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Development Of Oxide-Dispersion-Strengthened Nickel-Based Super Alloy Powders For Additive Manufacturing

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DEVELOPMENT OF OXIDE-DISPERSION- STRENGTHENED NICKEL-BASED SUPER ALLOY POWDERS FOR ADDITIVE MANUFACTURING

Sizhe Huang

Thesis submitted to the
College of Engineering and Mineral Resources at West Virginia University,
in partial fulfillment of the requirements for the degree of

**Master of Science
in
Material Science and Engineering**

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Keywords: Nickel, Oxide-Dispersion-Strengthened (ODS), Additive
Manufacturing (AM), Scanning Electron Microscope (SEM), X-ray diffraction
(XRD)

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ABSTRACT

DEVELOPMENT OF OXIDE-DISPERSION-STRENGTHENED NICKEL-BASED SUPER ALLOY POWDERS FOR ADDITIVE MANUFACTURING

Sizhe Huang

Oxide-Dispersion-Strengthened (ODS) Nickel-Based superalloy has been drawn a huge attention and developed with good oxidation resistance, corrosion resistance and high creep strength. It has been considered as critical materials for Additive Manufacturing (AM). The quality and the efficiency of fabrication methods of ODS limits the performance of itself on AM. The development of new type of ODS, new methodologies and evaluation techniques are required if the enhanced quality of ODS and enhanced efficiency of fabrication are to be achieved. Of the current fabrication techniques for AM, Gas Atomization (GA) is widely used since they can generate spherical powders with high qualities. However, GA is incapable of producing Ni-based ODS powders with uniform dispersion oxide contents since it requires the melting on constituent powders, and oxide contents have higher melting point than other major contents. Ball-milling (BM), is a prevailing and well-known technique for ODS and has been proven with the capability of producing particles with nanocrystalline structures. Mechano-Chemical-Bonding (MCB) is another new type of technique by using mechanical alloying effect without adding any binders to produce ODS.

In this research, MCB (MCB-only process) and its combined technique (MCB+BM process) were carried out to produce ODS powders with composition of Ni-20Cr-5Al-3W-1.5Y₂O₃ in wt%. The MCB is different with previous published techniques, raw element particles are subjected to breakdown, mixing, diffusion bonding, fracturing, shearing, and re-welding under different rotating speeds and different running durations. X-ray Diffraction (XRD) was adopted to prove that Y₂O₃ has been evenly distributed onto major particles. Also, the morphology, shape and size of particles are analyzed Scanning Electron Microscope (SEM). More spherical in shape and smoother particle surface produced by the MCB than the BM that benefits powder feeding during AM. Also, X-ray diffraction (XRD) was utilized to examine the lattice spacing of crystal structure. Three different batches of powders fabricated by the MCB process and its combined techniques were used in two different AM system. Results shows the powders were successfully deposited onto flat substrates and densified microstructures were obtained. In order to investigate the as-printed microstructure, X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) were employed.

In conclusion, MCB-only technique can manufacture desirable Nickel-base alloy for AM by determining the particle shape, surface and size characteristics, as well as, reasonable alloy status and profound microstructure.

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CHAPTER 1: INTRODUCTION

1.1 Background

The rapid development of industry has put forward more and more stringent requirements on the application range and properties of materials. People from science and industry now endeavor to open up new ways to seek new directions and effects of development. Additive manufacturing (AM) is a novel technology to build three dimensions objects by adding layer-upon-layer material which is typically plastic, metal and concrete. In metal-based AM, a direct source such as a laser or electron beam is applied to melt alloy powders locally gives rise to solidification. One of the most critical metal alloys that are applicable on AM is Ni alloy. Nonetheless, to 3D print conventional alloys such as high-strengthening-phase (γ' phase), Ni superalloys cannot accomplish desired solidification conditions since they are unweldable. Thus, a new system of Ni-based superalloy with efficient properties needs to be developed.

Ni superalloy has been extensively used in oil field, marine industry, and aviation industry because it alloy has excellent mechanical properties, reasonable creep resistance, sufficient fatigue resistance, excellent corrosion resistance, adequate ductility, and serviceable weldability. However, traditional Ni superalloy has been unable to meet industrial needs with the development of industrial technologies. The aviation industry has higher demands in the mechanical property of Ni superalloys, especially the mechanical behavior under high temperatures. The strengthened phase in the conventional superalloy is unstable when being subject to high temperatures ($>1000\text{ }^{\circ}\text{C}$).

Introducing a new strengthening element into superalloy is an important method to enhance the property of it. Dispersion strengthening is a useful metal strengthening mechanism besides strain strengthening; solution strengthening; fine-grain strengthening; precipitation strengthening in superalloy [1]. Oxide-dispersion-strengthening (ODS) has become one the dominant method to strengthen superalloys. It relies on the addition or formation of stable secondary phase particles in the metal matrix to strengthen alloys. Secondary phase particles are artificially added to the alloy matrix system with favorable thermal and chemical stabilities. They are generally fine and uniform presenting in the matrix and able to pin movements of dislocations, grain boundaries, and sub-grain boundaries to inhibit grain growth. Thus, the alloy is strengthened by secondary phase particles. However, it has been proven that oversize secondary phase particles undermined the fracture resistance and ductility of alloys even though they effectively hinder the movement of dislocations. Hence, to achieve the desired strengthening effect, secondary phase particles must be evenly distributed into the matrix system with fine size by other techniques.

ODS Ni-based superalloys (denoted as Ni-based ODS) is recently developed that strengthened by adding or in situ forming second phase particles with even and fine sizes (Nano sizes in general), i.e., Y_2O_3 , Al_2O_3 , Zr_2O_3 , and ThO_2 . At high temperatures, the strengthening γ' phase exists in conventional Ni superalloys reacts with carbon or carbon oxide to cause dissolve of itself into austenite matrix, thus leads to the failure of strengthening effect [2]. Nevertheless, Ni-based ODS can withstand high temperatures due to the existence of secondary phase particles since they do not dissolve themselves into matrix under high temperatures. Strengthening phases enable Ni-based ODSs to maintain high-temperature strength, and high-temperature creep performance and oxidation resistances near the melting point.

Ni-based ODS owns advantages as follows:

- I). High room temperature strength and high-temperature strength;
- II). High creep strength;
- III). Sufficient oxidation resistance and corrosion resistance;
- IV). Good ductility;
- V). Low swelling.

Therefore, Ni-based ODS is considered as a sufficient candidate for aircraft engines and gas turbines. Ni-based ODSs that apply to aircraft engines and gas turbines are MA6000 [3], IN738 with Y_2O_3 [4], and WAZ-D [5], etc. The high-temperature resistance of Ni-based ODS is significantly improved than conventional Ni superalloy with a maximum increase of about 100 °C [6]. Published results have shown that the fracture strength of ODS Ni-based superalloy (i.e., MA6000) is twice as conventional Ni-based superalloy at 1000 °C [7, 8].

Powder metallurgy technologies have gradually taken over the manufacturing of ODS superalloys. The ThO_2 powder was affiliated into tungsten to inhibit the trend of grain growth of tungsten at high temperatures. In 1949, Irmann [9] fabricated sintered aluminum powder (SAP) by Surface Oxidation, this was the first ODS that used as a structural material in the world. In 1962, Anders [10] from DuPont Company manufactured Ti-Ni alloy through Chemical Co-precipitation Method. But this method had limitations which were the difficulties of adding an active metal such as Ti and Al into the matrix system. Until the 1970s, Benjamin [11] successfully produced Ni-based ODS by Mechanical Alloying (MA) such that ODS techniques have been developed rapidly. MA has commercially produced various metal alloys, oxides and carbides which are widely used in nuclear reactors, advanced aircraft engines, gas turbines, and cars. The development of ODS materials is mainly concentrated in the United States, Britain, Japan, and Germany.

Ball-Milling (BM) machine and Mechano-Chemical-Bonding (MCB) machine are two primary instruments of the MA process. Laser-Engineering-Net-Shaping (LENS) system, Laser Cladding (LC) and Electro-Optical-System (EOS) are currently primary 3D printing methods in AM. This study aimed to develop new approaches to fabricate Ni-20Cr-5Al-3W-1.5Y₂O₃ in weight percentage ODSs

which are suitable for LENS, LC and EOS with reasonable particle size distributions, nearly spherical shapes, and excellent mechanical properties.

1.2 Research Objectives

The primary purpose of this study is to develop a material system to provide an improved level of thermal protection for hot-section components, such as turbine airfoils and gas turbines. To produce ODS Ni-based superalloy powders with proper sphericity and spreadability, which will be used in AM processes based on selective laser melting. The main strengthening phase of the Ni-based superalloy is γ' phase. It is precipitate strengthening in conventional superalloys. However, when the Ni-based superalloy is working at high temperature (near the melting point of the matrix), γ' phase will become dissolute which loses the strengthening purpose of the superalloy. But the added Y_2O_3 in ODS Ni-based superalloy will improve the mechanical properties at high temperatures since Y_2O_3 is the secondary particle in superalloys which satisfies the dispersion strengthening and able to pin the movements of dislocations and grain boundaries.

Strengthening Mechanism	Effective Temperature	Comments
Work Hardening	$\sim 0.3 T_m$	Dislocation/Dislocation Interaction
Grain Size Refinement	$\sim 0.3 T_m$	Grain Boundary Area – Dislocation Interaction
Solid Solution Strengthening	$\sim 0.4 T_m$	Lattice Strain Fields: Modulus Change, dislocation interaction
Precipitation Strengthening	$\sim 0.6 T_m$	Metastable 2 nd Phase Particles, impede dislocation motion
Dispersion Strengthening	$\sim 0.9 T_m$	Insoluble 2 nd Phase, stabilize grain, subgrains and creep

Figure 1-1. Types of strengthening mechanisms and corresponding effective working temperatures [7].

Figure 1-1 shows the types of strengthening mechanisms and corresponding effective working temperatures. ODS Ni-based superalloy falls in the dispersion strengthening category (Oxide-dispersion). T_m represents the melting points of alloys, and the melting point of Ni alloys is in the range of 1400~1500 °C. Thus, the effective working temperature of ODS Ni-based superalloys is in the range of 1260~1350 °C by calculating from Figure 1-1. Besides, for gas turbines, the temperature of exhaust entering the turbine can be as high as 1200~1400 °C while the effective working temperature of ODS Ni-based superalloys is in this range. Therefore, ODS Ni-based superalloys are suitable for providing high-level of thermal protection for turbines.

Atomization is the most used technique for superalloy fabrication. However, it is incapable of producing ODS superalloys since atomization requires the melting of metals and the known highest temperature of atomization is 1700 °C. The added oxides in ODS superalloys usually have melting temperatures more than 2000 °C. Recently, Joel R. et al. have proposed a novel method called reactive gas atomization to produce ODS Fe-based superalloys [12]. They used Cr as an oxygen vehicle to transport oxygen to add yttrium to form yttrium oxide thus achieve ODS. But the evidence of the even distribution of yttrium oxide was not clear in their research. And post heat treatment still needed for the alloy, they have shown that the yttrium oxide did not form until heat treated to 1200 °C [12]. Thus, an effective method for ODS superalloy fabrication needs to be developed.

Two techniques (the BM process and the MCB process) were employed to fabricate ODS Ni-based superalloy powders and investigate the efficiency of producing process. Except for Atomization methods, the MA process is the most widely used methodology to produce ODS superalloys. Since the difficulties of fabricating ODS by utilizing atomizations still exist. The BM machine is the instrument by using the mechanism of the MA process. It is capable of blending, breaking, and cold-welding the raw elemental powders and oxide compounds under high energy ball milling for long periods (usually up to 200 hours). The oxide compound is uniformly dispersed onto the hosting particles throughout the MA process. After the MA process, the processed powders are subjected to HIP to consolidate and heat treatment to relieve the residual stress. Furthermore, the HIPed material is usually processed by hot worked. Also, the hot worked material is heat treated to achieve the desired microstructures and mechanical properties to meet the requirements of multiple applications.

Since various post processes are involved after the MA process to fabricate ODS superalloys, commercially producing ODS superalloys become problematic which results in time-consuming and high cost. For instance, it costs about \$345/kg for Ni-based ODS MA 956 alloy. However, it only costs about \$30–35/kg for Ni-based superalloys such as INCONEL 718 and 617 [13]. Besides, the MA process usually needs an extended period to produce ODS superalloys which will cause contamination from milling debris and gaseous environment [14].

