\text{-Al}_2\text{O}_3$ and $\text{MoSi}_2\text{//WSi}_2$ thermocouples increased significantly with increasing temperature up to 600°-1000°C. At 500°C, $\text{MoSi}_2\text{//WSi}_2$ thermocouple displayed a thermoelectric voltage of 12.9 mV; whereas, the [50-50], [60-40], [75-25], [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3\text{//[50-50]$, [60-40], [75-25], [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouples showed 3.85, 5.41, 6.53 and 7.89 mV, respectively, at the same temperature. The thermoelectric voltage relatively increased with increasing metal silicide (MoSi_2 , WSi_2) content on both legs of the thermocouple from 50 to 90 vol%. It was also demonstrated that the thermoelectric voltage decreased from 12.9 to

Figure 86. (a) Thermoelectric voltage (E) and (b) effective Seebeck coefficients (S) measured for the $\text{MoSi}_2/\text{WSi}_2$ and various $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouples as a function of temperature difference.

7.89 mV at 500°C with the addition of 10 vol% Al_2O_3 into both legs of the thermocouple. At 1000°C, [50-50], [60-40], [75-25], [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[50-50], [60-40], [75-25], [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouples exhibited 15.2, 16.0, 14.1 and 17.5 mV, respectively. It is clear that the [60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[60-40] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouple could have relatively higher thermoelectric voltage than [50-50] and [75-25] at 1000°C based on the calculations. The [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouple performed better than the other composite thermocouples throughout the temperature range.

The effective Seebeck coefficients as a function of temperature difference for the composite thermocouples are presented in Figure 86(b). The MoSi_2 / WSi_2 thermocouple showed 25.4 and 25.7 $\mu\text{V/K}$ at 500°C and 1000°C, respectively. The effective Seebeck coefficients of the [50-50], [60-40], [75-25], [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[50-50], [60-40], [75-25], [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouples measured at 500°C were 15.0, 18.1, 17.1 and 17.5 $\mu\text{V/K}$, respectively. Therefore, the [60-40] and [90-10] revealed slightly higher Seebeck coefficients than the other composite thermocouples at 500°C. In addition, the effective Seebeck coefficients of all the composite thermocouples were relatively lower than the pure MoSi_2 / WSi_2 thermocouple at the same temperature. At 1000°C, the effective Seebeck coefficients of the [50-50], [60-40], [75-25], [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[50-50], [60-40], [75-25], [90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouples were measured as 31.3, 17.0, 10.3 and 20.9 $\mu\text{V/K}$, respectively. It is important to point out that [50-50] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[50-50] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouple exhibited relatively higher Seebeck coefficient than MoSi_2 / WSi_2 and other composite thermocouples at 900°C and 1000°C; although, it showed lower Seebeck coefficients than those thermocouples at the temperatures below ~200°C. This result may be related to the local compositional changes at the junction of the two composite legs of the [50-50] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[50-50] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouples. Furthermore, a non-linear thermoelectric response was observed for the [60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[60-40] $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite thermocouple as seen in Figure 86(a-b). Multiple samples of this composition showed similar responses, and from the characterization previously presented, a significant difference in chemistry was not identified. This data was included in the paper to

emphasize that there are some effects of phase formation and transformation at the junction that still require further characterization and understanding. Bhatt et al. [3] reported a similar non-linear behavior for the TiC/TaC thin-film thermocouples even after several cycles of heating and cooling, which was attributed to the lack of control over the temperature difference between the hot and cold junctions of the thin films resulting in noise, drift and voltage spikes in the thermoelectric response. In addition, the [90-10] MoSi₂-Al₂O₃//[90-10] WSi₂-Al₂O₃ composite thermocouple displayed a Seebeck coefficient of 20.9 $\mu\text{V/K}$ at 1000°C, which is found to be highly comparable to that of the MoSi₂/WSi₂ thermocouple (25.7 $\mu\text{V/K}$) and also significantly higher than that of the high alumina containing composite thermocouples (10.3-17.0 $\mu\text{V/K}$). This result may be related to the high content of the 5-3 metal silicide (Mo₅Si₃, W₅Si₃) phases formed during sintering, since the XRD/Rietveld results proved that there was 15.6 vol% increase in the volume percentage of the Mo₅Si₃ secondary phase with increasing metal silicide content in the composite from 50 to 90 vol%. Therefore, a significant increase in the thermoelectric voltage and Seebeck coefficient of the [90-10] MoSi₂-Al₂O₃//[90-10] WSi₂-Al₂O₃ thermocouple can be clearly seen at all temperatures, particularly at 1000°C. It also showed the most stable thermoelectric response in a wide temperature range in comparison to the other composite thermocouples, since its effective Seebeck coefficient increased only from 14.4 to 20.9 $\mu\text{V/K}$ with increasing temperature gradient from 27°C to 1000°C. In addition, both MoSi₂/WSi₂ and [90-10] MoSi₂-Al₂O₃//[90-10] WSi₂-Al₂O₃ thermocouples revealed higher sensitivity (14.4-25.7 $\mu\text{V/K}$) than the mostly used Pt-Rh//Pt high-temperature thermocouples; since it was reported that S-type (90% Pt-10% Rh//Pt) and R-type (87% Pt-13% Rh//Pt) thermocouples have sensitivity ranging from 5.5 to 13.0 $\mu\text{V/K}$ throughout the temperature range from room temperature to 1000°C [33].

As a review, the above results indicated that higher silicide content positively affects thermoelectric response of the composite thermocouples in general, where the measured Seebeck coefficient was shown to generally increase with decreased alumina content. Also, the results demonstrated that MoSi₂/WSi₂ thermocouple (25.1-25.7 $\mu\text{V/K}$)

Figure 87. Comparison of the estimated (*dashed lines*) and measured effective (*solid lines*) Seebeck coefficients of the various MoSi₂-Al₂O₃/WSi₂-Al₂O₃ (abbreviated as MA/WA) composite thermocouples as a function of temperature difference.

showed nearly nine times higher performance compared to that predicted for the pure MoSi₂/WSi₂ couples estimated from previously reported Seebeck coefficient data. For example; the effective Seebeck coefficient for a MoSi₂/WSi₂ couple should be near 2.8 μV/°C, estimated from the data presented by Bennethum and Sherwood [34]. As briefly discussed above, the raw precursors and sintered composites used in the current study showed the additional 5-3 metal silicide phases (within both Mo and W compositions), as characterized by both XPS and XRD. It is believed that the addition of the 5-3 metal silicide phases within the thermocouple is enhancing the thermoelectric effect for the sensors above that predicted for the pure MoSi₂/WSi₂ compositions. As shown in this

work, the amount of 5-3 metal silicide phase increases in both the MoSi_2 and WSi_2 compositions as the alumina content is decreased, resulting in a significant increase in the Seebeck coefficient of the [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouple at 1000°C . Unfortunately, the Seebeck data for pure Mo_5Si_3 and W_5Si_3 phases are not available in literature, and further work is being completed by the current authors to investigate the intrinsic thermoelectric characteristics of various 5-3 metal silicide phases.

In addition, Figure 87 presents both estimated (*dashed lines*) and measured (*solid lines*) Seebeck coefficients of the various $\text{MoSi}_2\text{-Al}_2\text{O}_3$ / $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite thermocouples. The measured Seebeck coefficients of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ / $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite thermocouples were acquired directly from the experiments of the composite thermocouples. The estimated Seebeck coefficients were calculated by using the data obtained with the metal silicide-oxide//Pt thermocouples and utilizing the equations (2-4). It was demonstrated that the measured Seebeck coefficients from the actual $\text{MoSi}_2\text{-Al}_2\text{O}_3$ / $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite thermocouples were higher than those estimated from the data of metal silicide-oxide//Pt thermocouples and Pt reference. It can be also seen that the [50-50], [60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[50-50], [60-40] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouples exhibited relatively higher effective Seebeck coefficients than the [75-25] and [90-10] compositions only at 700°C ; while they exhibited lower effective Seebeck coefficients at the temperatures ranging from 27°C to $\sim 480^\circ\text{C}$ (*solid lines* in the Figure 87). In addition, the [60-40] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ /[60-40] $\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouple could display relatively higher Seebeck coefficients than the [90-10] at the temperatures above 400°C based on the estimated Seebeck coefficients (*dashed lines*). This estimated trend was clearly observed in the measured effective Seebeck coefficients of these composite thermocouples at the temperatures above 500°C , as seen in Figure 87. As a review, these results indicated that a difference in 5-3 metal silicide content may not be the only aspect influencing the thermocouple performance; local compositional changes at the junction of the two composite legs may also be enhancing the thermoelectric behavior. Further work must be

Figure 88. Thermoelectric performance of the [90-10] MoSi₂-Al₂O₃/[90-10] WSi₂-Al₂O₃ long composite thermocouple (22.9 cm length, 0.6 cm width) up to 1350°C, as a function of cold- and hot-junction temperature, and time.

completed in order to isolate the influence at this location, possibly through more compositionally controlled thin-film experiments.