There is another technique by using the mechanism of the MA process called MCB machine being developed recently. The raw elemental powders are under high-speed compression and shearing force through a small gap between the vessel and a press head. The added oxide particles (i.e., Y₂O₃) are homogeneously coated onto the hosting particles, forming the composite powders. The MCB process is a dry process without adding any binders to form alloys through the solid state diffusion. At present, the MCB technique has been used to make various composite materials applied in the area of pharmaceuticals, batteries, fuel cells, functional gradient materials, and cermets [14]. Kang et al. have shown that the MCB process was able to disperse Y₂O₃ particles onto the based and hosting particles homogeneously to form the composite powders [15]. Furthermore,

the newly developed MCB processing technique is simple, environmentally friendly, and can be scaled up to 300 liters per batch. Thus, MCB or its combination technique is considered as an enhancement or alternative to the conventional MA process using balling milling.

Another technique called Additive Manufacturing was utilized in this research since it can produce bulk and densified samples by laser or electron beam in three dimensions. It has gained significant academic and industry interests because it is capable of creating complex geometries with customized materials properties. Comparing to the post-processing of BM process alloy powders consolidation, AM technique is a much easier way to achieve densified samples. This research aimed to develop ODS Ni-based superalloy powders for AM techniques and investigate the feasibility of using BM processed and MCB processed alloy powders in the field of AM.

1.3 Challenge of Research

I). Particle size distribution

Based on the existing results of powder granulometry requirements for AM techniques, a Gaussian size distribution (Figure 1-2) of powder is desirable. BM and MCB techniques could achieve this Gaussian model. However, the size of the particle for AM also has strict requirements: the mean particle size of widely used GA powders is 20~40 μm . The particle size control of BM and MCB is a challenge.

Figure 1-2. A schematic of the Gaussian model of powder size distribution [16].

II). Particle strengthening phase

It is known that the strengthening phase of ODS Ni-based superalloys is the γ' phase. Fabricating powders with γ' phase is still a challenge in this area. Even

the widely used atomization is only capable of generating pre-alloyed powders. It is noted that the BM process could produce powders with γ' phase, but the difficulty of MCB-only generating γ' phase still exists.

III). Particle shapes

Atomization process produces the most spherical powders. But, BM and MCB could not generate perfectly spherical particles comparing to atomization process which would influence the flowability of powders during the AM process. The highest degree of roundness produced by MCB is known as 0.93.

IV). Microstructure control of post-printed samples

The dimensional accuracy of AM technique is still a problem since shrinkage usually happens after depositing alloy powders onto a substrate. Also, the flowability of powder, input laser energy, and laser scanning speed directly affect the shrinkage and density of as-printed samples. If the input energy density is relatively low, the as-printed will have more shrinkage and low density (i.e., more pores than conventional consolidation method). Thus, the processing parameter control is a big challenge for this research.

CHAPTER 2: REV IEW OF LITERATURE

2.1 Superalloys

Superalloy refers to the alloy which uses Fe, Ni, and Co as the matrix, and is capable of working over 600 °C and under stress for a long time. Superalloy is also called refractory alloy or high-temperature alloy. Superalloy has good high-temperature strength, excellent oxidation resistance, good corrosion resistance, high creep strength, and good ductility. Superalloys are generally Ni, Fe, and Co-based alloys used above temperature 540 °C [2]. The Fe-Ni-base superalloys such as the popular alloy IN718 is an extension of stainless steel technology and generally is wrought. Co-base and Ni-base superalloys may be wrought or cast, depending on the application/composition involved [2]. Table 2-1 shows the composition of conventional superalloys.

However, when the working temperature comes to 50% (on an absolute scale) of the melting point of an alloy, the strength must be weakened with the increase of time. Therefore, current superalloys could not meet the requirement of the industrial application. A new type of superalloys needs to be developed by adding dispersion to strengthen superalloys. Introducing a new strengthening element into superalloy is an important method to enhance the mechanical property. Dispersion strengthening is a useful metal strengthening mechanism besides strain strengthening; solution strengthening; fine-grain strengthening; precipitation strengthening in superalloys

Table 2-1. Components of common Superalloys (wt. %) [17]								
Alloy	Ni	Fe	Cr	Ti	Al	Mo	C	others
<i>Powder processed Superalloys</i>								
IN 100	Bal	-	12.4	4.3	5	3.2	0.07	18.5Co
Rene 88	Bal	-	16.0	3.7	2.1	4	0.03	13Co4W0.7Nb
<i>Wrought Superalloys</i>								
IN 718	50	30	18	0.8	0.6	3	0.05	5.2Nb
Waspaloy	58	-	19	3	1.4	4.4	0.08	13Co
<i>Casting Superalloys</i>								
Rene 80	Bal	-	14	5	3	4	0.17	9.5Co4W

2.2 Oxide -Dispersion-Strengthened (ODS) Superalloys

ODS superalloys are one type of dispersion strengthened superalloys, the strengthening mechanism of ODS is dispersion strengthening by adding a new element which is harder than the matrix metals. The added compound is called the secondary phase particle. Ordinary strengthening particles are refractory Oxides (i.e., Y₂O₃, Al₂O₃, HfO₂, and ThO₂), Carbides (i.e., TiC, SiC, and WC), Nitrides (i.e., TiN, BN, and Si₃N₄), and Borides (i.e., TiB₂, ZrB₂, and CrB₂).

ODS superalloys are primarily distinguished from conventional superalloys by the dispersion strengthening γ' phase. There are two main categories of commercial ODS superalloys, the ODS Ni-based superalloy, and the ODS Fe-based superalloy. The temperature of the solid solution limits the maximum working temperature for ODS superalloys. When ODS superalloys are working over 1000 °C, the aggregation, coarse and dissolve of strengthening γ' phase is inevitable thereby impair the high-temperature strength of the ODS superalloys.

The choice of oxide is critical in ODS superalloys. The oxide with a high melting point, high chemical stability, the ability of insoluble in the matrix, low diffusion rate, and low interface energy is preferred for ODS superalloys. ThO₂ was the earliest oxide that added into ODS superalloys, but Y₂O₃ substituted it since it has radioactivity. Plus, Y₂O₃ can form a more stable metal composite oxide with the excess oxygen and Al in the matrix (3Y₂O₃ • 5Al₂O₃). Significant evidence has shown that the dispersion actually consists of mixed oxides, i.e., Y₃Al₅O₂ (YAG), YAlO₃ (YAP), YAH, etc. [18]. Al₂O₃ is another alternative for ODS superalloy due to its well-known stability. The ODS Ni-based superalloy and the ODS Fe-based superalloy are the most studied and applied alloys.

Table 2-2. Components of common ODS superalloys (wt. %) [19]								
Alloy	Ni	Fe	Cr	Ti	Al	C	Y ₂ O ₃	others
MA 754	Bal	1.0	20	0.5	0.3	0.05	0.6	
MA 757	Bal	-	16	-	4.5	-	1	
MA 758	Bal	-	20	0.5	0.3	-	0.6	
PM 1000	Bal	-	20	-	0.3	-	0.6	0.5Mo
MA 6000	Bal	-	15	2.5	4.5	0.05	1.1	2Mo4W2Ta
MA 956	-	Bal	20	1	4.5	0.02	0.5	
PM 2000	-	Bal	20	0.5	5.5	<0.04	0.5	

2.2.1 ODS Ni-based Superalloys

Material scientists have been conducting researches since the 20th century concerning ODS superalloys. The first ODS Ni-based superalloy was produced in the 1950s by DuPont company through co-precipitation method. The company had generated some conventional alloys such as Ti-Ni alloys. Until the 1970s, Benjamin et al. invented MA to produce ODS superalloys thus he boosted the development of ODS superalloys, especially ODS Ni-based superalloys. Currently, MA753, MA754, MA6000, and MA956 ODS Ni-based superalloys have been produced and commercialized [17]. MA754 was the first commercialized ODS Ni-based superalloy. It could be working at 1250 °C. In the 1970s, it was applied to some aircraft high-temperature components, i.e., American military engines F404, F110. It was adopted to machine blades and ring units. MA6000 has a tensile strength of 222 MPa, Yield strength of 192MPa at 1100 °C [20].

In ODS Ni-based superalloys, the selection of an oxide particle is the crucial point. The choice of oxide particle should be in line with these characteristics:

Chemically stable, non-dissoluble in a matrix, low diffusion coefficient, and low interphase energy. The first chosen oxide particle was ThO_2 . But it was eliminated from the ODS since it is radioactive. Y_2O_3 was then researched mostly to produce ODS superalloys. Its creep strength at 850 °C could sustain over 185 MPa over 6000 hours. Russia OKBM considered MA6000 was the only standard materials for turbine disk. MA6000 was mainly used on turbine blades [3].

The strength of most alloys normally decreases with temperatures, except some intermetallic compounds, such as γ' - Ni_3Al which increases with temperatures up to about 900 °C. Precipitates of γ' - $\text{Ni}_3(\text{Al}, \text{Ti})$ is considered as the primary strengthener for Ni-based superalloys. However, because the precipitates are metastable, they will coarsen when heated at high temperatures, so that the mechanical properties decrease with time. Efforts have been made to involve more stable nanosize oxide particles such as Y_2O_3 , ThO_2 , and ZrO_2 which can disperse homogeneously in the alloy grains through the ODS Ni-based superalloy is currently much more widely used than ODS Fe-based superalloy, and ODS Co-based superalloy because the working temperature of ODS Ni-based superalloy is 150~250 °C higher than ODS Fe-based superalloy and ODS Co-based superalloy [17].

In conclusion: the development of ODS Ni superalloys went through three stages [21]:

- I). From 1905 when Ni-Cr electro resistance alloy was produced to 1940 when Nimonic80 alloy was fabricated, Ni superalloys improved from single crystal to γ' phase strengthening alloy. The working temperature rose from 650 °C to 750~800 °C.
- II). The compositions of alloys were continuously adjusted. The work temperature rose to 950~980 °C.
- III). New synthesis processes were employed such as directional casting, welding. And oxide particles were added to achieve ODS Ni-based superalloys which have better performances.

ODS Ni-based superalloy falls into two main categories. The first class is represented by alloys that contain a low content of Al and Ti, i.e., MA754, MA758, and PM 1000, etc. These alloys do not include strengthening γ' phase. Their high-temperature strengths mainly depend on the solid solution strengthening of Cr. Adding Cr and Al also improves the oxidation resistance of alloys. But their medium-temperature strength is not as good as expected. The MA process produces these ODS Ni-based superalloys with Y_2O_3 as secondary phase particle. Extrusion, rolling and hot compressing are usually applied on these alloys to obtain desired columnar grain structures which grow along the deformation direction. The columnar grain structures improve the endurance strength and creep resistance of

alloys. The second class is represented by alloys that composed of higher Al and Ti contents. This leads to more strengthening γ' phase existing in the matrix (up to 60% or higher). Mo, W, and Ta play an important role in stabilizing strengthening γ' phase. These alloys have higher medium-temperature strength than the first class alloys.

Figure 2-1. SEM images of γ' phase in conventional Ni-based superalloys: (a). Wrought alloy (x 3000); (b). Cast alloy (x 5000) [2]

Figure 2-1 shows the γ' phase of conventional Ni-based superalloys. It is noted that γ' phase is spheroidal and cuboidal with some degree of coherence. It has been noted that γ' phase tends to occur as spheres for 0 to 0.2% mismatches, becomes cuboidal for mismatches of about 0.5 to 1%, and is plate-like at mismatches above about 1.25% [2]. Another significant strengthening phase of Ni-based superalloy is γ'' phase. It is not discussed in this study since the designed nominal composition does not contain the γ'' phase former elements: Nb and Ta.

2.2.2 ODS Fe-based Superalloys

Cr and Mo were added into ODS Fe-based Superalloy to induce solid solution strengthening. Oxidation resistance of ODS Fe-based Superalloy was improved by adding Cr and Al. The nanosize added Y_2O_3 not only pinned the movement of dislocation but also inhibited the migration of atoms to cause the formation of oxide layers on the surface. This enhances the oxidation resistance and corrosion resistance. Studies of ODS Fe-based Superalloy are mostly about ODS low-activity ferrite steel and ODS low-activity ferrite steel/double-phase martensitic steel; the main difference is the content of Cr. Low activity ferrite steel has 14~20 wt. % Cr, low activity ferrite steel/double-phase martensitic steel has 9~12 wt. % Cr. The common ODS Fe-based Superalloys are: ODS ferrite steel-PM2000 [22], MA 957 [23], 14YWT [24], ODS ferrite steel/double-phase martensitic steel-ODS Eurofer97 [25], 9Cr-ODS [26] etc.

In general, ODS ferrite steel has higher creep strength than ODS ferrite steel/double-phase martensitic steel. And ODS ferrite steel has lower stability than ODS ferrite steel/double-phase martensitic steel in anisotropy. The characteristics of ODS Fe-based superalloys are as follows: 1). The ODS Fe-based superalloy powders processed by MA when after hot sintering, has fine grains from 100 to about a few hundred nanometers. 2). Y-Ti-O, $Y_2Ti_2O_7$, and $YTiO_5$ were observed to present in the matrix with 2~5 nm [27]. These two characteristics ensure that the ODS Fe-based superalloy has a stable grain structure which provides excellent conditions for high-temperature creep strength.

The strengthening phases of ODS Fe-based superalloy are as follows: TEM characterization of MA957 has shown that the strengthening phase is the $Y_2Ti_2O_5$ particle with a smaller size of added Y_2O_3 [23]. Ukai et al. found that Ti could be dissolved into the matrix and acted as a refiner of the strengthening phase. The strengthening phase Y-Ti-O was formed through reaction $TiO_2 + Y_2O_3$, the strengthening phase could be refined down to 2nm [26]. TEM was frequently used to analyze the strengthening phase in ODS steels. Based on previous TEM researches, the major strengthening phases of ODS steels are Y_2TiO_7 and $YTiO_5$ [27].

In order to improve the corrosion behavior of ODS steels, Al was later added into the system. For instance, PM2000 ODS steel has four types of Y-Al-O strengthening phases [22]. They are $YAlO_3$ with Yttrium-Al-Perovskite (YAP) and Yttrium-Al-Hexagonal (YAH) structure; Y_4AlO_9 with Yttrium-Al-Monoclinic (YAM) structure; $Y_3Al_5O_{12}$ with Yttrium-Al-Garnet (YAG) structure.

2.2.3 ODS Al-based Superalloys

ODS Al-based superalloys are different from other ODS superalloys since a dense alumina film naturally exists on the surface of Al powders. ODS Al-based superalloys can be achieved by compression, extrusion and strengthened by alumina when subject to severe deformation. Common Al superalloys are age strengthening Al alloys and particle strengthening Al alloys. Age strengthening Al superalloys mainly depends on the secondary phase precipitate during age strengthening, common alloys in this category are 2000 series and 7000 series Al alloys. Age strengthening Al superalloys have a limitation which is the secondary phase would dissolve into the matrix at high temperatures. Particle strengthening Al superalloys are strengthened by added hard particles, the standard alloy in this category is SiC strengthened Al alloy. But SiC is usually coarsened in the matrix which affects the ductility of Al superalloys. Besides, the unevenly distributed SiC in the matrix influences the mechanical properties of ODS Al-based superalloys.

ODS Al-based superalloys have been developed since the 1940s; they are mostly fabricated by surface oxidation method and the MA process. They also contain nanosize secondary strengthening particles, i.e., Al_2O_3 , Al_4C_3 , and AlN. The commercialized ODS Al-based superalloys are A19052 and A19021 [28].

A19052 has higher corrosion resistance than 7000 series alloys. A19021 has better ductility than other common Al superalloys. These alloys above involve multiple strengthening mechanisms, i.e., Mg solid solution strengthening, super fine strengthening, and Al_2O_3 , MgO , and Al_4C_3 dispersion strengthening.

2.2.4 ODS Cu-based Superalloys

The first ODS Cu-based superalloy was Cu- Al_2O_3 produced by internal oxidation processing in the 1970s by SCM company. Al_2O_3 was added to the ODS Cu-based superalloy to improve the high fracture strength and low processing cost. And the Al_2O_3 particle in the matrix is usually small. The Cu- Al_2O_3 can be produced by using several routes which include the mixing of Cu and Al_2O_3 powder followed by casting, such as the Comalco process [29], and internal oxidation of Cu-Al alloy powders [30] followed by consolidation.

2.2.5 ODS Co-based Superalloys

Most of the Co-based superalloys have a low forgeability because they contain more carbon than other superalloys. And these carbons would form carbides in superalloys which impairs the forgeability [31]. γ' precipitates also strengthen ODS Co-based superalloy. Also, the added oxide particle play as a secondary phase would improve the medium and high-temperature strength of ODS Co-based superalloys [31]. When the ODS Co-based superalloy is working at medium temperatures, the γ' precipitation is treated as more useful to strengthen the alloy. However, the oxide dispersion enhances the high-temperature mechanical properties due to the thermal stability of oxide particles. It is generally accepted that the components of Al and W in Co-Al-W alloy can hardly dissolve into Co matrix except at high temperature [31].

2.3 Fabrication Techniques of ODS Superalloys Powder

2.3.1 Mechanical Alloying (MA)

The MA process is a technique that combines two different or more powders into a high energy ball milling machine to obtain fine-grained powders [sy dashu]. In the initial stage of MA, the base powders are mixed with other raw elemental powders and blended in stainless steel jars or ceramic jars that contain different sizes of balls. Figure 2-1 shows the early stage of MA processing, and the powder particles are relatively soft before plastic deformations. The ball to powder ratio is usually in the range of 1:10~1:20. The powders are sealed in the jars with Argon or Nitrogen gas to prevent oxidation during the process, and the jars are placed and rotated on a horizontal or vertical level.

Figure 2-2. A schematic of mixture powders in the early stage of the MA process [32].

The powder particles are impacted and crashed by the balls, in such way, compression, impaction, break-down, cold welding and extrusion might happen among powders, balls, and walls of jars. The powder particles are subjected to intense plastic deformation when they are under break-down and extrusion. Thus, the surface area of powder particle enlarges, thereby results in the appearance of atomized surfaces of metals. The surfaces are clean and fresh, and they are bonded to each other under cold welding and compression which leads to lamellar structures existing in particles. They tend to deform and grow when the grinding hour increases, work hardening of powder particles happens. Larger particles will have cracks and be broke apart. The processing tends to arrive equilibrium stage, so the size distribution of powder particles is narrow.

For ODS Ni-based superalloy, the raw elemental powders are still distinguishable in the early stage. However, the oxide dispersoid is distributed into matrix powders. In addition, the oxide dispersoid is dispersed along the welding surfaces and adjacent powder particles (Figure 2-2). Cold welding and breaking keep repeating during the processing, which results in the refinement of matrix powders and the exposure of fresh unreacted powder particles. It observably increases the contact area between particles, decrease the diffusion range of metal atoms and increase the diffusion coefficient. Generally, the MA process is dominated by solid diffusion. Because high-density crystal defects emerge during the process, thus providing a thermal driving force, to actuate the metal atoms diffuse and grow along the free surface of crystals, grain boundaries and lattice until the raw components deplete to form alloys [11]. Figure 2-3 shows a schematic of a schematic of powders in the final stage of the MA process. The dispersion was coated onto the surface on metal A and metal B. And metal A and metal B were interrelated.

Figure 2-3. A schematic of mixture powders in the final stage of the MA process [11, 32].

This technique usually requires a long duration to achieve alloyed powders. According to published results, the MA process requires 10~70 hours for most of common ODS superalloys [14]. Figure 2-4 shows the morphologies and shapes of the MA processed powder particles. As indicated by the red circle in Figure 2-4, the lamellar structure of MA processed powders is clear shown (refer to Figure 2-3). And the powders are in irregular shapes. Usually, the particle size range of mechanical alloying is 20~45μm which is narrow. Lamellar structures of particles were observed, suggesting powders were under cold-welding and fracture during the process.

Figure 2-4. An SEM picture of powders under ball milling 400 rpm 41 hours.

2.3.2 Mechano-Chemical Bonding (MCB)

The MCB processing is a dry complex mechano-chemical technique for applying mechanical energy to different material particles to cause a mechano-chemical interaction between particles. The advantage of the MCB process is that it is a process by only using the internal mechanical energy without using any binders comparing to the BM process. The BM process usually adds a processing control agent to the powder to boost the MA effect. The solid solution may form during the process, i.e., smaller particles may diffuse onto or through the hosting particles. In principle, the MCB technique takes the advantages of passing dry powder mixtures with preferred particle size ratios through a narrow gap, so that smaller guest particles are bonded and coated onto the surface of larger core particles under the influences of various types of mechanical forces [14].

This instrument is capable of producing Ni-based and Fe-based ODS superalloy powders. The MCB machine is composed of three parts: Control panel, Motor Box and Main Vessel. As shown in Figure 2-5, the main vessel contains a rotor and blades with press heads. The powder mixture could be imported through the feeding port. The rotor and blades rotate at high speeds when the machine is working. As shown in Figure 2-6, a powder casing may form during the process, and the rotating speed of MCB could be up to 6000 Revolutions per Minute (rpm). When the blade and rotor are rotating, and the press head is passing through, the powder particles are under compression and friction, and the particle casing might migrate along the rotation direction which both will cause short local temperature spikes between the powders, i.e., at the contact points of powder particles. Thus, the powder particles are under plastic deformation.

Figure 2-5. A schematic of the MCB machine.

Figure 2-6. The principle of the MCB process: (a). A schematic of the main inner vessel; (b). Structural patterns of nanocomposite particles [33, 34]

By applying the MCB treatment, powders can achieve particle coating, precision mixing, sphericalzation, and surface modification in one processing step [26]. Figure 2-6 (b) shows the basic principle of structural patterns of nanocomposite particles processed by the MCB process. It is noted that pattern is similar to the final stage of the BM process. In the final stage of the BM process, the element A and element B were interrelated with each other, and the dispersoids were coated onto the surface of element A and element B. While for the MCB process, it could achieve the interrelation of element A and element B, or the coating from A onto the surface of B, and even coated on the surface of other major particles such as element C and element D. The coating is depending of the selected size of each added element.

In this research, the MCB processing provides a unique way to produce ODS Ni-based Superalloy powders with the composition of Ni-20Cr-5Al-3W-1.5Y₂O₃ (in wt. %) through a drying processing without using any binders or introducing any contaminations. Although, individually, there are various types and sizes of ODS superalloy powders fabrication methods. Separately, however, the MCB processing has three significant advantages:

- I). Shapes of particles: The MCB processing could achieve particle coating, precision mixing, sphericalzation, and surface modification, in such way powder particles would come out with high roundness that could be up to the degree of 0.93. Figure 2-7 shows the powder particle morphologies after MCB processing.

Figure 2-7. An SEM picture of powders under MCB processing 5000 rpm 11 hours.

- I). Uniform distribution of Y_2O_3 : Y_2O_3 could be evenly distributed onto the hosting particles as a coating to form solid solution through surface diffuse. It is also possible to create other alloy phases and different microstructures. For the currently available MA process, Y_2O_3 could be diffused onto the hosting particles, but it is difficult to achieve uniform distribution since MCB has precision mixing, sphericalization, and surface modification. For the current available Atomization, since Y_2O_3 or other oxide dispersion has a high melting point, Atomization could only achieve up to 1700 °C. Y_2O_3 will be difficult to melt and form a composite with other content. However, according to published results (As shown in Figure 2-8) [35], MCB is capable of distributing and coating Y_2O_3 at lower temperatures. Figure 2-7 (a) shows a roughly 25 nm thin film coating in lighter contrast coated onto the hosting particles in darker contrast (Ni and Cr in this study), 2-6(b) implies that the thin film coating is amorphous Y_2O_3 [35].

Figure 2-8. TEM images of MCB processed ODS Ni-based superalloy powders (a) TEM BF image, (b) HRTEM image [35].

- II). Forming alloys: The MCB process has the capability to pre-alloy the powder mixture. As shown in Figure 2-9, the XRD analysis shows that the γ matrix (NiAl phase) exists. In addition, the absence peak of Y_2O_3 indicates that Y_2O_3 is uniformly distributed and coated as an amorphous coating onto hosting particles.

Figure 2-9. An XRD analysis of powders under MCB processing 5000 rpm 11 hours.

2.3.3 Atomization

Atomization is a process that uses the principle of low mechanical strength of liquid metal to break apart liquid metal droplets. It is easier to break the molten metal droplet than when it is solid. High-pressure gas (i.e., H₂, air, and inert gases) or solution (i.e., Water and Oil) is adapted to be sprayed at high speeds on liquid metal droplets to force the metal to solidify in a high cooling rate. The solidified metal particle is spun and filtered by ordinary rotation. Atomization processes are capable of producing high-quality metal powders, such as Ni, Fe, and Al superalloys with uniform particle distribution and spherical shapes.

Atomization is a two-step process. First, shearing of liquid metal occurs; second, freezing of liquid droplets takes place. In the first step, a relatively large volume of liquid is sheared into smaller liquid particles. The energy needed for shearing is supplied by such sources as high-velocity gas jets, water jets, centrifugal action, and by plasma jets [advance GA processing for Ti and Ti Alloy powder manufacturing]. Major Atomization processes are Gas Atomization (GA) and Water Atomization (WA).