To investigate the thermoelectric performance of a long thermocouple (22.9 cm length, 0.6 cm width, ~400 μm thickness) at higher temperatures, a composite thermocouple with a configuration of [90-10] MoSi₂-Al₂O₃/[90-10] WSi₂-Al₂O₃ was selected for an extended demonstration of the thermoelectric performance at higher temperatures and durations (1350°C for 10 h in argon). The thermoelectric performance of a long [90-10] MoSi₂-Al₂O₃/[90-10] WSi₂-Al₂O₃ composite thermocouple is presented as a function of temperature and time in the Figure 88. A reference thermocouple was placed near the cold and hot junction of the sensor sample; the temperature versus measurement

time data collected from both reference thermocouples was also included in the Figure 88. A slightly different testing configuration (compared to the smaller thermocouples discussed in this work) was needed for testing at the higher operation temperatures. The longer thermocouple was measured within a high-temperature tube furnace with alumina fiber-insulation placed around the cold-junction. Even with this insulation, the cold-junction reached a temperature of $\sim 460^{\circ}\text{C}$ when the 1350°C maximum isothermal was achieved. The thermoelectric voltage linearly increased with increasing temperature, and it exhibited a maximum thermoelectric voltage of 19.3 mV at 1350°C . It is also clear that its thermoelectric performance was adequately stable during the isothermal hold for 10 h. The slight changes in the thermoelectric voltage data during the isothermal hold were found to be caused by small temperature fluctuations ($\sim 0.02^{\circ}\text{C}$) of the high-temperature furnace; and therefore, it does not indicate any stability issue of the composite thermocouple. As a result, this thermoelectric response shows promise for future high-temperature applications for replacement of precious metal-based sensors.

6.4 Conclusions

Various thermocouples were fabricated by using two metal silicides (MoSi_2 , WSi_2), $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites, and platinum. The phase development, microstructural analysis and thermoelectric characterization studies were performed on various combinations of these materials. It was determined that 5-3 metal silicides (Mo_5Si_3 , W_5Si_3) were formed in the composite thermocouples as secondary phases during sintering. Small amounts of silica and tungsten oxide (WO_3) phases were also found to be formed on the surface of the thermocouples. In addition, an increase in the concentration of secondary 5-3 silicides with increasing metal silicide content in the composites was shown for the composites. Thermoelectric voltage and Seebeck coefficients of the thermocouples mostly increased with increasing temperature and metal silicide content. Significant improvements in the thermoelectric performance of the composite thermocouples ($\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$, $\text{WSi}_2\text{-Al}_2\text{O}_3/\text{Pt}$ and $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{WSi}_2\text{-Al}_2\text{O}_3$) were achieved particularly at the [90-10] volume percentage. It was proposed that the increased presence of the 5-3 metal silicide

(Mo_5Si_3 , W_5Si_3) phases formed within the composite systems having high metal silicide content (75-90 vol%) may be influencing the increased thermoelectric performance. In addition, the measured effective Seebeck coefficients of the $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{WSi}_2\text{-Al}_2\text{O}_3$ thermocouples were significantly higher than their estimated Seebeck coefficients from the Pt reference measurements, possibly indicating further compositional effects at the thermocouple junction. A long composite thermocouple with a configuration of [90-10] $\text{MoSi}_2\text{-Al}_2\text{O}_3$ //[90-10] $\text{WSi}_2\text{-Al}_2\text{O}_3$ embedded within an alumina preform displayed stable thermoelectric performance at 1350°C with a maximum thermoelectric voltage of 19.3 mV. This study presented that the $\text{MoSi}_2\text{-Al}_2\text{O}_3/\text{WSi}_2\text{-Al}_2\text{O}_3$ thick-film ceramic composite thermocouples have great potential for high-temperature measurements, and the ceramic-based composite thermocouples are relatively robust and stable, and substantially less costly compared to the mostly used precious metal-based thermocouples.

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CHAPTER 7: EFFECT OF ALUMINA PHASE AND HIGH-TEMPERATURE PREOXIDATION TREATMENT ON OXIDATION BEHAVIOR OF COMPOSITES

7.1 Introduction

Molybdenum silicide (MoSi_2) and tungsten silicide (WSi_2) were extensively studied due to their great potential for use in a broad range of structural and electrical applications subjected to elevated temperatures and harsh conditions such as gas turbine blades, heating elements and gate electrodes. Their high melting points ($>2000^\circ\text{C}$), good mechanical strength/hardness, excellent high-temperature oxidation resistance above 1000°C , and high electrical conductivity are described as their major advantages [1-6]. However, at relatively lower temperatures ($\sim 400^\circ\text{C}$ - 800°C), these silicides undergo catastrophic oxidation, as commonly referred as pest oxidation or pesting, resulting in dramatic structural disintegration from the bulk into a powder [7-10]. This accelerated internal oxidation phenomenon is found to be caused by simultaneous oxidation of metals (Mo, W) and silicon to form highly volatile molybdenum oxide (MoO_3) and tungsten oxide (WO_3) phases, which inhibit the formation of a protective and highly dense silica (SiO_2) layer on the surface [10-12]. The MoSi_2 - and WSi_2 -based materials are also known to be more prone to pest oxidation in the presence of high porosity, microcracks and internal stresses [13,14].

For greater application, these metal silicides need to be capable of operating under cyclic oxidation conditions in a wide temperature range ($\sim 400^\circ\text{C}$ - 1600°C) for long operation hours, and thus, it is crucial to improve their low-temperature (pest) oxidation resistance for enhancing their lifetime, reliability and performance. Therefore, different engineering approaches have been applied over the years to improve their oxidation resistance by controlling their oxidation kinetics. The substitutional alloying with metals and reinforcing with ceramic materials (composite approach) are the most widely used techniques in this

field [3,7,15]. The most common alloying elements for these silicide systems are aluminum, boron, chromium and vanadium, while carbides (e.g. SiC, TiC), borides (e.g. TiB₂, MoB) and Si₃N₄ are commonly used as a secondary reinforcing phase with these silicides. Some improvements on their low-temperature oxidation resistance were achieved mostly by the addition of different carbides and borides [12,16-18]. These achievements were attributed to the reduced oxygen diffusion rates owing to selective oxidation of the additive phases and the formation of relatively dense surface silica layers along with different oxide phases (e.g. TiO₂, Mo₉O₂₆). In addition, it was reported that the addition of 10-30 vol% Al₂O₃ phase could relatively lower the pest oxidation of MoSi₂ coatings at 500°C, but the molybdenum oxide (MoO₃) phase was still detected after exposure to air for 16 h [19]. However, it should be noted that the high-temperature oxidation of the MoSi₂ coatings was adversely influenced by the increased alumina content due to the formation of the mullite phase and pores within the surface [19,20]. There are limited studies conducted on the effect of alumina addition for the metal silicide-based (MoSi₂, WSi₂) material systems, and thus, further oxidation studies are highly needed.

Another approach to enhance the low-temperature oxidation of the metal silicides is through a high-temperature preoxidation treatment, which aims to form a protective surface layer without any reinforcement. To the author's knowledge, this alternative approach was first reported in open literature on hot isostatically pressed MoSi₂ samples by Berztiss et al. [21]. They preoxidized the MoSi₂ samples at 1000°C for 26 and 54 h, and directly cooled the samples to 500°C for performing the oxidation tests in an oxygen atmosphere. The results showed that the preoxidized MoSi₂ samples still oxidized after ~75-110 h of isothermal oxidation period at 500°C, but the process highly limited the internal oxidation. The clay-bonded MoSi₂-based composite samples were preoxidized at 1400°C for an hour in another study [22]. Their isothermal oxidation experiments at 500°C for 288 h showed that the specific mass change could be reduced from +0.466 to -0.007 mg/cm² by forming the protective surface silica (low-cristobalite) layer via the preoxidation treatment. This result demonstrated that the structural disintegration and pest oxidation of the MoSi₂ could

be highly restrained using this approach. However surprisingly, there are very limited studies investigating the effect of a high-temperature preoxidation treatment on the post oxidation of the transition metal silicides (e.g. MoSi₂, TiSi₂) [21-23], and no study was found on the WSi₂ system to the best of our knowledge. Therefore, the conceptual understanding of the high-temperature preoxidation treatment is very limited. Further studies are essential to better understand the mechanism and kinetics of the high-temperature preoxidation treatment, formation of surface oxide layers (surface characterization), and their effect on the low-temperature oxidation behavior of the transition metal silicides and their composites.