2.3.3.1 Gas Atomization (GA)

GA is a conventional and widely used method for metal powder production. As shown in Figure 2-10, GA uses inert gas jets to atomize molten metal powders into fine droplets, which cools down as the droplets drop in the chamber and form spherical powders with uniform size distribution. During the GA process, the molten metal is atomized thanks to inert gas jets into fine metal droplets which cools down during their fall in the atomizing tower. And pre-alloyed powders form.

GA is widely used in metal powder metallurgy and is capable of producing spherical and uniform structured superalloy powders (As shown in Figure 2-10a), the known highest melting temperature that GA could achieve is around 1700 °C which is lower than the melting temperatures of most of the oxides. The low melting temperature of the GA process introduces the difficulties of adopting GA to produce ODS superalloy powders, i.e., Y₂O₃ could not be uniformly distributed into the matrix metals since it has a higher melting point (2425 °C) and it would not be melted in the first step. However, post-processing and alternation usually are introduced after gas atomization in order to achieve ODS superalloy powders. Conventionally, gas atomized powders are mechanically alloyed post process with Y₂O₃ in order to obtain uniform oxide dispersion and monocrystalline microstructure [14].

Figure 2-10. A schematic of a gas atomization process
[\[https://www.lpwtechnology.com/technical-library/powder-production/\]](https://www.lpwtechnology.com/technical-library/powder-production/)

Figure 2-11. SEM images showing characteristic morphologies of as-produced atomized powder: (a). Gas atomized 316 stainless steel [36]; (b). Water atomized 316 stainless steel [36]; (c). Gas atomized Ti-6Al-4V [37]; (d). Gas atomized IN718 [38]; (e). Cross sections of gas atomized IN718 [38]

In addition, there are pores trapped inside the GA particles during the solidification as shown in Figure 2-11 (c) and (e) (indicated by red arrows). Narra et al. have found that pores inside of the particles would affect the density and microstructure of AM as-printed samples [39]. A reactive gas atomization synthesis method to produce Fe-based ODS superalloy powders was published by I.E Anderson et al. [12]. The surface of gas atomized particles was oxidized at an elevated temperature by utilizing MA to obtain uniform oxide dispersion. Figure 2-12 demonstrates the presence of the oxide dispersoid during all stages for the aforementioned reactive gas atomization process. It is evident from the XRD plot of the as-atomized powder, and the hot isostatic pressed (HIP) powder does not show oxide dispersoid formation until after heat treatment at 1200° C [12].

It is noted that Y_2O_3 was coated as an amorphous thin film onto the hosting particles, and the XRD result of MCB powders confirms that. Even though the absence of Y_2O_3 peak of the reactive gas atomized powders is apparent, no

evidence has shown that Y_2O_3 was evenly distributed into the matrix. Y_2O_3 did not appear until HIP and heat treatment. Besides, heat treatment will alter the strengthening phase of powders. Alternation is still required which is time-consuming. Moreover, the formation of the dispersoids did not appear until further heat treatment of the atomized powders, which in turn will cause coarsening of the grain size. However, the MCB process excels in the production of ODS superalloy powders with uniformly distributed oxide dispersoid without extra processing.

Figure 2-12. XRD data revealing dispersoid formation after heat treatment of powders under different chemical compositions [12]

2.3.3.2 Water Atomization (WA)

This technique uses water jets to atomize the molten metal (Figure 2-13). The metal is melted in a furnace in the first step and poured into a tundish. The resulting metal stream is blown out in a fine jet while water from a high-pressure pump blows until the metal becomes atomized. The resulting powder is dried and classified for particle size depending on its intended usage [40].

Figure 2-13. A schematic of a water atomization process [40]

WA is similar to GA which is also capable of producing high-quality metal powders, such as Ni, Fe, and Al superalloys with uniform particle distribution. But Figure 2-11 (b) shows that the shape of WA particles is not perfectly spherical with some irregular shapes. And the difficulties of using WA to produce ODS particles still exist.

2.3.4 Surface Oxidation

Surface Oxidation is a method that obtains oxide dispersion through oxide thin film which exists on the surface of particles. Compression and extrusion usually are employed after surface oxidation to produce ODS superalloy. *Irmann et al.* adopted surface oxidation to produce sintering Al. Flaky Al powders were chosen to form a 0.1~0.2 μm thin film on the surface of Al powders. The oxidized Al powders are then compressed and extruded to break apart the oxide film and blend it into the matrix in order to obtain powders with evenly distributed oxide dispersions [9].

2.3.5 Internal Oxidation

The internal oxidation method is designed according to the principle of preferential oxidation of solute elements in dilute solid solution. Hence, this method requires that the solute elements have a higher free energy of formation of an oxide with oxygen than the solvent elements. The typical dispersion strengthened alloy fabricated by internal oxidation is Cu-Al₂O₃ alloy. Cu and Al were first melted into metal liquid and then atomized to powder forms, and the atomized powders were then mixed with oxidant and heated at 1073~1223 K to utilize internal oxidation.

During this processing, the decomposed oxygen from the oxidant reacts with Al since Al is more reactive than Cu. The extra oxygen was then drained from the system. Hence, ODS Cu-based superalloy powders were produced with distributed Al_2O_3 [30].

2.3.6 Co-precipitation

Co-precipitation is a methodology that utilizing chemical reaction to obtain ODS. A mixed solution is made with nitrate, ammonium carbonate, ammonium nitrate, and oxide gel to form a metallic oxide on oxide particles. The mixture is then filtered, washed, dried, ball milled and dehydrogenized to achieve ODS superalloy powders. DuPont company has produced ODS Ni-based superalloy by using this method:

Figure 2-14. A craft routine of the fabrication of TD-Ni [10]

2.3.7 Mechanical Mixing

Mechanical Mixing is using a roller mixer, a ball milling machine, and a rotating arm mixer to mix matrix metal powders with oxide particles through a dry or wet processing. This method has limitations: when the size of matrix particles and oxide particles have big difference, bigger particles tend to float, and smaller particles tend to sink during the mixing. Especially, when the oxide particle is nanosize, agglomeration would happen between oxide particles.

In summary, all these methods above could fabricate ODS superalloy powders with different mechanical properties, sizes, morphologies, and shapes. In order to obtain densified ODS superalloys, powders produced by these methods could be subjected to sintering, cold pressing, extrusion, hot isostatic pressing and spark plasma sintering. However, in this research, the aim is to develop fine ODS Ni-based superalloy powders for AM which is a novel and under-developed technique. Even though Atomization is the principal and widely used technique for producing superalloy powders, the difficulties of fabricating ODS superalloy powders still exist comparing to BM and MCB.

2.4 AM Techniques

AM is the latest manufacturing technique that has high degree-of-freedom and allows product customization. To be specific, AM is defined as "a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies", referred from ASTM's definition. Since there are several ways to deposit materials and different energy sources (laser and electron beam) can be chosen, the systems are categorized into three different types according to the material feeding: powder bed systems, powder feed systems, and wire feed systems [41].

Figure 2-15. A schematic of a general powder bed system [41]

2.4.1 Powder bed systems

Powder bed systems typically have lower unit build volumes which are smaller than 0.03 m^3 . Figure 2-15 shows a schematic diagram of a typical powder bed system. A roller rakes powder from the reservoir across the work area. The energy source is then delivered to the surface of the bed, and the powder is either melted or sintered into a desirable shape. By repeating the process of racking and melting/sintering, a 3D solid is formed. The workpiece of powder bed systems has higher resolution features so that the dimension of the work piece can be produced

precisely. The most prevailing powder bed system is the EOS M290, which has been fully commercialized and widely applied in many top notch industries for customizing tool parts and for some research purposes [36].

2.4.2 Powder feed systems

Instead of racking a layer of material powder by a roller, powder feed systems utilize a nozzle to convey powders onto the build surface of the workpiece. The energy source melts a monolayer or more of the powder into the shape desired, and a 3D solid is formed by repeating the process (Figure 2-16). There are two types of feeding system that either the workpiece remains static and the energy source/powder nozzle moves, or work piece moves while the energy source/powder nozzle fixed in a position. The powder feed systems have a larger build volume, Optomec450 LENS (Laser Engineered Net Shaping-LENS) as an example, which has 1.2m³ build volume. Also, powder feed systems can be utilized to refurbish and repair damaged part of the workpiece. LENS is the most popular direct energy deposition AM process for powder development and testing. Thus it is suitable for research applications.

Figure 2-16. A schematic of a general powder feed system [41]

2.4.3 Wire feed systems

Wire feed systems can use plasma arc as energy source besides electron beam and laser. At first, a single bead of material is deposited and upon subsequent passes is built upon to develop a 3D structure. Although wire feed systems have a high deposition rate, the extensive machining and polishing are required.

Figure 2-17. A schematic drawing of a general wire feed system [41]

Figure 2-18. Metal AM processes [16]

The overall metal AM processes are all summarized in Figure 2-18. Besides the three widely utilized AM processes mentioned above, there are some other metal powder deposition methods, for instance, the binder jetting that uses an organic binder to coagulate the metal powder together and cures in the oven to form a green body that is ready for sintering in the next step. The critical challenge for binder jetting is the shrinkage of sample dimension after sintering process (up to 40% length shrinkage).

On the other hand, an electron beam is another energy source that can reach ~60kW, which is superiorly higher than laser beam (450W). The electron beam could provide sufficient energy for metal powder to melt and form desirable microstructures with faster scanning speed. The downside is the electron beam system needs to be operated in a vacuum. Thus, electron beam melting is less widespread than laser melting due to its high requirement in vacuums.

Selective laser melting (SLM) is another prominent powder bed AM technique that has higher precision and has better as-built surface quality with compare to electron beam and LENS. It has been fully commercialized (EOS Company) and becomes the leading technology in AM. The only restriction for the SLM is the size requirement of metal powder, which is lying in a narrow range between 40 μm ~ 60 μm , and spherical in morphology. The purpose of setting this restriction is to ensure the powder bed has high packing density, and the GA processed powder is the only way to provide the desired powder size and morphology. Other powder processes, such as the BM process, has very few reports in SLM application. However, another type of AM technique called Laser Cladding (LC) has a higher tolerance for powder shapes and sizes. The input energy of LC is much higher than LENS, and it is widely used in the industry. The objective in LC is to fuse an alloy layer or coating, onto the surface of a substrate.

In accordance with above, LENS system and LC are two appropriate candidate AM techniques ore this study:

- I). Higher tolerance with powder size and morphology
- II). requirement in a vacuum environment
- III). The processing parameters control determines the density of the printed sample.

In summary, LENS system and LC are suitable for metal powder development for AM, and in this thesis, the ODS powder processed by MCB-only and its combined technique (MCB+BM) was utilized.

CHAPTER 3: THEORETICAL BACKGROUND

3.1 Strengthening Mechanisms of ODS Ni-Based Superalloys

3.1.1 Dispersion Strengthening

Dispersion strengthening is a mechanism that adding chemically stable secondary or ternary phase particle into matrix metals to strengthen alloys. Secondary phase particles are artificially added into the matrix, they are uniform, fine, thermally stable and chemically stable and are capable of pinning dislocation, grain boundaries, and sub-grain boundaries. The secondary phase particle is also sufficient to inhibit the migration and movement of dislocations and prevent grain from growing. Therefore, the mechanical properties of alloys are enhanced.

Although secondary phase particles could improve the mechanical property, they could also weaken the ductility and breaking resistance. Secondary phase particle usually has high melting points which enable dispersion strengthened metals to have high yield strength, tensile strength, creep resistance and abrasive resistance. The working temperature of dispersion materials could be up to $0.8\sim0.9T_m$ [42].

The theory of dispersion strengthening is the theory of dislocation. The effect of secondary phase particle mainly depends on the pinning of dislocations by the secondary phase particle. Common secondary phase particle is refractory Oxides (i.e., Y_2O_3 , Al_2O_3 , HfO_2 , and ThO_2), Carbides (i.e., TiC , SiC , and WC), Nitrides (i.e., TiN , BN , and Si_3N_4), and Borides (i.e., TiB_2 , ZrB_2 , and CrB_2). They are harder than the matrix metals, so they are obstacles of the migration and movement of the dislocation line. The dislocation line needs higher stress as a driving force to migrate. Secondary phase particle falls into two categories: deformable particle and non-deformable particle. These two types of particles interact with dislocation differently in two different theory.

3.1.1.1 Orowan Theory

Figure 3-1. The dislocations pass particles by bowing mechanism [43]

Orowan proposed this theory in 1948 [44], as shown in Figure 3-1. When the dispersion strengthened alloy is under external loading, the dislocation which migrates along glide plane meets the harder non-deformable secondary particle,

the particles bow the dislocation line. As the loading increases, the bowing part becomes stronger, and the dislocation line bypasses the particles so that a positive dislocation meets a negative dislocation. Positive dislocation tends to counteract the negative dislocation. Therefore, a dislocation ring forms which increases the density of dislocation and the resistance of dislocation migration. Figure 3-2 shows a TEM picture of a dislocation ring which confirms this theory.

Figure 3-2. A TEM picture of a dislocation ring [45]

Figure 3-3. General view of the mechanical balance of the dislocation line

As shown in Figure 3-3, when the dislocation line bypasses the particle, the resistant force from particle to dislocation line F and the tension T of dislocation line satisfies:

$$F = 2T \sin \theta \quad (3.1)$$

Where θ is the angle of dislocation line where it bypassed. When $\theta = \frac{\pi}{2}$, the dislocation ring is a semicircle. When F reaches its maximum value, $T = \frac{1}{2}Gb^2$ where G is the shear modulus, b is the Burgers Vector of a dislocation. Therefore, $F_{\max} = Gb^2$ Apply balancing condition, $F_{\max} = \lambda b \tau_c$. Substitute $F_{\max} = \lambda b \tau_c$ into formula (1) will get:

$$\tau_c = \frac{Gb}{\lambda} \quad (3.2)$$

Where τ_c is the critical stress, G is the shear modulus, b is the Burgers Vector of a dislocation, and λ is the distance between secondary particles. Only when the external stress exceeds the critical stress, the dislocation line is able to migrate and bypass. From formula (3.1), the yield stress is inversely proportional to λ . When the distance is smaller, metals perform high yield strength which explains the size of added secondary phase particle is usually around 50 nm.

3.1.1.2 Ansell-Lenel Theory

Ansell et al. [46] proposed this theory after Orowan. When the secondary phase particle is deformable, the dislocation line will cut the secondary phase particle instead of bypassing and encircling it. They used the crack of secondary phase particle which caused by dislocation pile up as the criterion of yielding.

Figure 3-4. A schematic drawing of Ansell-Lenel Theory [47]

Figure 3-5. A TEM picture of a dislocation cutting a secondary phase particle [46]

When the stress applied on the particle is equal to the breaking stress of particle, the dislocation line will move as this pattern. Thus, the metal will yield. The cracking of secondary phase particle consumes the driving force of dislocation migration, which increases the resistance of dislocation. This theory could be formulated as follows:

$$\tau_c = \sqrt{\frac{GbG^*}{2\lambda C}} \quad (3.3)$$

Where G is the shear modulus of the matrix, G^* is the shear modulus of secondary phase particle, b is the Burgers Vector of a dislocation, and λ is the distance between secondary particles, C is a constant ≈ 30 .

3.1.2 Strain Strengthening [42]

Strain strengthening is a mechanism that metals are cold processed or deformed below the temperature of recrystallization. Hence the density of dislocation is increased. Every single dislocation is more challenging to migrate since density is increased. The resistance between different grains is stronger. Thus the mechanical properties of metals are improved. This method is usually applied to ductile superalloys. But the recrystallization temperature of most metals is in the range of $1/3 \sim 1/2 T_m$, where T_m is the melting temperature of metals. When heat the cold-deformed metals to their recrystallization temperature would deduce the dislocation which caused by the deformation.

3.1.3 Solution Strengthening [42]

Solution strengthening is a method that adding other metal elements into the matrix system to utilize lattice distort of γ' phase, thus the atomic binding force of metal atoms is increased, the diffusion rate of elements is decreased, and the growth of defects is prevented. For FCC solid solution, the deformation is non-homogenous. And such this deformation is through the climbing of dislocations which is associated with short-range domain boundary energy. These short-range domain boundary energy will induce friction stress to inhibit dislocation. Therefore, the alloy is strengthened. Pettinary et al. published researches about Ni-Cr alloys that contain Mo, W, Re, etc. instead of Al and Ti which are elements of forming γ' . They confirmed that the short-range domain boundary energy in FCC solid solution caused the non-homogenous distribution of dislocations, hence caused the non-homogenous deformation. It could be summarized for ODS nickel-based superalloys as follows:

- I). Soluble elements in the Ni matrix is capable of forming an infinite solid solution so that the degree of solution strengthening is increased.
- II). Most of the metal atoms have a larger radius than Ni, thus adding these elements into solid solution will increase the lattice constants.
- III). The non-homogenous dislocation and clustering particle is a stable phenomenon. It is helpful for the mechanical property at high temperatures.
- IV). Added elements could pin non-homogenize dislocation which inhibits dislocation climbing. Thus the mechanical property at high temperatures is improved.

3.1.4 Fine-grain strengthening

Hall-Petch [48] proposed that fine-grain strengthening is an effective strengthening mechanism for superalloys. The alloy is strengthened by the fine grain and grain boundaries. The finer the grain, and the more grain boundaries, the higher mechanical properties at room temperature. This theory could be presented in a formula as follows:

$$\sigma_s = \sigma_0 + Kd^{-\frac{1}{2}} \quad (3.4)$$

Where σ_s --Yield strength of the alloy

σ_0 --The resistant force inside the grain in terms of dislocation

K --Coefficient

d -- The diameter of the grain

3.1.5 Precipitation Strengthening [42]

Precipitation strengthening is a mechanism that adds elements into the matrix and then quenching of rapid cooling to obtain a metastable solid solution. When the alloy is heat treated after rapid cooling, metallic compound forms as clustering group or particle. These groups and particles interact with dislocation within the elastic stress field in order to prevent dislocation from migrating. These particles are commonly small and uniform in the matrix. Precipitation Strengthening is one of the most effective strengthening methods for superalloys. Even though γ' is coherent with the matrix, their lattice parameters are different. When γ' is coherently precipitate from the γ matrix, γ' will cause elastic stress field around itself. The mismatch degree of γ' and γ could be formulated as follows:

$$\delta = \frac{2(a_{\gamma'} - a_{\gamma})}{a_{\gamma'} + a_{\gamma}} \quad (3.5)$$

Where $a_{\gamma'}$ -- Lattice parameter of γ' phase

a_{γ} -- Lattice parameter of the γ matrix.

The mismatch stress field exists on the interfaces of γ' , and γ is capable of inhibiting the migration of dislocation which strengthens the alloy.

3.2 The Effect of Elements

Table 3-1. Compositional ranges of major alloying additions in Ni-based superalloys [2]	
Elements	Ranges (wt. %)
Cr	5~25
W	0~12
Al	0~6
Ni	-

Table 3-1 shows the compositional ranges of principal alloying additions in Ni-based superalloys. Table 3-2 shows that role of added elements in ODS Ni-based superalloys. There were only five elements added into the developed material system. The effect of each added element is discussed below.

Nickel: Ni has Face-center-cubic (FCC) unit cell. It has high chemical stability, and the structure stability enables it maintains FCC from room temperature to melting point. Ni matrix is capable of fully forming alloys with other elements through solid solution strengthening instead of generating harmful phases. Thus, Ni is a good candidate for matrix system. More importantly, Ni forms strengthening γ' phase with L12 structure by interacting with other metal elements in the system during aging processing [13]. All Ni-base alloys contain this phase as the matrix. And it is also the element of forming the γ matrix and γ'' phase with Nb and Ta. This makes Ni alloy suitable for producing ODS superalloys.

Chromium: Cr is the solid solution strengthener in ODS Ni-based superalloys. Cr could enhance the corrosion resistance and high-temperature oxidation resistance. It is a significant component in ODS superalloys. Cr could form a densified Cr_2O_3 oxide film on the surface of metals to improve the passivation ability of metals. But high content of Cr could promote the formation of alpha phase which would undermine the ductility of alloys. Considering the corrosion resistance and ductility of ODS superalloys, Cr was chosen as 20 wt. % in this research.

Tungsten: W is the element to facilitate the solid solution strengthening in ODS superalloys. According to published results, the creep strengths of ODS super alloys increases with W contents. But when W is over 3 wt. %, the creep strength reaches saturated, W could cause some unstable phases such as Laves phase which would weaken the creep strengths of ODS super alloys. So W was chosen as 3 wt. % in this study.

Aluminum: Al forms the γ matrix with Ni. It goes into solid solutions to provide oxidation resistance since a stable Al_2O_3 film could form on the surface of Ni-based superalloys. It is also a booster for the γ' precipitates which enhance the mechanical properties of Ni-based superalloys. But existing results have shown

that when Al is over 5 wt. %, the γ' phase tends to mismatch with the γ matrix. So the content of Al is set to 5 wt. % in this study.

Yttrium Oxide: Based on previous results, when Y_2O_3 is over 0.2 wt. %, the strengthening of metals is apparent. But when it is higher than 0.5 wt. %, microvoid would form along with grain boundary which increases the diffusion of oxygen to decrease the oxidation resistance of alloys: the higher content of Y_2O_3 , the higher oxidation rate of alloys.

Other elements: Generally, N, O, and C, etc. would decrease the ductility of metals. But recent results showed that the influence of Nitrite, Oxide, and Carbide which formed by N, O, and C in metals depends on the size, distribution, and shape of these compounds. When V and Ti are contained in alloys, moderate content of N, O, and C could form $MxCy$ compounds with V and Ti, which would enhance the high-temperature strengths of alloys, especially the creep strength. When C is high in alloys, C will combine with Cr forming carbides which would cause the loss of Cr to decrease the corrosion resistance of alloys. When alloys contain S, P, Si, and Cu, these elements will impair the ductility.

Table 3-2. Alloying elements present in ODS Ni-based superalloys [2]	
γ former	Ni, Fe, Co, Cr, W, Mo, V, Y
γ' former	Al, Ti
Minor alloying additions	Zr, Hf, B, C

CHAPTER 4: EXPERIMENT

4.1 Experiment Procedure

Figure 4-1. A flow chart of experiments

4.2 Experiment Materials

I). Raw elemental powders

Table 4-1. The information of raw powder.			
Elemental powder	Average Size	Degree of purity	Weight Percentage
Nickel	3~7 μm	99.9%	70.5%
Chromium	3~7 μm	99.2%	20%
Aluminum	4.5~7 μm	97.5%	5%
Tungsten	<1 μm	99.95%	3%
Yttrium Oxide	50~70 nm	99.995%	1.5%

The raw powders that were used in this study are from Alfa Aesar. The average size, degree of purity and weight percentage are shown in Table 4-1. These powders were storage separately and sealed in bottles with Argon gas. The just-blended powder was mixed, sealed in bottles with Argon gas, and stored in a glove box with Argon atmosphere. A digital scale with accuracy 0.001g was used to weight powders. Each bottle contained the just-blended powder sample which had weights approximately 300 g. Considering the short processing time of MCB and no ball to ball, ball to powder, and powder to container wall collision happened during MCB process, the average size of starting raw powders are from 50 nm to 7 μm in this study [49-52]. Figure 4-2 shows SEM morphology of raw powders. As shown in Figure 4-2, the Ni particle is spiky with some degree of roundness. Al is the most spherical powder. Cr particle is chunky. Tungsten particle is block-like with a smaller size. And Y_2O_3 particle is nanosize plate.

Figure 4-2 SME morphology of (a). Pure Nickel powder; (b). Pure Chromium powder; (c). Pure Aluminum powder; (d). Pure Tungsten powder; (e). Pure Yttrium Oxide powder; (f). As-just-blended powder (unprocessed).

II). Processing control agent

A processing control agent (PCA) was used to function as a lubricant and to enhance powder flowability [53]. The PCA is stearic acid from Alfar Aesar with a formula of $\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$. The purity of stearic acid is 98%.

4.3 Experiment Methods and Instruments

Two types of processing technique, MCB + BM and MCB-only were employed to process as-just-blended starting powder to fabricate experimental ODS Ni-based superalloy powders. In order to investigate and compare the MA effect of the MCB process, a BM process under 400rpm 41hours (denoted as BM-only) was employed. And the powder processed by the BM-only process is used a benchmark material in further research. Note: BM experiments were carried out with the corporation from another Master student Markova Macpherson under Dr. Bruce S. Kang's supervision. Markova Macpherson shares the credits in BM experiments.

I). The MCB machine

The model of MCB machine is NOBILTA-130 from HOSOKAWA Micron LTD. The capacity of the main chamber is 0.5 liters, and 350g powder can be produced for each batch. The maximum inner pressure of the main vessel is 0.49 MPa. A thermal couple is attached in the powder feeding port to monitor the temperature of the inner vessel wall. Figure 5-3 shows the actual image of HOSOKAWA NOBILTA-130 MCB machine.

Figure 4-3. HOSOKAWA NOBILTA-130 MCB machine.

In this study, the raw powder was weighed on a digital scale in a glove box. And then the raw powder was mixed and sealed in a polyethylene bottle with Argon gas. Before feeding the raw mixed powder into the vessel, Argon gas was used to purge out the air in the vessel for three times. Each time is 15 seconds. After feeding the powder into the vessel, Argon gas was filled for 10 seconds. Figure 4-4 shows the craft routine of MCB processing.