The high-temperature preoxidation treatment is a very promising approach for enhancing the low-temperature oxidation resistance of the transition metal silicides and their performance for high-temperature structural and electrical applications. This could be highly beneficial particularly for the high-temperature electrical applications (e.g. interconnects, sensors), since the intrinsic electrical properties of the transition metal silicides could be theoretically preserved at the same time, unlike the common alloying approaches which focus on structural applications. Therefore, in this study, MoSi₂-Al₂O₃ and WSi₂-Al₂O₃ composites were preoxidized at 1000°-1200°C to understand the combined effect of the alumina addition and high-temperature preoxidation on surface oxide formation and their low-temperature oxidation behavior. Their electrical properties were additionally characterized to examine the influence of the preoxidation treatment on their high-temperature electrical performance.

7.2 Materials and Method

7.2.1 Processing of the MoSi₂- and WSi₂-Al₂O₃ composites

Commercial MoSi₂ (99.5%) and WSi₂ (99.5%) powders were purchased from Alfa Aesar (Tewksbury, MA) as starting metal silicide powders, while the starting corundum Al₂O₃ powder (99.8%) was provided by Almatix (Leetsdale, PA). These powders were initially characterized by X-ray diffraction (XRD, Panalytical X'Pert Pro, Westborough, MA) and field emission scanning electron microscopy (FE-SEM, Hitachi S-4700F, Tokyo,

Japan). The results (not shown) displayed that starting metal silicide powders consisted of metal disilicides (MoSi_2 , WSi_2) and 5-3 metal silicides (Mo_5Si_3 , W_5Si_3), all with a tetragonal structure, and remaining metal phases (Mo, W). The average grain sizes of the starting MoSi_2 , WSi_2 and Al_2O_3 powders were 4.2, 5.3 and 0.4 μm , respectively, as measured using the ImageJ software [24]. The metal silicide powders had random morphology, while the equiaxed morphology was identified for the alumina powder as presented in our previous publication [25]. The $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite powders were prepared by the addition of 70 vol% of alumina phase via ball-milling in ethanol for 24 h. Since the metal silicide-oxide volume percentages kept constant at 30-70 vol%, only composite compositions ($\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$) were used throughout the paper. After the drying process at around 50°C , the cylindrical pellets with 13-26 mm diameter were pressed using a uniaxial press, followed by sintering at 1600°C for 2 h under 50 sccm of argon flow. The heating and cooling rates were kept constant at $3^\circ\text{C}/\text{min}$ during sintering processes. In addition, baseline MoSi_2 and WSi_2 pellets were sintered under similar conditions without the addition of the alumina phase for initial comparison.

7.2.2 High-temperature preoxidation treatment

Prior to the preoxidation treatment, very small square/rectangular specimens having 0.10-0.19 cm^2 surface area were prepared from the as-sintered composites by cutting and fine polishing with a 600 grit SiC polishing paper. Larger rectangular bar samples ($\sim 15 \times 4 \times 2$ mm) were also prepared from the selected samples for further high-temperature electrical measurements. This was followed by cleaning of the samples in ethanol under ultrasonication for 10 minutes. The as-prepared specimens were placed in a tube furnace within an alumina crucible. They were all preoxidized isothermally at $1000^\circ\text{-}1200^\circ\text{C}$ under 10 sccm of air flow for different time periods ranging from 10 to 120 minutes. After the preoxidation treatment was completed, they were further heated to 1300°C by $2^\circ\text{C}/\text{min}$ and held there for 2 h to densify the surface oxide layer formed. It should be noted that all steps (heating, cooling and isothermal hold at 1300°C), except for the isothermal preoxidation treatments, were conducted in argon (50 sccm) to avoid any other oxidation reactions.

Table 16. High-temperature preoxidation (PO) treatment conditions and sample denotations.

Preoxidation temperature	Preoxidation time (minutes)	PO sample denotation
1000°C	10	PO-1000-10
	30	PO-1000-30
	60	PO-1000-60
	120	PO-1000-120
1100°C	10	PO-1100-10
	30	PO-1100-30
	60	PO-1100-60
	120	PO-1100-120
1200°C	10	PO-1200-10
	30	PO-1200-30
	60	PO-1200-60
	120	PO-1200-120

The air and argon volumetric flow rates were controlled by a LabVIEW program (National Instruments, Austin, TX) as a function of time and temperature. For simplicity, the preoxidized composite samples (*abbreviated as **PO***) were labeled in this paper based on the preoxidation conditions; for example, a composite sample preoxidized at 1000°C for 30 minutes was termed as “PO-1000-30”. All preoxidation conditions and sample denotations are additionally listed in Table 16. The optical macrographs of the samples were recorded before/after preoxidation treatments using a digital microscope (Dino-Lite, New Taipei City, Taiwan).

7.2.3 Oxidation tests and material characterization

A thermogravimetric analyzer (TGA, Pyris 1, PerkinElmer, Shelton, CT) was used to perform the non-isothermal oxidation tests in an ambient air atmosphere (20 ml/min) at the temperatures ranging from 50°C to 870°C. The heating rate was kept constant at 10°C/min for all oxidation experiments conducted on the reference silicide samples (MoSi₂, WSi₂), as-sintered composites (without preoxidation, *termed as w/o PO*) and preoxidized composites (*termed as w/ PO*). The optical images of the samples were also taken after the non-isothermal oxidation tests. The densities of the as-sintered composites were measured by applying the Archimedes technique using ethanol as the immersion liquid. The apparent porosity levels of the non-preoxidized MoSi₂-Al₂O₃ and WSi₂-Al₂O₃ composites were then calculated as 10.4 (± 0.81) and 8.3% (± 2.10), respectively. The bright-field optical images of the composite surfaces were taken by a light microscope (Axio Lab.A1, Zeiss, Jena, Germany) using a contrast enhancing blue color filter. For microstructural analyses, the cross-sectional areas of the composite samples were polished using SiC polishing sheets (600-1200 grits) followed by a diamond paste (0.5 μm). After 10 minutes of overall polishing process, the as-polished samples were subsequently ultrasonicated in deionized water and ethanol, each for 10-15 minutes. The cross-sectional microstructural analysis of the samples was performed using a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700F, Tokyo, Japan).

The phase analysis of the composite samples was initially conducted by X-ray diffraction (XRD, Panalytical X'Pert Pro, Westborough, MA) with CuK_α radiation source. The surface characterization of the composite samples before/after high-temperature preoxidation treatments were performed by X-ray photoelectron spectroscopy (XPS, Physical Electronics, PHI 5000 VersaProbe, Chanhassen, MN) and Raman microscope (Renishaw InVia Raman, New Mills, UK). The XPS analyses were conducted using a focused monochromatized Al-K_α radiation (1486.6 eV), and the peaks were recorded with a constant pass energy of 0.5 eV in the 0 to 1400 eV spectral range. Raman spectra of the composites were measured with 532 nm Ar laser excitation, where the laser beam was

focused on the sample with a 50× microscope objective with a 100% laser power. Standard 4-point DC electrical conductivity measurements were conducted at the temperatures up to 950°C using the as-prepared rectangular bar samples, which were attached to the test setup made of a four-bore alumina tube and platinum (Pt) wires (99.95% pure, Surepure Chemetals, Florham Park, NJ). The electrical measurements were carried out in argon atmosphere for a better comparison of the electrical data of the composite samples with (and without) subjected to the high-temperature preoxidation treatment. It should be also noted that the surface oxide layers formed after preoxidation were removed via fine polishing using 1200 grit SiC polishing paper for ~30-40 seconds before electrical tests due to the insulating characteristics of the surface layers and difficulty of making continuous Pt electrical connections. A digital multimeter (Keithley 2100, Tektronix, Beaverton, OR) was controlled by LabVIEW (National Instruments, Austin, TX) and Keithley software to measure the electrical resistance of the composite samples as a function of temperature, which was simultaneously recorded by a B-type of thermocouple.