Figure 4-4. A craft routine of MCB process

Table 4-2. Unique configurations of raw powder for the MCB-only, BM-only and MCB+BM process

Configuration	Rotation Speed (rpm)	Running Mode	Time (hours)
M1	4000	Normal	1
M2	4000	Normal	18
M3	4000	Normal	32
M4	4000	Normal	50
M5	5000	Normal	22
M6	5000	Normal	32
M7	5000	Normal	50
M8	5000	Step-running	8
M9	5000	Step-running	11
BM-only	400	-	41
MCB+BM	MCB 4000+BM 400	MCB Normal	1+40

Table 4-2 shows 11 different process parameters for the MCB-only, BM-only and MCB+BM process. Where, Normal mode denotes: The just-blended powder was processed for varying periods with the duration of 4 hours of each, the total running hours accumulated up to 50 hours. Step-running mode denotes: The just blended powder was processed for different periods with the duration of 1.5 hours of each, the off interval was 10 mins, the total running hours accumulated up to 11 hours. And the MCB main vessel was shook and hammered by a plastic hammer during the off intervals.

II). The BM machine

MCB first processed As-just-blended power under 4000rpm 1 hour in an Argon gas atmosphere. Each run has a yield of 300g. It was expected to have Y_2O_3 nanoparticles evenly dispersed and bonded onto the surfaces of Ni and Cr particles (host particles) which created oxide dispersion and MA effects. The MCB processed powder was then processed by a planetary BM with 4 stainless still jars under different rotation speed (i.e., 300rpm and 400rpm), different Ball to Powder (BPR) ratio (i.e. 10:1, 15:1 and 30:1), and different processed durations (i.e. 15 hours, 20 hours, 25 hours, 40hours and 45hours). A PCA Stearic Acid with the composition of $C_{17}H_{35}CO_2H$ at 0.5 wt. % was added to each jar to boost the MA effect. Size distribution of four 20 mm balls, four 15 mm balls, two 10 mm balls and

two 5 mm balls were used. And each run has a yield of 64g which is relatively low comparing to the MCB process. The powder was processed in Argon atmosphere during the BM process. The optimization of BM parameters has been investigated by Markova Macpherson. In this study MCB-4000rpm-1hour+BM-400rpm-40hours-BPR 15:1 (denoted as MCB+BM) was used as a reference to investigate the MA effect of MCB+BM, MCB-only, and BM-only processed powders.

Figure 4-5. The MTI planetary BM machine

Figure 4-6. A craft routine of MA process

III). Particle size distribution

The size distribution of particle is analyzed by a Laser particle analyzer from Malvern Panalytical company (Model: Master Sizer 2000). The solution that was used to disperse the powder into the laser system was distilled water. And the chamber of the analyzer was purged by distilled water after each test.

IV). Laser engineering net shaping (LENS)

Produced MCB+BM and MCB-only powders were sent to the University of Pittsburgh to conduct experiments on LENS 450 system. The LENS system in the University of Pittsburgh is LENS 450 system. Three input laser energies were selected: 200W, 250W, and 275W refer to the nominal parameters of LENS 450 system. Two laser scanning speeds were chosen: 33 mm/s and 10 mm/s. Two powder feeding rates were used: 8 rpm and 11rpm. Two different flat substrates

were adapted: MAR-247R (Ni alloy) and Stainless steel. The hatching spacing was 0.1524 mm and the layer thickness was 0.1 mm. Hatching lines were made at 0 ° horizontally in the first layer and then were rotated 90 ° for the next layer by repeating this order. Figure 4-7 shows the schematic of the hatch spacing.

Figure 4-7. A schematic of hatching patterns employed in LENS 450 system.

V). Laser Cladding

The MCB-only processed powders were sent to Siemens Company, Pittsburgh to conduct Laser Cladding. The input laser power was ~5kW. A MAR-247R flat substrate was chosen. The laser scanning speed, hatch spacing, laser thickness, and hatching patterns are confidential from Siemens Company. So the as-printed samples will be used a reference to compare the as-printed microstructure between large input laser energy and low input laser energy.

VI). Density Testing

The density testing is based on Archimedes drainage. Since voids and cracks cannot be totally eliminated after printing, achieving the theoretical density of as-printed samples is difficult. A relative density should be employed to examine the density of as-printed samples:

$$\rho_R = \frac{\rho_E}{\rho_T} \times 100\% \quad (4.1)$$

Where, ρ_R -- Relative density

ρ_E -- Experimental density of as-printed samples measured by Archimedes drainage

ρ_T -- Theoretical density of as-printed samples

$$\rho_T = \rho_a \cdot W_a + \rho_b \cdot W_b + \dots + \rho_x \cdot W_x \quad (4.2)$$

Where, ρ_x -- The theoretical density of component x

W_x -- The weight fraction of component x

Figure 4-8. A schematic of Archimedes drainage.

The as-printed samples were tested for density in an alcohol solution. The steps of the test and calculation are as follows:

$$m_1 = \rho_E V - \rho_1 V \quad (4.3)$$

$$m_2 = \rho_E V - \rho_2 V \quad (4.4)$$

Combine (4.3) and (4.4) would get

$$\rho_E = \frac{m_1 \rho_2 - m_2 \rho_1}{m_1 - m_2} \quad (4.5)$$

Where m_1 and m_2 are the weights of the as-printed sample in air and in the alcohol solution respectively. ρ_1 and ρ_2 are the density of the as-printed sample in air and in the alcohol solution respectively. Table 4-3 shows that theoretical density of components in this study. Thus, the calculated theoretical density of as-printed sample should be 8.51 g/cm³.

Table 4-3. Theoretical density of components					
Component	Nickel	Chromium	Aluminum	Tungsten	Yttrium Oxide
Theoretical Density (g/cm ³)	8.908	7.190	2.699	19.300	5.100
Weight Fraction (%)	70.5	20	5	3	1.5

VII). The grinding and polishing of as-printed samples.

All the as-printed were grinding and polishing under the same condition for the following characterization. The as-printed samples were cut cross-sectionally, grinded with sandpapers in according grit size: 240, 400, 800, 1200, 2000, and polished with diamond suspension 9 μm , 3 μm , and 1 μm . Buehler Vibromet was employed for final polishing in 0.05 diamond suspension. The samples were then etched by Marble's Reagent for 2 seconds etching time.

Figure 4-9. The Buehler Vibromet instrument [<https://www.azom.com/equipment-details.aspx?EquipID=3101>].

4.4 Characterization Methods

After the MCB-only, BM-only and MCB+BM processes, a small amount of powders (5~20 g) were taken and sealed in glass vials and stored in an inert environment. And then they were subjected to the non-destructive micro-structural analysis: X-ray Diffractometer (XRD), Scanning Electron Microscope (SEM) and Energy Dispersive Spectrum (EDS).

I). XRD

The X-ray Diffractometer is PANalytical X'Pert Pro with a CuK alpha radiation (45kV, 40mA) from SRF WVU. A spinner stage was used. The mixed raw powder, MCB processed powder, BM processed powder, MCB+BM processed powder and as-printed samples were analyzed by PANalytical X'Pert Pro. And the powders were consolidated into a disk. For the as-printed powder, the laser deposited layers were analyzed by the XRD and the signal of the substrates have been removed by curve fitting. The XRD patterns were recorded at room temperature with step-sizes of 0.0167 ° of 2 θ and 40 s per step which ranges in 10 ° to 90 °.

II). SEM

The scanning electron microscope is Hitachi S-4700 from SRF WVU. The mixed raw powder, MCB-only processed powder, BM-only processed powder, MCB+BM processed powder, and as-printed samples were analyzed by Hitachi S-4700. The processed powders were dispersed into an alcohol solution to become a suspension solution. And then they were dispersed and fixed onto a carbon tape for SEM characterizations. The as-printed samples were also fixed onto a carbon tape for cross-section characterizations.

III). EDS

EDS was utilized to analyze the distribution of elements in the cross section as-printed samples. Especially, point scan was used to pinpoint the location and analyze the distribution, density, and phases. Mapping was also employed to observe the element distribution, but the result will be considered as a reference in the appendix.

CHAPTER 5: RESULTS AND DISCUSSION

The processed powders were analyzed by XRD, SEM, and XPS. In order to investigate the MA effect of the MCB-only process, BM-only process and MCB+BM process. An experiment denoted as BM-only (refers to Chapter 5) was carried out under Ball Milling 400 rpm 41 hours. XRD patterns and SEM images of BM-only would be considered as a benchmark to compare with MCB-only, and MCB+BM processed powders.

5.1 Analysis of Fabricated Powder

5.1.1 XRD Analysis

The processed powders were characterized by XRD using a PANalytical X'Pert PRO X-Ray diffractometer with a CuK α radiation (45kV, 40mA) and a spinner stage. The processed powders were consolidated into a disk. The XRD patterns were recorded at room temperature with step-sizes of 0.0167 ° of 2 θ and 40 s per step which ranges in 10 ° to 90 °. The XRD pattern broadening effect would be calculated to investigate the MA effect.

Figure 5-1. XRD patterns of pure elemental starting powders.

Figure 5-1 shows the XRD patterns of as-received pure elemental starting powders. The Al powder shows three major peaks around 38 °, 45 °, and 65 ° respectively. The W powder also shows three major peaks around 40 °, 58 °, and 73 ° respectively. The base material Ni shows three major peaks around 45 °, 52 °, and 78 ° respectively. While there is only one obvious major peak for Y₂O₃ and Cr powders which are around 30 ° and 45 ° respectively. It is noted that the first major peak is overlapped with the only major peak of Cr and the second major peak of Al. Since the Y₂O₃ is nanosize, the spectrum of Y₂O₃ displays line-broadening effect.

Figure 5-2. XRD patterns of the processed powders: (a). MCB-4000rpm-1hour+BM-400rpm-40hours process (MCB+BM); (b).BM-only-400rpm-41hoursprocess (BM only); (c) As-just-mixed (0 hour); (d) MCB-only-4000rpm-1hour process (MCB only).

As shown in the XRD spectrums, the as-just-mixed (0 h) powder still displays Y₂O₃ (211) peak. But since the content of Y₂O₃ is low, the intensity of Y₂O₃ (211) peak is low. Also, Al (111) and W (110) are apparent in as-just-mixed powder. However, Ni (111) and Cr (110) overlapped at 45 ° and the overlapped of Al (200) with Ni (111) and Cr (110) is hidden.

When the as-just-mixed powder was under MCB-4000rpm-1hour, the Y₂O₃ (211) peak disappeared which confirms that Y₂O₃ was uniformly distributed onto the hosting particles as an amorphous thin film. The Y₂O₃ (211) peak also disappeared after MCB+BM process and the BM-only process. It is because Y₂O₃

was decomposed as yttrium and oxygen during the BM process. But the uniform distribution of Y_2O_3 during the BM process is still unclear. The spectrums of the MCB-only process and BM-only process are identical, residual Al (111) and W (110) peaks are still observed, meaning powder particles did not form fully alloys during these processes. But the NiAl (110) is observed after the MCB-only process and BM-only process, suggesting the MCB-only process and the BM-only process could generate pre-alloys. The Al (111) disappeared after the MCB+BM process, indicating the Al went into the matrix to form solid solution with hosting Ni and Cr particles. Also, Ni_3Al (111) and NiAl (110) are observed in MCB+BM processed powders. Individual elemental peaks except for W are not observed in MCB+BM processed powder and the major peak is the broadest among these spectrums, suggesting a significant change of crystallographic structure due to the formation of solid solutions formed during the MCB+BM process. In addition, the existence of NiAl and Ni_3Al is evidence of solid solutions. Also, the strong broadening effect of MCB+BM means severe plastic deformation happened during the process. Therefore, the MCB+BM process could generate powder with a better crystallographic structure from Figure 5-2.

Figure 5-3. XRD spectrums of the MCB-only processed powders: Normal mode under 4000rpm: (a).18 hours; (b). 32 hours; (c). 50 hours. Normal mode under 5000rpm: (d). 22 hours; (e). 32 hours; (f) 50 hours; Step mode under 5000rpm: (g). 8 hours; (h) 11 hours.

I). The influence of milling time on powders

Figure 5-3 shows the XRD spectrums of the MCB-only processed powders under different milling time, rotation speed and running mode. The spectrums are almost identical but have some tiny differences. Cr (110), Ni (111) and NiAl (110) peak are displayed in every XRD spectrum, meaning the smaller particle was coated onto the surface of the hosting Ni and Cr particle according to the principle of the MCB process. And Al formed a small amount of NiAl with Ni when it was coated onto the surface of Ni particle. Figure 5-3 (a), (b) and (c) are the XRD patterns of powders under the same rotation speed 4000rpm (i.e., input energy) and different milling time. Residual Al (111) and W (110) peak still exist in these three patterns, but the intensity of Al (111) and W (110) peak decreased as the increase of milling time. However, the NiAl (110), Ni (111) and Cr (110) peaks did not change significantly. Similarly, Figure 5-3 (d), (e) and (f) are the XRD patterns of powders under the same rotation speed 5000rpm and different milling time. Residual Al (111) and W (110) peaks still exist in these three patterns, but the intensity of Al (111) and W (110) peak also decreased as the increase of milling time. Other peaks in these three XRD spectrums also did not change significantly. In the same way, Figure 5-3 (g) and (h) are the XRD patterns of powders under the same rotation speed 4000rpm, step mode and different milling time. Residual Al (111) and W (110) peak still exist in these three patterns, but the intensity of Al (111) and W (110) peak also decreased as the increase of milling time. Other peaks in these two XRD spectrums also did not change significantly.

II). The influence of rotation speed (input energy) on powders

It is obvious that a higher rotation speed would provide more shearing force, compression, and break-down during the process when confining powder particles through the narrow gap. Figure 5-3 shows, the higher the rotation speed, the less the residual elemental content. For instance, the intensity of Al (111) and W (110) peaks in spectrum (d), (e) and (f) are lower than spectrum (a), (b) and (c), meaning a higher rotation speed would force the Al and W to go into the matrix to form solid solutions.

III). The influence of running mode on powders

Figure 5-3 shows the MCB running mode has a higher efficiency for blending and generating powders since spectrums (g) and (h) has lower Al (111) and W (110) peak intensity than other spectrums in Figure 5-3, suggesting there was more NiAl matrix forming in MCB-only step mode processed powders. In addition, the step mode processed powders were only milled for up to 11 hours, but the normal mode processed powder was milled up to 50 hours which is time-consuming. Because when the powders were under normal mode, they tended to stick on the inner vessel wall due to the high centrifugal force. A thermal couple of the main vessel recorded that the temperature of the inner vessel wall rose in the

first couple of hours. Then dropped to a constant temperature and remained at this temperature until the end. However, for the step mode, the milling times were divided into 90 minutes of each. The temperature of the inner vessel wall rose to a spike and then the machine is off for a 10 minutes break. During this break, the main vessel were shaken by a plastic hammer to force the powder particles to fall from the inner vessel wall. It was noted that each cycle of step mode has a relatively inner vessel temperature comparing to the normal mode.

There could be two different kinds of temperature effects during the MCB process. One is due to the plastic deformation and friction of the particle squeezing through the confined gap between the blades and the inner chamber wall. And the efficiency of heat transfer is also part of the reason. The second one is the overall temperature in the main chamber. The temperature rose during the MCB process is mainly due to powder to wall collision and frictional effects among particles, blade tips, and the inner vessel wall. The overall temperature rose during the MCB process can be due to more than one reason. First, as mentioned above, one is the plastic deformation and frictional effects due to the kinetic energy of the rotation speed rise the temperature of powder. The higher the energy (i.e., rotation speed, size of the particle, size of the confined gap and running time, etc.), the higher is the temperature rise. Second, it is possible that exothermic processes occurring during MCB process cause the particles to ignite and generate additional heat. While the temperature of the vessel increases gradually with running time in the early stages, a sudden increase in temperature is noted when an exothermic reaction occurs among the particles, i.e. ignite occurs in the particles. Third, the transfer of energy from the blade to the vessel wall might also cause intrinsic temperature rise. Therefore, the step mode was adjusted and adopted in order to decrease the processing time of the MCB process. And the XRD results show that the MCB step mode has a higher efficiency than the MCB normal mode.

In order to investigate the difference among MCB milling time, rotation speed and running mode. The major peak of spectrums which is around 45° is magnified as shown in Figure 5-4. It is obvious in the spectrums of the MCB-only processed powders that the MCB-only process did not generate Ni_3Al phase in powders which implies it is only capable of producing pre-alloys with a uniform distribution of Y_2O_3 . As shown in Figure 5-4, the XRD of the MCB+BM processed powder is the broadest, indicating powders were under severe plastic deformations. When powders were subject to MCB normal mode under different milling time and rotation speed, as indicated by spectrums (k) ~ (f), the peak did not shift and the intensity did not change significantly, meaning there was no much lattice deformation during the MCB normal mode process. However, the peaks of MCB step mode processed powders shifted toward higher diffraction angles, meaning solid diffusion happened during the process and lattice deformation occurred. It is possible that the large grain was substituted the small grain to decrease the lattice parameters. In other words, the MCB step mode would cause more lattice defects. For the BM-only processed powder, as displayed in spectrum (j), the major peak

is much similar to the XRD of the MCB-only processed powders, meaning the MCB-only process is a potential alternative method of the BM process.

Figure 5-4. XRD spectrums of the processed powders: Normal mode under 4000rpm: (a).18 hours; (b). 32 hours; (c). 50 hours. (k). 1 hour; Normal mode under 5000rpm: (d). 22 hours; (e). 32 hours; (f). 50 hours; Step mode under 5000rpm: (g). 8 hours; (h). 11 hours; (i). MCB+BM; (j). BM-only.

Utilizing the Full Width at High Maximum (FWHM) of XRD spectrums of processed powders, the peak broadening effect could be employed to estimate the micro-strain and crystal size of powder particles. Micro-strain, fine crystal size, and a systematic error of instrument usually contribute to XRD peak broadening. The following equation could represent the effect of XRD peak broadening [14]:

$$B_r \cos \theta = \frac{k\lambda}{L} + \eta \sin \theta \quad (5.1)$$

Where, B_r —FWHM

θ — Diffraction Angle

K— Constant (0.89~1.39), in this study is 0.93

λ — X-ray wavelength, in this study is 1.54060 Å

L—Crystal Size

η — Micro-strain of crystal

Figure 5-5. Analysis of line-broadening effect of processed powders: B. BM-only Normal mode under 4000rpm; C. 1 hours; D. 18 hours; E. 32 hours; F. 50 hours; Normal mode under 5000rpm: G. 22 hours; H. 32 hours; I. 50 hours; Step mode under 5000rpm: J. 8 hours; K. 11 hours; L. MCB+BM.

Equation (5.1) was plotted by using the FWHM B_r times $\cos$ (corresponding diffraction angle θ) as Y-axis, and $\sin$ (corresponding diffraction angle θ) as X-axis. Figure 5-5 and 5-6 show $B_r \times \cos \theta$ as a function of $\sin \theta$. The scattered points were linearly fit and analyzed by linear regression in Origin. The intercept and slope of the fitting line represent the crystal size of powder and micro-strain. In order to observe the line-broadening effects of the XRD of the MCB-only process and the BM-only process except for the MCB+BM process. Figure 5-5 B ~ K is enlarged in Figure 5-6. All the scattered points were linearly fit and analyzed by linear regression in Origin. The slope and intercept were calculated in the Origin for each linearly fit line. And the micro-strain and crystal size calculated from the XRD spectrums are shown in Table 5-1.

Figure 5-6. Analysis of peak broadening effect of processed powders.

Table 5-1. Micro-strain and crystal size of processed powders.

Processed Powders	Rotation Speed (rpm)	Milling hours	Micro-strain	Crystal Size (nm)
BM-only	400	41	0.77%	272
MCB+BM	4000+400	1+40	1.50%	119
M1	Normal 4000	1	0.65%	280
M2	Normal 4000	18	0.55%	291
M3	Normal 4000	32	0.53%	287
M4	Normal 5000	50	0.43%	308
M5	Normal 5000	22	0.53%	287
M6	Normal 5000	32	0.55%	265
M7	Normal 5000	50	0.55%	297
M8	Step 5000	8	0.67%	270
M9	Step 5000	11	0.65%	260

Table 5-1 shows that when powders were under the MCB-only normal mode, the crystallographic structure did not change significantly since the micro-strain of powder particles almost remain at the same value. However, the micro-strain of the MCB-only step mode processed powder particles is 0.1% higher the MCB-only

step mode processed powder particles. In general, the crystal size of the MCB-only processed powders is almost identical, suggesting the MCB-only process would not significantly change the crystallographic structure and powder size under different running mode and running duration, but it is capable of uniformly distributing nanosize Y_2O_3 into the matrix materials resulting in the disappearance of Y_2O_3 . BM-only also would not change the crystallographic structure and powder size. But, the uniform distribution of Y_2O_3 during the BM-only process is still not clear. Although the BM-only and the MCB-only process did not change the crystallographic structure greatly, the combined MCB+BM process generated large micro-strain because the Y_2O_3 was homogeneously distributed during the MCB process. And since Y_2O_3 is nanosize, the large lattice strain was introduced during the BM process since high energy balls could produce a large amount of plastic deformation in powder by ball to ball, ball to wall, and ball to powder collisions. In this condition, the Y_2O_3 satisfied the Orowan strengthening mechanism and serve as a hard secondary phase. Therefore, the MCB+BM process has the best performance.

5.1.2 SEM Analysis

SEM imaging was conducted on the MCB-only, BM-only and MCB+BM fabricated powder samples showing morphology, topology and dimension. In order to compare the MA effects, BM-only powder sample was used as a reference benchmark. Figure 5-7 shows the SEM micrographs of the BM-only and MCB+BM processed powder at different magnification, suggesting the conventional BM-only process produced randomly shaped particles and the surface of the BM-only processed powders is rough, lamellar structure is clearly shown in the picture (shown as the red circle). But the MCB+BM process generated more spherical powders, and the surface of powders is smoother than the BM-only processed powders. The lamellar structure is not clear in the MCB+BM processed powders, meaning the MA effect was in the final stage.

Figure 5-7. SEM micrographs of: (a).BM-only (x 10k); (b). BM-only (x 1.5k) (c). MCB+BM (x 1k); (d). MCB+BM (x 3k).

Figure 5-8 shows the morphology, shape and size distribution of the MCB-only processed powders under different milling time, rotation speed and running mode. In general, the powder particles from 1 hour to 50 hours under different rotation speed remain with some degree of sphericity. The chunky, bulky, and flaky microstructure did not appear in the MCB-only processed powders comparing to the BM processed powders. Figure 5-8 (a) shows the morphology of powders under MCB normal mode 4000rpm after 1hour. Some large size of spherical particles were observed, and some small particles were scattered in the background, suggesting the powder was under mixing and break-down. It is noted that some small particles were bonded onto the surface of the larger spherical particle, meaning the coating of particles started in the early stage.

Figure 5-8 (b) ~ (d) show the morphology of particles under the same rotation speed 4000 rpm for different milling time. The sphericity improved as the increase of the milling time, there were small particles scattering around in the background in (b), but as the milling time increased, the amount of the smaller particles decreased, and the surface of larger spherical particles were coated by the smaller particles. Figure 5-8 (e) ~ (g) show the morphology of particles under the same rotation speed 5000 rpm for different milling time. Similarly, the amount of smaller particles decreased as the milling time increased. However, when the input mechanical energy was increased from 4000rpm to 5000rpm, less small particles were observed in Figure 5-8 (e) ~ (g) than Figure 5-8 (b) ~ (d) respectively. Besides, Figure (f) and (g) show almost no smaller particles in the background, and the size and shape of larger spherical tended to be uniform and homogeneous, meaning higher input mechanical energy would improve the MA effect during the process and enhance the morphology of powders.

Figure 5-8. SEM images of the processed powders: Normal mode under 4000rpm: (a). 1 hours; (b). 18 hours; (c). 32 hours; (d). 50 hours; Normal mode under 5000rpm: (e). 22 hours; (f). 32 hours; (g). 50 hours; Step mode under 5000rpm: (h). 8 hours; (i). 11 hours (x 1k); (j). 11 hours (x 600).

Figure 5-8 (h) ~ (j) show the morphology of particles under MCB step mode 5000rpm for different periods. The morphology, shape, and size in Figure 5-8 (h) is similar to Figure 5-8 (e), indicating that the MCB step mode could obtain almost the identical morphology, shape and size of the particle in a shorter amount of time. This confirms the conclusion drawn from the XRD that the MCB step mode has a higher efficiency than the MCB normal mode. Figure 5-8 (j) and (i) display the best morphology and shape of the processed powder. The surface of particles was smoother, and the particles were more spherical with an overall degree of roundness up to 0.93 which is near perfect shape. This makes the MCB-only step processed powder a potential candidate for AM applications.