7.3 Results

7.3.1 Non-isothermal low-temperature oxidation

The oxidation-induced mass changes for the as-sintered (non-preoxidized) silicides (MoSi_2 , WSi_2) and their composites with the addition of 70 vol% alumina phase are presented in Figure 89 as a function of oxidation temperature ranging from 50°C to 870°C. A negligible mass gain ($\leq 0.12 \text{ mg/cm}^2$) was observed for the MoSi_2 and $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite samples up to around 400°C. It is apparent that there was a notable mass gain at the temperature region of 400°-780°C due to low-temperature oxidation of MoSi_2 leading to the formation of MoO_3 and SiO_2 as oxidation products [21,26,27]. The overall mass gain at 780°C for the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite (0.44 mg/cm^2) was relatively lower than that for the MoSi_2 (0.72 mg/cm^2). The mass loss was detected above this temperature, which is related to the evaporation of the volatile MoO_3 phase [12]. However, no pest oxidation was observed for both MoSi_2 -based samples during non-isothermal oxidation, since pesting usually refers to the formation of volatile oxide species, followed by a structural disintegration of the bulk samples into powders [28]. Similar to the MoSi_2 -based materials,

Figure 89. Mass change per unit surface area of the as-sintered (non-preoxidized) (a) MoSi₂ and 30-70 vol% MoSi₂-Al₂O₃, and (b) WSi₂ and 30-70 vol% WSi₂-Al₂O₃ samples as a function of oxidation temperature in air (“w/o” term refers to non-preoxidized samples).

there was a very low mass gain ($< 0.27 \text{ mg/cm}^2$) for the as-sintered WSi_2 and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite samples at the temperature region of $50^\circ\text{-}500^\circ\text{C}$ (Figure 89b). The significant mass gain for both samples is apparent starting from 500°C , but it was found to be more drastic at the temperatures ranging from $\sim 730^\circ\text{C}$ to 870°C . However, the overall mass gain at 870°C for the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite (12.81 mg/cm^2) was substantially lower than that of the WSi_2 (26.34 mg/cm^2). Unlike the MoSi_2 -based samples, these bulk samples completely disintegrated into a powder form owing to the poorer oxidation resistance of the WSi_2 , which resulted in the formation of WO_3 and SiO_2 as oxidation products leading to their pest oxidation [6,10]. In brief, the addition of the 70 vol% alumina highly reduced the mass gain, which could be attributed to the less interaction of the metal silicide phases with open environment owing to their coverage with the oxide phase. However, the level of decrease in mass gain ($\sim 38.9\text{-}51.4\%$) was not proportional to the decrease in the silicide content (70 vol%), which implied possible differences in porosity levels between the samples, and heterogeneous composite microstructures.

After examining the influence of the alumina addition on the oxidation behavior, the high-temperature preoxidation treatment was applied to the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites in order to understand the kinetics and to further improve their oxidation resistance by lowering or eliminating their pest oxidation behavior. Figure 90 displays the oxidation-induced mass change for (a-c) $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (d-f) $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites, which were all preoxidized (*termed as w/ PO*) at $1000^\circ\text{-}1200^\circ\text{C}$ for a period of time ranging from 10 to 120 minutes. The non-isothermal oxidation data of the non-preoxidized (without preoxidation, *termed as w/o PO*) composite samples was also included here for a better comparison. For the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites, the overall mass gain significantly increased after preoxidation at 1000°C for 10-30 min, in comparison with the non-preoxidized sample (Figure 90a). The formation and evaporation curves of a volatile phase were clearly observed for these two samples. At the peak points around 700°C (before evaporation or mass loss), the mass gain increased from 0.40 to $1.31\text{-}2.39 \text{ mg/cm}^2$, which could be due to the formation of a porous surface layer with a remaining volatile oxide

Figure 90. Mass change per unit surface area of the non-preoxidized (w/o) and preoxidized (w/) (a-b-c) 30-70 vol% MoSi₂-Al₂O₃, and (d-e-f) 30-70 vol% WSi₂-Al₂O₃ composites as a function of oxidation temperature in air (*a-d*, *b-e*, *c-f* presents the samples preoxidized at 1000°C, 1100°C and 1200°C, respectively).

Figure 90. (continued) Mass change per unit surface area of the non-preoxidized (*w/o*) and preoxidized (*w/*) (a-b-c) 30-70 vol% MoSi₂-Al₂O₃, and (d-e-f) 30-70 vol% WSi₂-Al₂O₃ composites as a function of oxidation temperature in air (*a-d*, *b-e*, *c-f* presents the samples preoxidized at 1000°C, 1100°C and 1200°C, respectively).

Figure 90. (continued) Mass change per unit surface area of the non-preoxidized (*w/o*) and preoxidized (*w/*) (a-b-c) 30-70 vol% MoSi₂-Al₂O₃, and (d-e-f) 30-70 vol% WSi₂-Al₂O₃ composites as a function of oxidation temperature in air (*a-d*, *b-e*, *c-f* presents the samples preoxidized at 1000°C, 1100°C and 1200°C, respectively).

species during preoxidation treatment at 1000°C for a short period. Therefore, a partial pest oxidation was observed for these samples. However, it is evident that the overall mass gain was highly reduced by preoxidizing the composites for 60-120 min at the same temperature. At higher preoxidation temperatures (1100°-1200°C), the critical preoxidation time was much shorter for the MoSi₂-Al₂O₃ composites, as seen in Figure 90b-c. The overall mass gain at 870°C was significantly lowered from 0.45 to 0.09-0.15 mg/cm² by preoxidizing the samples, even only for 10 min. For the WSi₂-Al₂O₃ composites, preoxidation treatment at 1000°C for 10 min did not affect the low-temperature oxidation behavior, since the overall mass gain of the preoxidized sample at 870°C (12.42 mg/cm²) was quite similar to that of the non-preoxidized sample (12.81 mg/cm²). It should be noted that further preoxidation studies at 1000°C were not conducted for the WSi₂-Al₂O₃ samples due to the formation of porous surface layers and pest oxidation during preoxidation treatment. However, significant reductions in the overall mass gain were clearly observed as a function of increasing preoxidation time at 1100°-1200°C (Figure 90e-f), indicating the requirement of longer preoxidation time periods (≥ 60 min) for the WSi₂-Al₂O₃ composites. The overall mass gain at 870°C was decreased from 12.81 to 0.11-0.15 mg/cm² by preoxidizing the composite samples at 1100°C for 60-120 min and at 1200°C for 120 min.

After non-isothermal oxidation tests, the overall mass gain values recorded at 870°C for the preoxidized composite samples are summarized as a function of preoxidation time in Figure 91a-b to understand the kinetics of the high-temperature preoxidation treatment at three different temperatures. It is apparent that there is a critical preoxidation time at different temperatures, which is necessary to achieve a protective layer on the composite surfaces and to highly improve their low-temperature oxidation resistance. As additionally reviewed in Figure 91c, the oxidation-induced mass gains in their specific pest oxidation regions (~400°-750°C for the MoSi₂-Al₂O₃; ~400°-870°C for the WSi₂-Al₂O₃) were determined to be ~0.02-0.05 mg/cm² after high-temperature preoxidation treatment for 120 min. Therefore, further studies (e.g. microstructure, surface chemistry) were only performed on the selected preoxidized composite samples (at 1000°-1200°C for 120 min),

Figure 91. Effect of preoxidation time and temperature on the overall mass gain at 870°C for the (a) 30-70 vol% MoSi₂-Al₂O₃, (b) 30-70 vol% WSi₂-Al₂O₃ composites, and (c) mass change per unit surface area in the pest oxidation temperature regime for the composites preoxidized at 1000°-1200°C for 120 min.

Figure 91. (continued) Effect of preoxidation time and temperature on the overall mass gain at 870°C for the (a) 30-70 vol% MoSi₂-Al₂O₃, (b) 30-70 vol% WSi₂-Al₂O₃ composites, and (c) mass change per unit surface area in the pest oxidation temperature regime for the composites preoxidized at 1000°-1200°C for 120 min.

along with the non-preoxidized samples, to better understand how high-temperature preoxidation treatment improved their oxidation resistance.

7.3.2 Optical micrographs and SEM microstructures of surface layer morphologies

The optical micrographs of the protective surface features of the preoxidized MoSi₂- and WSi₂-Al₂O₃ composites are shown in Figure 92. For baseline, the surface images of the non-preoxidized samples are also included. It is evident that different surface morphologies with glassy type of features were formed on the surface of the composite samples during high-temperature preoxidation treatment conducted at 1000°-1200°C for 120 min. For MoSi₂-Al₂O₃ system, the surface features were identified to be very similar

Figure 92. Optical micrographs of the surface of the non-preoxidized (*w/o PO*) and preoxidized (*w/ PO*) (a-b-c-d) 30-70 MoSi₂-Al₂O₃ and (e-f-g-h) 30-70 WSi₂-Al₂O₃ composites (non-preoxidized sample surfaces are presented as baseline).

Figure 92. (continued) Optical micrographs of the surface of the non-preoxidized (*w/o PO*) and preoxidized (*w/ PO*) (a-b-c-d) 30-70 MoSi₂-Al₂O₃ and (e-f-g-h) 30-70 WSi₂-Al₂O₃ composites (non-preoxidized sample surfaces are presented as baseline).

Figure 92. (continued) Optical micrographs of the surface of the non-preoxidized (*w/o PO*) and preoxidized (*w/ PO*) (a-b-c-d) 30-70 $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (e-f-g-h) 30-70 $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites (non-preoxidized sample surfaces are presented as baseline).

Figure 92. (continued) Optical micrographs of the surface of the non-preoxidized (*w/o PO*) and preoxidized (*w/ PO*) (a-b-c-d) 30-70 $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (e-f-g-h) 30-70 $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites (non-preoxidized sample surfaces are presented as baseline).

after preoxidation at 1100°-1200°C, but glassy regions seemed to be different and more clear after preoxidation at 1000°C. Significant differences on the surface features formed can be similarly seen for the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites preoxidized at different temperatures. As also described in the previous section, the preoxidation treatment at 1000°C was found to be not applicable for the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites due to the pest oxidation and structural disintegration of the samples during preoxidation process, as shown by the optical images.

Figure 93 presents the cross-sectional SEM microstructures of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after high-temperature preoxidation treatment at 1000°-1200°C for 120 min. The highly dense protective surface layers were clearly observed on the surfaces of the preoxidized composite samples. The average thicknesses of the protective surface layers after preoxidation of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite samples at 1000°C, 1100°C and 1200°C were 4.94 μm (± 1.008), 14.16 μm (± 0.605) and 6.45 μm (± 0.900), respectively. For the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites, the average thickness of the surface layer decreased from 4.81 (± 1.013) to 3.05 μm (± 0.147) with increasing preoxidation temperature from 1100°C to 1200°C. The protective surface layers formed more homogeneously on the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ (w/ PO-1100-120) and $\text{WSi}_2\text{-Al}_2\text{O}_3$ (w/ PO-1200-120) composite samples, since the thicknesses of the surface layers were found to be more similar at different regions. In addition, different features were detected on the outer surface (bright regions) of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite preoxidized at 1000°C, as similarly identified on its optical micrograph. The metal disilicide (MoSi_2 , WSi_2) and 5-3 metal silicide (Mo_5Si_3 , W_5Si_3) grains were identified within the composite microstructures, as marked in Figure 93. The secondary 5-3 metal silicide phases were formed at the regions closer to the surface layer during the preoxidation processes, as dictated by the thermodynamics of the high-temperature (above ~1000°C) oxidation reactions of the starting metal disilicides [6,28,29]. These results are in good agreement with the reported research studies, since it is known that these metal silicides react with oxygen at high temperatures to form 5-3 metal silicide phases mostly underneath the surface layer [25,30].

Figure 93. Cross-sectional SEM microstructures of the (a-b-c-d-e) 30-70 $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (f-g-h-i) 30-70 $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after preoxidation at 1000°-1200°C for 120 min.

Figure 93. (continued) Cross-sectional SEM microstructures of the (a-b-c-d-e) 30-70 $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (f-g-h-i) 30-70 $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after preoxidation at 1000°-1200°C for 120 min.

Figure 93. (continued) Cross-sectional SEM microstructures of the (a-b-c-d-e) 30-70 $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (f-g-h-i) 30-70 $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after preoxidation at 1000°-1200°C for 120 min.

Figure 93. (continued) Cross-sectional SEM microstructures of the (a-b-c-d-e) 30-70 MoSi₂-Al₂O₃ and (f-g-h-i) 30-70 WSi₂-Al₂O₃ composites after preoxidation at 1000°-1200°C for 120 min.

Figure 93. (continued) Cross-sectional SEM microstructures of the (a-b-c-d-e) 30-70 $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (f-g-h-i) 30-70 $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after preoxidation at 1000°-1200°C for 120 min.

7.3.3 Structural analysis of the composites

The structural analysis of the non-preoxidized (*w/o PO*) and preoxidized (*w/ PO*) $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites was initially performed using XRD to identify the possible phase changes after the high-temperature preoxidation treatment. Figure 94 presents the XRD patterns taken from the surfaces of the composite samples. As baseline data, the XRD patterns of the non-preoxidized composites revealed the presence of the starting metal disilicide (tetragonal-structured MoSi_2 , WSi_2) and alumina. In addition to their high intensity peaks, low intensity peaks were also detected mostly at the 2θ range of 36-46°, referring to the tetragonal-structured Mo_5Si_3 and W_5Si_3 phases existing within the composites even before preoxidation treatments. After preoxidation of the composites at 1000°-1200°C for 120 min, significant structural changes were observed. The peak intensities for the Mo_5Si_3 phase increased as a function of preoxidation temperature (1000°-1200°C), which implies an increase in its amount within the preoxidized $\text{MoSi}_2\text{-Al}_2\text{O}_3$

Figure 94. XRD patterns of the 30-70 vol% (a) $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (b) $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after preoxidation at 1000°-1200°C for 120 min (XRD results of the non-preoxidized samples are used as baseline).

composites. In addition, the peak intensities for the MoSi_2 decreased significantly, while $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ as a ternary intermetallic phase and Al_2SiO_5 (a mullite polymorph) phases were formed (Figure 94a). Similar structural changes were also detected within the preoxidized $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites, since $\text{W}(\text{Si}_{1-x}\text{Al}_x)_2$ and Al_2SiO_5 were identified after high-temperature preoxidation treatment at $1100^\circ\text{-}1200^\circ\text{C}$. However, the W_5Si_3 peaks were found to be more intense after preoxidation at 1100°C for 120 min (Figure 94b). The notable reduction in the peak intensities of the starting metal silicides (MoSi_2 , WSi_2) could be related to the significant thickness of the protective surface layers, and also, the presence of alumina, mullite and 5-3 metal silicide (Mo_5Si_3 , W_5Si_3) as major phases beneath the surface layers. These results indicate that different reactions took place simultaneously during high-temperature preoxidation treatments, referring to the formation of the complex surface structures.

7.3.4 Surface chemistry of the protective surface layers

The Raman spectra of the surfaces of the non-preoxidized (*w/o PO*) and preoxidized (*w/ PO*) $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites are shown in Figure 95. The Raman spectrum of the non-preoxidized $\text{MoSi}_2\text{-Al}_2\text{O}_3$ baseline sample revealed two sharp strong peaks located at 326 and 441 cm^{-1} , which were attributed to the A_{1g} and E_g Raman active lattice modes of the tetragonal MoSi_2 [31]. Similarly, two sharp strong peaks located at 331 and 453 cm^{-1} for the non-preoxidized $\text{WSi}_2\text{-Al}_2\text{O}_3$ were assigned to the tetragonal WSi_2 , and the related vibration of silicon atoms in x-y planes and along z-direction [32,33]. Significant changes in the surface chemistry of the composite structures were clearly observed after high-temperature preoxidation treatments. Four weak Raman peaks were detected at 154 , 170 , 215 and 292 cm^{-1} for the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ sample preoxidized at 1000°C . These peaks imply the presence of remaining molybdenum oxide species (e.g. MoO_3) and/or a silica polymorph (tridymite or cristobalite) on the surface layer in small amounts [34-37]. These peaks were not observed after preoxidation at $1100^\circ\text{-}1200^\circ\text{C}$, possibly indicating the formation of molybdenum oxide-free surface layers at higher temperatures. After the preoxidation of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ at 1100°C , four very small peaks

Figure 95. Raman spectra taken from the surfaces of the 30-70 vol% (a) MoSi₂-Al₂O₃ and (b) WSi₂-Al₂O₃ composites after preoxidation at 1000°-1200°C for 120 min (Raman spectra of the non-preoxidized samples are presented as baseline).

were detected at 637, 794, 854 and 928 cm^{-1} , which may be due to the presence of a mullite polymorph or $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$ phase. However, after preoxidation of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ at 1200°C, five highly broad and strong peaks were identified at 196, 337, 490, 580 and 736 cm^{-1} . It was determined from the peaks located at 337 and 490 cm^{-1} that there was a significant Raman peak broadening and shifting to higher energy levels compared to the baseline MoSi_2 peaks. This could be due to the Al substitution into the MoSi_2 lattice to form the ternary intermetallic phase, $\text{Mo}(\text{Si}_{1-x}\text{Al}_x)_2$, on the surface layer during preoxidation, since the Raman spectroscopy is well-known as an important tool to study the solid solution and ternary phase formations. The peak located at 196 cm^{-1} could be attributed to a silica polymorph (tridymite or quartz) [36,37]. Similar peak shifts were also observed for the other two peaks (580 and 736 cm^{-1}), which were close to the Raman modes of the bulk Al_2O_3 [38]. For the $\text{WSi}_2\text{-Al}_2\text{O}_3$ system, similar peaks located at 331, 376, 442, 453 and 497 cm^{-1} were identified after preoxidation at 1100°C and 1200°C (Figure 95b). The broadening of the two peaks (331 and 453 cm^{-1}) could be similarly correlated to the formation of the ternary intermetallic phase ($\text{W}(\text{Si}_{1-x}\text{Al}_x)_2$) within the surface layer. The close three peaks located at 376, 422 and 497 cm^{-1} implied the presence of an amorphous silica layer along with a cristobalite- SiO_2 [37,39]. Also, after preoxidation at 1100°C, three different peaks were observed at 578, 643 and 748 cm^{-1} , which may indicate the presence of Al_2O_3 and remaining tungsten oxide species (e.g. WO_3) within the surface layer [38,40,41]. It should be noted that the Raman modes of W_5Si_3 at 117, 170 and 270 cm^{-1} were not detected [42], referring to the formation of 5-3 metal silicide phases beneath the protective surface layer, not within that layer.

The surface chemical characteristics of the composite samples were comprehensively examined by X-ray photoelectron spectroscopy (XPS). It should be noted that these results only represent the surface composition of the protective layers due to the high surface sensitivity of the XPS instrument, which is only a few nanometer of penetration depth [43]. Figure 96 presents the XPS survey spectra of the surface features of the non-preoxidized and preoxidized $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite samples.

Figure 96. XPS survey spectra taken from the surfaces of the 30-70 vol% (a) MoSi₂-Al₂O₃ and (b) WSi₂-Al₂O₃ composites after preoxidation at 1000°-1200°C for 120 min (XPS spectra of the non-preoxidized samples are used as baseline).

The existence of the C 1s peaks detected could be due to the phenomenon of the adventitious carbon layer formation [44]. For the baseline non-preoxidized MoSi₂-Al₂O₃ composite sample, the Mo 3d, Al 2p and Si 2p peaks indicate the presence of the MoSi₂, Al₂O₃ and SiO₂ phases, respectively (Figure 96a). The Mo 3d and Al 2p peaks were not observed after its preoxidation at 1000°C, and the Si 2p peaks also became more intense. This indicated the predominant existence of the silica phase on the surface. At higher preoxidation temperatures (1100°-1200°C), the Mo 3s peak at around 500 eV and Al 2p peaks were clearly identified. In addition, a decrease in the intensity of the Si 2p peaks, as well as, a significant change in the peak shapes were observed, which could be attributed to the formation of an intermetallic phase containing Mo, Al and Si elements. Moreover, increasing the preoxidation temperature from 1100°C to 1200°C resulted in peak shifts of the Mo 3s, Si 2p and Al 2p, which may be interrelated with the possible compositional changes within the ternary (Mo-Si-Al) intermetallic phase. As displayed in Figure 96b, a similar trend was also observed for the WSi₂-Al₂O₃ composite system. The presence of the WSi₂, Al₂O₃ and SiO₂ phases within the baseline non-preoxidized WSi₂-Al₂O₃ composite sample was determined by the detected W 4f, Al 2p and Si 2p peaks. The W 4p_{3/2} peak became less intense after preoxidation at 1100°C, but completely disappeared after preoxidation at 1200°C. On the other hand, the W 4p_{1/2} peaks were detected only after preoxidation treatments, along with shifting of the Al 2p and Si 2p peaks. These changes could be an indication of the formation of an intermetallic phase (W-Al-Si) on the surface of the composites.

To better understand the influence of the high-temperature preoxidation treatments on the formation of protective surface layers and their chemistry, it is necessary to determine the chemical composition and chemical state of the elements. Therefore, for all these composite samples, deconvolution of the Si 2p and Al 2p XPS peaks was carried out by a peak-fitting method to determine the peak positions precisely from their high resolution XPS spectra. The deconvoluted peaks of the Si 2p are presented in Figure 97. The non-preoxidized MoSi₂-Al₂O₃ composite revealed two different oxidation states of

Figure 97. Deconvoluted high-resolution XPS peaks of the Si 2p for the non-preoxidized and preoxidized (a-b-c-d) 30-70 vol% MoSi₂-Al₂O₃ and (e-f-g) 30-70 vol% WSi₂-Al₂O₃ composites.

Figure 97. (continued) Deconvoluted high-resolution XPS peaks of the Si 2p for the non-preoxidized and preoxidized (a-b-c-d) 30-70 vol% $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (e-f-g) 30-70 vol% $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites.

Figure 97. (continued) Deconvoluted high-resolution XPS peaks of the Si 2p for the non-preoxidized and preoxidized (a-b-c-d) 30-70 vol% $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (e-f-g) 30-70 vol% $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites.

Figure 97. (continued) Deconvoluted high-resolution XPS peaks of the Si 2p for the non-preoxidized and preoxidized (a-b-c-d) 30-70 vol% MoSi₂-Al₂O₃ and (e-f-g) 30-70 vol% WSi₂-Al₂O₃ composites.

silicon, where Mo-Si and Si-O bonding were identified from the binding energies of 99.74 and 102.09 eV, respectively [45,46]. After preoxidation of the MoSi₂-Al₂O₃ composite samples at 1000°-1200°C, only a single peak was observed at around ~102 eV, corresponding to the Si-O bonding. The Si 2p spectrum of the non-preoxidized WSi₂-Al₂O₃ composite sample exhibited three peaks at the binding energies of 98.25, 99.68 and 102.43 eV. The former two peaks were found to belong to the W-Si bonding [47,48], which could be assessed as evidence of two different W-Si phases (WSi₂, W₅Si₃). The Si-O bonding was identified from the single peak located at 102.43 eV. After high-temperature preoxidation treatment at 1100°-1200°C, only one peak at ~101.5 eV remained, which belongs to the Si-O bonding, similar to the preoxidized MoSi₂-Al₂O₃ composites. These results clearly prove the presence of the silica phase on the outer surface of the protective layers. Figure 98 displays the deconvolution of the Al 2p peaks for the composite samples.

Figure 98. Deconvoluted high-resolution XPS peaks of the Al 2p for the non-preoxidized and preoxidized (a-b-c) 30-70 vol% $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (d-e-f) 30-70 vol% $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites.

Figure 98. (continued) Deconvoluted high-resolution XPS peaks of the Al 2p for the non-preoxidized and preoxidized (a-b-c) 30-70 vol% MoSi₂-Al₂O₃ and (d-e-f) 30-70 vol% WSi₂-Al₂O₃ composites.

Figure 98. (continued) Deconvoluted high-resolution XPS peaks of the Al 2p for the non-preoxidized and preoxidized (a-b-c) 30-70 vol% MoSi₂-Al₂O₃ and (d-e-f) 30-70 vol% WSi₂-Al₂O₃ composites.

The non-preoxidized $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites revealed a single peak centered at ~ 74 eV, representing the Al-O bonding. After preoxidation of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composites at 1100°C - 1200°C , two deconvolution peaks at around 73.2 and 74.5 were identified, which are related to the Al-O and Al-Si bonding, respectively [49,50]. The preoxidized $\text{WSi}_2\text{-Al}_2\text{O}_3$ samples displayed three peaks in the Al 2p spectra at the binding energies around 72.8 (Al-Si), 73.3 and 74.0 eV (Al-O). The unidentified third peak located at around 73.3 may be related to the Al-W bonding.

7.3.5 High-temperature electrical properties of the composites

The electrical conductivities of the composites were measured up to $\sim 950^\circ\text{C}$ in argon atmosphere for better comparison of the high-temperature electrical properties of the non-preoxidized and preoxidized samples. The electrical data was measured at temperatures above 300°C , since their significantly higher electrical conductivities caused relatively inaccurate measurements for the low resistances acquired in the lower temperature region. Figure 99 presents the electrical conductivities of the non-preoxidized and preoxidized $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composite samples as a function of temperature. It is evident that the electrical conductivity of all the composites decreased with increasing temperature, showing their metallic-type electrical conduction behavior due to the presence of the metallic transition metal silicides within the composite structures [51]. As a baseline, the electrical conductivities of the non-preoxidized $\text{MoSi}_2\text{-Al}_2\text{O}_3$ composite at 800°C and 900°C were measured as 58.9 and 52.1 S/cm, respectively (Figure 99a). At the low temperature region ($\leq 500^\circ\text{C}$), all preoxidized samples exhibited relatively higher electrical conductivities. However, the electrical conductivities of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ samples were relatively lower (45.1-55.3 S/cm at 800°C ; 40.1-47.3 S/cm at 900°C) after preoxidation at 1000°C and 1200°C . In addition, the electrical conductivity significantly increased after preoxidation at 1100°C , where the electrical conductivities at 800°C and 900°C were 78.6 and 69.1 S/cm, respectively. Similar trend in the low temperature region can be also seen for the $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites (Figure 99b). At high temperatures, the preoxidized samples displayed slightly lower electrical conductivity values with respect to

Figure 99. Electrical conductivity of the 30-70 vol% (a) $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and (b) $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites after preoxidation at 1000°-1200°C for 120 min (Electrical data of the non-preoxidized samples are also presented as baseline).

the non-preoxidized sample. The electrical conductivity at 800°C decreased from 54.7 to 49.7 S/cm with preoxidation process and increasing preoxidation temperature. These results demonstrated that the high-temperature intrinsic electrical properties of the bulk composites could be highly preserved. It is evident that the internal oxidation process was limited to the surfaces of the metal silicides in the porosities, which implied that the oxygen diffusion into the silicide-silicide grain boundaries may be highly inhibited by the alumina phase. Thus, the preoxidation process did not suppress the electrical percolation network between the silicide grains (MoSi₂-MoSi₂ and WSi₂-WSi₂). Small changes in the electrical conductivities could be attributed to the structural changes, particularly to the formation 5-3 metal silicide phases beneath the protective surface layers.

7.4 Discussion

The non-isothermal oxidation tests revealed that the oxidation-induced mass gain of the transition metal silicides (MoSi₂, WSi₂) at the low-temperature region (~400°-850°C) could be reduced up to a certain level (~38.9-51.4%) by addition of 70 vol% alumina phase. This mass gain is due to the characteristic low-temperature (pest) oxidation behavior of these metal silicides and simultaneous formation of highly volatile oxide species along with a silica phase as dictated by the following oxidation reactions (1-2) thermodynamically favored in this temperature regime [6,12,26,28,52]:

Their high-temperature structural and electrical applications require a safe and reliable operation under cyclic oxidation conditions for extended hours in a broad temperature range [19,22,25,53]. However, it is evident that the addition of the alumina phase could only be a partial solution for improving their low-temperature oxidation resistance, based on the evidence of the oxidation-induced mass gain for both composites and complete structural disintegration for the WSi₂-Al₂O₃ composite. Therefore, the non-preoxidized MoSi₂-Al₂O₃ and WSi₂-Al₂O₃ composites cannot fulfill all the requirements for high-

temperature applications due to their projected short lifetime particularly under cyclic oxidation.

The preoxidation treatment at 1000°C for 10-30 min was found to be not effective, which could be due to the formation of molybdenum and tungsten oxide species (e.g. MoO₃). Studies on the MoSi₂-based material systems reported that the temperature range of 600°-1000°C is where the transition from non-protective to protective surface layer formation occurs [21,27]. This transition is known to be at relatively higher temperatures (~800°-1200°C) for the WSi₂-based materials [6,18]. Therefore, initial reactions (1-2) still took place during short-term preoxidation at 1000°C, possibly causing to the formation of non-protective, porous surface layer including Mo- and W-oxide species in a silica phase [21,54]. For the WSi₂-Al₂O₃ composites, it is apparent that the reaction (2) predominantly controls their preoxidation at 1000°C, since pest oxidation was still observed. However, low-temperature (pest) oxidation of the MoSi₂-Al₂O₃ composite was highly hindered by preoxidizing at 1000°C for longer times (60-120 min), since the preoxidation time was enough for the evaporation of the molybdenum oxide species and formation of the glassy-type protective surface layer with a ~4.94 μm thickness. Furthermore, the preoxidation treatments, which were conducted at higher temperatures (1100°-1200°C), revealed significant improvements on the low-temperature oxidation resistance of the MoSi₂-Al₂O₃ and WSi₂-Al₂O₃ composites. At these temperatures, the critical preoxidation time for the MoSi₂-Al₂O₃ composites was determined to be relatively lower (10 min), particularly compared to that of the WSi₂-Al₂O₃ composites (≥ 60 min), which indicated different kinetics and thermodynamics controlling the preoxidation processes of two composite systems. In the specific pest oxidation regions, the oxidation-induced mass gains were substantially lower in the range of 0.02-0.05 mg/cm² after high-temperature preoxidation treatment. This indicates ~82.1-99.8% reduction in the mass gain during non-isothermal oxidation owing to the formation of highly dense, protective surface layers with average thicknesses ranging from 3.05 to 14.16 μm. It should be noted that it is difficult to compare these data with the earlier research studies, where nearly all of them reported isothermal

Figure 100. Optical micrographs of the edges of the composite samples (top surfaces): (a) MoSi₂-Al₂O₃ preoxidized at 1200°C for 120 min, and (b) WSi₂-Al₂O₃ preoxidized at 1100°C for 120 min.

oxidation data. However, in the same temperature region, the mass gain for the MoSi₂ sample was measured as ~0.55 mg/cm² after non-isothermal exposure to air [23]. This is substantially higher than the values achieved after high-temperature preoxidation treatment. Additionally, it is important to point out that the slight oxidation of the preoxidized composites could be attributed to the small gaps, which remained on the edges of the composite surfaces after preoxidation (Figure 100 for example optical images). This could be explained with structural changes on the surface of the composites, which may lead to changes in volume and dewetting of the protective surface layers or volumetric shrinkage during high temperature heat treatment following the preoxidation processes [55].

The highly protective nature of the surface layers formed via high-temperature preoxidation treatments was determined to be due to the very complex structures and surface chemistries, as identified by XRD, XPS and Raman spectroscopy. The presence of ternary intermetallic phases (Mo(Si_{1-x},Al_x)₂, W(Si_{1-x},Al_x)₂) and a mullite polymorph (Al₂SiO₅), along with starting metal disilicides and alumina, were determined within the composite structures by XRD. As supporting data, identification of different Raman active modes and peak broadening/shifting for the MoSi₂ and WSi₂ modes implied the presence of mullite, silica (e.g. tridymite, cristobalite), alumina and ternary intermetallic phases within the protective surface layers (inner/outer layers), due to the lower penetration depth of the Raman spectroscopy. It is related to its better surface sensitivity and the lower penetration of the excitation energy, particularly compared to the X-rays [56,57]. Additionally, the XPS results displayed the disappearance of some peaks (e.g. Mo 3d), appearance of new peaks (e.g. Mo 3s, W 4p), increments in the peak intensities of Si 2p and Si 2s and peak shifts after high-temperature preoxidation treatments. The deconvolution of the Si 2p and Al 2p XPS peaks also revealed the presence of Si-O, Al-O and Al-Si bonding. These results supported the existence of ternary intermetallic phases, silica, alumina and mullite within the outer surface layers formed via high-temperature preoxidation, due to the greater surface sensitivity of the XPS (less than 10 nm in depth) [58]. The structural and surface characterization studies demonstrated the complex

structures of the protective surface layers, implying the possible occurrence of the following reactions (3-8), along with the above-mentioned reaction (2), simultaneously during preoxidation treatments at high-temperatures [6,9,19,20,59-62]:

Therefore, it is apparent that the alumina phase has a significant effect on the preoxidation process and surface reactions, since it caused side reactions taking place at elevated temperatures; and thus, modified the surface layer features (e.g. wetting) and their composition. This could be explained with the limited solubility of aluminum (Al) in MoSi_2 , and hence, partial substitution of Al with silicon [15,56]. It is important to point out that the formation of the Mo-Al-Si and W-Al-Si ternary intermetallic phases (aluminosilicides) on the surface of the $\text{MoSi}_2\text{-Al}_2\text{O}_3$ and $\text{WSi}_2\text{-Al}_2\text{O}_3$ composites could also positively influence their oxidation resistance at elevated temperatures. These intermetallic phases are considered to be promising alternative high-temperature heating elements and protective coatings [15,63]. The studies reported that they could exhibit a better oxidation resistance at both low- and high-temperature regimes compared to the metal disilicides due to the formation of a highly dense, protective oxide surface layer composed of alumina and mullite, instead of silica [15,64-66].

The high-temperature electrical conductivities of the composites relatively changed after preoxidation treatments, which is most likely related to the structural changes leading to the reduction in metal disilicide (MoSi_2 , WSi_2) content and increment in 5-3 metal silicide (Mo_5Si_3 , W_5Si_3) amount within the composite structures. However, the results demonstrate that the alumina phase blocked the oxygen diffusion into silicide-silicide grain boundaries, which highly protected the percolation and electrical conductivity of the

composites. Kobel et al. (2004) reported that the electrical conductivity of the 25 vol% MoSi₂-75 vol% Al₂O₃ composite was to be ~25 S/cm at 700°C [67]. Therefore, the electrical results achieved for the preoxidized MoSi₂-Al₂O₃ composites (~55.9-99.6 S/cm at 700°C) are comparable. No electrical data for the WSi₂-Al₂O₃ composites was found in the literature for comparison. In brief, these results are highly promising for high-temperature structural and electrical applications, since their high-temperature electrical properties could be highly preserved, along with their metallic conduction behavior, while substantially improving their oxidation resistance, and also lowering the grain growth rates of the metal silicides by using the alumina phase as a grain growth inhibitor [25].

7.5 Conclusions

The influence of the alumina phase and high-temperature preoxidation treatment on the low-temperature (pest) oxidation behavior was studied using the fabricated 30-70 vol% MoSi₂-Al₂O₃ and WSi₂-Al₂O₃ composites. The results demonstrated that the low-temperature oxidation resistance of the composites could be highly enhanced in the presence of alumina and particularly after preoxidation treatment at elevated temperatures (1000°-1200°C) for a certain period of time. The SEM microstructures displayed the formation of highly dense and protective surface layers with average thicknesses ranging from 3.1 to 14.2 µm. The protective nature of the complex surface structures was due to the presence of the ternary intermetallic phases (Mo-Al-Si, W-Al-Si), alumina, silica and mullite phases, as identified by a series of structural and surface analyses performed via XRD, XPS and Raman spectroscopy. The preoxidized composites still exhibited a metallic-type of conduction behavior with highly preserved electrical conductivities of 45.1-78.6 S/cm at 800°C and 40.1-69.1 S/cm at 900°C. These results are highly promising for an improved performance, lifetime and reliability of metal silicide-based materials in a broad range of high-temperature structural and electrical applications. The high-temperature preoxidation treatment was shown to be a very efficient and practical method, and thus, could be successfully applied to other transition metal silicides and different material systems. Further studies are essential to study and understand the influence of different

parameters (e.g. alumina content, preoxidation atmosphere, gas flow rate) on controlling the surface layer formation, and the kinetics of the preoxidation treatment (e.g. change in thickness as a function of time).

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Conclusions and Future Work

Due to the challenging high temperature and harsh environment conditions, there is a need for the development of electrical and advanced sensing materials, which can operate with high reliability, accuracy and sensitivity for extended operation hours without any degradation under such conditions. Therefore, in the three chapters (Chapter 2-3-4) of this research, the main objectives were to fabricate the various transition metal silicide-refractory oxide composites, and to achieve materials possessing high chemical/thermal stability, improved microstructural stability with reduced grain growth rate, enhanced oxidation resistance and high electrical conductivity. Different transition metal silicides (MoSi_2 , WSi_2 , NbSi_2 , TaSi_2 , CrSi_2) were incorporated with refractory oxide phases (Al_2O_3 , ZrO_2 , Cr_2O_3), and composite materials were successfully fabricated. Their phase and microstructural stability, oxidation kinetics and electrical properties were extensively investigated at high temperatures. All the composites exhibited high phase stability at temperatures of 1400°C - 1600°C , only with the formation of secondary metal silicide phases with 5-3 stoichiometry. On the other hand, solid-state reactions between starting chromium silicide and chromia resulted in the formation of different type of chromium silicide phases, depending on the initial silicide/oxide volume ratio. The results also demonstrated that grain growth rates were significantly reduced by addition of oxide phases into the composite structures, which could be highly beneficial for long-term use. Furthermore, increasing sintering temperature and oxide phase addition highly increased the oxidation resistance, particularly compared to the monolithic metal silicides. The chromium silicide-based composites, which were fabricated via solid-state reactions, also displayed enhanced oxidation resistance. All the composites exhibited a metallic type electrical conduction with substantially high electrical conductivities up to around 1000°C .

In the Chapter 5, a microstructural image analysis method was developed based on free-path spacing between neighboring grains to determine the degree of homogeneity or mixedness of the composites quantitatively. This could be beneficial for understanding the

microstructure-property relations better (e.g. percolation). In the Chapter 6, the transition metal silicide-refractory oxide thick-film ceramic composite thermocouples were fabricated, and their thermoelectric properties were extensively studied. Like bulk composites, the significant influence of the 5-3 metal silicide phases on the thermoelectric response was identified. Depending on the silicide/oxide volume ratio on the thermocouple legs, the fabricated composite thermocouples exhibited higher sensitivity than mostly used Pt-Rh-based thermocouples in a wide temperature region. In the Chapter 7, the results clearly presented that the alumina addition and high-temperature preoxidation treatment substantially lowered the oxidation rates and enhanced their oxidation resistance due to the formation of complex-structured, highly protective surface layers.

Based on the results of this research, further studies are needed as listed below:

- Thermal stability studies should be conducted at high-temperatures for extended hours (>100 hours) to understand their long-term phase stability and capability for high-temperature applications.
- The influence of the oxide phase concentration on the grain growth kinetics should be studied.
- The effect of the refractory oxide phase addition and its volume percentage should be examined by fabricating the composites with a very low amount of porosity.
- Isothermal and cyclic oxidation studies are needed to determine the oxidation kinetics at different temperatures (both in low- and high-temperature regime).
- The results clearly demonstrate that the secondary 5-3 silicide phases have significant influence on their properties. Their physical properties are also not well-known in the literature. Therefore, it is crucial to synthesize these compounds and study their physical properties, to better understand the composite structures.
- Transmission electron microscopy (TEM) studies are important to characterize the amorphous silica grain boundary phase, and to better understand its effect on the microstructures (e.g. grain boundary wetting).

- Their electrical properties need to be measured at higher temperatures ($>1000^{\circ}\text{C}$) by changing the platinum electrical connections.
- Thermoelectric characterization studies implied that there may be compositional changes at the junction, which influence the thermoelectric output. The junction of the two composite legs needs to be well characterized to understand their thermoelectric properties better.
- The high-temperature preoxidation treatment was shown to be a very efficient and practical method; and thus, it is essential to study the influence of different parameters (e.g. type of oxide phase, alumina concentration, preoxidation atmosphere, gas flow rate) on controlling the surface layer formation, and kinetics of preoxidation process. The high-temperature preoxidation studies should be also conducted on monolithic metal silicides to better understand the influence of the refractory oxide phase addition on preoxidation kinetics and surface layer composition.
- The high-temperature preoxidation method should be applied to the thick-film composite thermocouples, which are not embedded between alumina substrates, to enhance their oxidation resistance by forming a protective surface layer. Afterwards, their thermoelectric characterization needs to be carried out in air atmosphere to study their performance in real conditions. However, the preoxidation conditions should be carefully adjusted for thick-films based on the results achieved with bulk samples.

Curriculum Vitae

Education

West Virginia University	Ph.D. in Material Sci. Eng.	2014-2018
Anadolu University	M.Sc. in Nanotechnology	2008-2011
Anadolu University	B.Sc. in Materials Sci. Eng.	2003-2008

Thesis/Dissertation

Ph.D. Thesis	Processing, stability and high-temperature properties of transition metal silicide-refractory oxide composites for electrical applications
M.Sc. Thesis	Synthesis of size and shape controlled titanium dioxide particles
B.Sc. Thesis	Hydrothermal synthesis of alpha-alumina (α -Al ₂ O ₃) particles

Publications

(1) Yakaboylu, G.A., Sabolsky, K., Sabolsky, E.M., “*Phase stability, microstructure and high-temperature properties of NbSi₂- and TaSi₂-oxide electroconductive ceramic composites*”, Journal of Materials Science, published online on 17 April 2018 (volume/issue/page numbers to be assigned).

(2) Yakaboylu, G.A., Pillai, R.C., Sabolsky, K., Sabolsky, E.M., “*MoSi₂- and WSi₂-based embedded ceramic composite thermocouples for high-temperature and harsh-environment sensing*”, Sensors and Actuators A: Physical 272, 139-152 (2018).

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Presentations

- (1) Yakaboylu, G.A., Pillai, R.C., Sabolsky, K., Yumak, T., Sabolsky, E.M., “*Transition Metal Silicide-Based Ceramic Composites for High Temperature and Harsh Environment Sensing*”, Oral presentation, to be presented at the Materials Science and Technology MS&T’18, Columbus OH, October 14-18 (2018).
- (2) Yakaboylu, G.A., Pillai, R.C., Sabolsky, K., Haynes, D.J., Sabolsky, E.M., “*Metal Silicide-Refractory Oxide Ceramic Composites for High-Temperature and Harsh-Environment Sensing: Processing, Stability and Thermoelectric Properties*”, Oral presentation, to be presented at the 233rd ECS Meeting, Seattle WA, May 13-17 (2018).
- (3) Yakaboylu, G.A., Pillai, R.C., Sabolsky, K., Sabolsky, E.M., “*Metal Silicide-Refractory Oxide Electroconductive Ceramic Composites for High-Temperature and Harsh-Environment Sensing Applications*”, Oral presentation, Materials Science and Technology MS&T’17, Pittsburgh PA, October 8-12 (2017).

- (4) Yakaboylu, G.A., Pillai, R.C., Sabolsky, K., Sabolsky, E.M., “*Processing of Metal Silicide/Refractory Oxide Composites for High-Temperature and Harsh-Environment Sensing Applications*”, Poster presentation, Gordon Research Conference (GRC), Ceramics, Solid State Studies in, South Hadley MA, July 31-August 5 (2016).
- (5) Yakaboylu, G.A., Pillai, R.C., Armour, B., Sabolsky, K., Sabolsky, E.M., “*Conductive Ceramic Composites for Fabricating High Temperature and Harsh Environment Sensors: Thermal Processing, Stability and Properties*”, Oral presentation, International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach FL, January 24-29 (2016).
- (6) Yakaboylu, G.A., Pillai, R.C., Armour, B., Sabolsky, K., Sabolsky, E.M., “*Development of Refractory Oxide/Metal Silicide Composites for High Temperature Harsh-Environment Sensor Applications*”, Oral presentation, Materials Science and Technology MS&T’15, Columbus OH, October 4-8 (2015).
- (7) Yakaboylu, G.A., Pillai, R.C., Chockalingam, S., Armour, B., Palmisiano, M., Sabolsky, K., Sabolsky, E.M., “*Thermal Processing and Properties of Conductive Refractory Composites for High-Temperature Electrical Applications*”, Oral presentation, International Conference and Exposition on Advanced Ceramics and Composites, Daytona Beach FL, January 25-30 (2015).