Figure 5-9 shows SEM micrographs taken at a higher magnification in order to observe the surface of the powder particles. Figure 5-9 (a) shows the powder particles remained unchanged and spherical, and the spiky, chunky and flaky particles were not observed in the image. And it is obvious that some fragments of smaller particles were bonded onto the surface of the larger spherical particle. Figure 5-9 (b) ~ (d) show the surface of particles under the same rotation speed 4000 rpm for different milling time. The surface became smoother as the milling time increased. But the shape and sphericity changed comparing to Figure 5-9 (a), meaning the powder particles were under mechanical deformations. Figure 5-8 (h) ~ (i) show the surface of particles under the same rotation speed 5000 rpm for different milling time. The surface also became smoother as the milling time increased. But the surface roughness and shape of the powder particles under 4000rpm and 5000rpm are similar; they did not change significantly during the process.

Figure 5-9. SEM images of the surface of the processed powders: Normal mode under 4000rpm: (a).1 hours; (b). 18 hours; (c). 32 hours; (d). 50 hours; Normal mode under 5000rpm: (e). 22 hours; (f). 32 hours; (g). 50 hours; Step mode under 5000rpm: (h). 8 hours; (i). 11 hours (x 1k); (j). 11 hours (x 600).

Figure 5-8 (h) and (i) show the surface of particles under MCB step mode 5000rpm for different periods, the MCB step processed particle has a smoother surface than other powder particles. And the coating of hosting particle could be finished in a shorter amount of time under the MCB step process. In summary, the composite and topography were observed in these MCB processed powder particles, indicating small particles were bonded on the surface of major particles or bonded with major particles forming the composite structure as seen in Figure 5-9. All MCB processed powder particles remained spherical, suggesting small micro-strain calculated from the XRD patterns.

5.1.3 Size Distribution of Processed Powders

The laser diffraction method is popularly used as a large number of measurement can be obtained within shorter timeframes and repeatable results are ensured through proper sample dispersion, referred to ASTM B822. The processed powders were analyzed by a Laser Particle Analyzer (Model: Malvern Panalytical's Master Sizer 2000). The size distribution results of this Master Sizer 2000 could be formulated as $D(x) = \text{sizes}$, where D is the diameter of particle as measured by laser diffraction, for which x is the mass percent of particles with measured diameter less than D . As shown in Figure 5-9, five variations of powder size distribution were discussed in published results [16].

Additionally, distribution widths can be obtained through standard deviation measurements from the central tendency while the span ($D_{90}-D_{10}/D_{50}$) is sometimes used to represent the width of a Gaussian size distribution based on size metrics computation. Typically, a higher standard deviation, larger span or size width are common indicators of a wider distributed powder and vice-versa [16].

Many commercial feedstocks used in SLM processes follow a Gaussian distribution whilst the addition or removal of powder particles through mixing and sieving operations could substantially affect the behavior of the distribution curve resulting in other model variants as shown in Fig 5-10. In Gaussian (normal) distributions, the mode, mean and median coincides at a single central tendency of the curve while negatively and positively skewed distributions are asymmetrical as a result of higher fractions in coarsened and fine particles respectively.

Figure 5-10. Variations of powder size distribution [16]

$D(0.1) = 7.836\mu\text{m}$, $D(0.5) = 14.296\mu\text{m}$, $D(0.9) = 26.846\mu\text{m}$

Figure 5-11. Powder size distribution of MCB+BM processed powder

Figure 5-12. Powder size distribution of the BM-only processed powder

Figure 5-13. Powder size distribution of the MCB-only processed power (MCB-normal-4000 rpm-50 hours).

Figure 5-14. Powder size distribution of the MCB-only processed power (MCB-normal-5000 rpm-50 hours).

Figure 5-15. Powder size distribution of the MCB-only processed power (MCB-step-5000 rpm-8 hours).

Figure 5-16. Powder size distribution of the MCB-only processed powder (MCB-step-5000 rpm-8 hours).

Figure 5-11 to 5-15 show that the powders processed by MCB+BM, the BM-only process, and the MCB-only normal mode processes satisfy the desired Gaussian model. However, the MCB-only step mode processed powder under 5000 rpm 11 hours (Figure 5-16) is a while negatively skewed distribution, indicating the amount of smaller particles is larger than other processed powders. The disadvantage of the negatively skewed distribution the smaller particles agglomerate easily due to the Vander Waals force.

Figure 5-17 summarizes the size distribution of the processed powders. It is obvious that the MCB+BM processed powder has the largest average particle size which is desirable for AM applications. The BM-only processed powder has a lower average particle size comparing to the MCB-only normal mode processed powders. As the rotation speed increased during the MCB-only processed, the average particle size did not change significantly. However, the size of 90% (D 0.9) of the larger particle decreased which narrowed the distribution range which indicates that the higher rotation speed improves the spheroidization and surface modification of powder particles. Figure 5-16 (f) shows that the MCB-only step mode could generate the highest input mechanical energy which results in smaller particle sizes.

To sum up and combine the XRD and SEM analysis, the MCB+BM process has the best performance in powder fabrication. The BM-only process is similar to the MCB-only process based on the XRD and SEM results, but the duration of the BM-only is relatively long. Also, the production of a BM machine is only 64 g of each batch, while the MCB-only process has a production yield of 300~350 g of each batch. Therefore, MCB-only process is a suitable alternative process for producing ODS superalloy powders for AM applications. Since the powders

processed by MCB+BM process, the MCB-only normal mode process and the MCB-only step mode process own a large, medium and small particle size range respectively. Powder fabricated by these three processes were chosen to conduct AM experiments on Laser systems to investigate the feasibility of the produced powders applying to AM technique.

Figure 5-17. Powder size distribution of different processed powders: (a). MCB+BM process; (b). The BM-only process; the normal MCB-only process: (c). 4000 rpm 50 hours; (d). 5000 rpm 50 hours; the step MCB-only process: (e). 5000 rpm 8 hours; (f). 5000 rpm 11 hours.

5.2 Analysis of As-printed Samples

5.2.1 LENS As-printed Samples

I). The First Batch of Samples

The MCB+BM processed powders were applied on LENS 450 system with a nominal laser spot size of 240 µm. A MAR-M247A flat plate was selected as the substrate. As shown in Figure 5-18, three as-printed samples were additively manufactured. Samples were fabricated with a laser travel speed of 33 mm/s. The laser power was selected as 200W, 250W and 270W, producing linear energy-defined as laser power (J) /laser travel speed (mm) [54]. Therefore the linear energy is 6.06 J/mm, 7.57 J/mm and 8.18 J/mm respectively. Hatching lines were made at 0 ° horizontally in the first layer and then were rotated 90 ° for the next

layer. The hatch spacing was 0.1524 mm, and the layer thickness was 0.1 mm. The powder feeding rate was 8 rpm.

Figure 5-18. A schematic of the first batch of LENS as-printed samples.

Table 5-2. The experimental density, relative density, and input linear energy of as-printed samples.

As-printed samples	Experimental Density (g/cm ³)	Relative Density (. %)	Input Linear Energy (J/mm)
200W	5.67	66.63%	6.06
250W	6.33	74.38%	7.75
275W	7.13	83.78%	8.33

Table 5-2 shows the experimental density and relative density of as-printed samples. The as-printed density of samples increased with the increase of the linear energy, meaning the more linear energy, the densifier microstructure and the more chance of forming a melt pool. Figure 5-18 shows the SEM images of the cross-section of 200W-6.06J/mm, 250W-7.75J/mm, and 275W-8.33J/mm as-printed samples. It shows the influence of the laser linear energy on the microstructure of as-printed parts observed at a low magnification (under the same magnification). In order to examine the characteristic microstructure clearly, higher magnifications on the specific locations were investigated and shown in Figure 5-19.

Figure 5-19 (a) shows clear pores existing in the as-printed ODS part which explains the low density of this as-printed sample. Columnar structures were found clearly in Figure 5-19 (b) and (c), but not in (a), suggesting a higher input linear energy would cause columnar structure since it could provide a more thermal driving force for the grain growth of the microstructure. No clearly pores were found in a low magnification in Figure 5-19 (b) and (c). The growth directions of columnar structure and the building direction of the as-printed ODS parts are displayed by arrows in the SEM image. The growth direction of the columnar structure was found that it was approximately 45 ° from the building direction.

Figure 5-19. SEM showing images of the characteristic microstructures of as-printed ODS parts at different laser powder and input linear energy: (a). 200W-6.06J/mm; (b). 250W-7.75J/mm; (c). 275W-8.33J/mm

As the laser power increased, the columnar structure arrays became finer, exhibiting a typical epitaxial growth along the growth direction. However, in Figure 5-19 (b), as the building direction forwarded, the columnar structure became dispersed and unclear (shown by the circle). But the columnar structure in Figure 5-19 (c) was still clearly found as the building direction forwarded, meaning the input energy of 250W-7.55J/mm sample was not sufficient and decreased with advancement of the building direction comparing the 275W-8.33J/mm sample.

Figure 5-20 shows the characteristic microstructures of as-printed ODS parts in the specific locations (as indicated in the red block in Figure 5-19) at a higher magnification. No columnar structures were found in Figure 5-20 (a), but some tiny upright γ 'phase was observed. It was hard to identify every columnar dendrite in Figure 5-20 (b) since severe clustering occurred during the solidification process within the melt pool. Also, short cracks were found in the inter-dendritic region in Figure 5-20 (b). The continuous columnar dendrites are still clearly observed in Figure 5-20 (c). But small and short cracks were still found in the inter-dendritic region.

Figure 5-20. High-magnification of SEM micrographs showing the characteristic microstructures of as-printed ODS parts in: (a). Figure 5-19 (a); (b). Figure 5-19 (b); (c). Figure 5-19 (c).

Unlike the ambiguous epitaxial characteristics shown in Figure 5-20 (b), the columnar dendrites generally displayed the epitaxial growth with a higher degree of clustering on increasing the laser power. Generally, the major input energy and heat induced by laser radiation were transmitted through the substrate of previous as-printed layers, which in turn facilitated the formation of typical columnar dendrite structures along the building direction [54-56]. Furthermore, residual thermal stress as a result of the repeated rapid melting and solidification at a higher laser power was remained in the workpiece [57], which results in the generation of thermal cracks in both dendrite and inter-dendritic regions that were observed in the SEM micrographs.

As regards the increasing of the laser power, the instantaneous and overall temperature within the melt pool increased remarkably due to more heat and energy induced by the laser beam generated during the process. As a consequence, the heat accumulated during the process which caused the internal energy and thermodynamic potentials improved. The improvement enhanced the epitaxial growth of the columnar dendrites and the dispersion performance [56].

In order to examine the chemical composition of the columnar dendrites and the inter-dendrite zones that were observed in different process conditions. EDS point scan was conducted to identify the chemical composition as shown in Figure 5-21. For EDS spot 1, it shows C, O, Cr, Al, Ni, and Y. And the major component is Cr, Al, and O, meaning it formed complex oxides and carbide during the process. And the Y_2O_3 tended to grow on the grain boundary. EDS spots show C, O, Ni, Cr, Al, and W. The yttrium was not found in this spot. The major composition is C, Ni, and Cr, meaning a complex carbide formed at this location.

EDS point analysis indicated that carbon was introduced during the process. It is because the powders were processed by MCB+BM process. A processing control agent with the composition of $CH_3(CH_2)_{16}CO_2H$ to boost the MA effect during the BM process. Some of the carbon remained after the BM process and reacted with major elements Ni, Cr, and Al to form carbides during the printing process.

Figure 5-21. EDS point analysis of as-printed ODS parts at different laser powder and input linear energy: (a). 250W-7.75J/mm in mid-layer; (b). 275W-8.33J/mm in mid-layer.

II). The Second Batch of Sample

The first batch of samples has reviewed the influence of different laser powder on as-printed microstructure. In order to investigate the influence of different laser scanning speed on as-printed microstructure. A second batch of sample was conducted on LENS 450 system. Also, for the purpose of exploring the feasibility of the MCB-only processed powders being applied in AM process. The as-printed sample was deposited by the MCB-only-step-5000 rpm 11 hours processed powders. Since the MCB-only process only generates pre-alloys, the laser scanning speed was decreased to improve the input linear energy. Thus, more thermal and grain growth driving force would be provided for grain growth to form densified macrostructures.

Figure 5-22 shows a schematic and images of the second batch printed sample. A stainless steel flat plate was selected as substrate. The laser power was selected as 250W. The hatching line remained the same as previous experiments. But the laser travel speed was decreased to 10 mm/s, therefore, providing a 25 J/mm linear energy which is a significant enhancement from previous experiments. The layer thickness was still 0.1 mm. 20 layers were printed. The size of the as-printed sample is 10 mm x 10 mm x 2~3 mm, as indicated as 1 in Figure 5-22 (b). The as-printed experimental density of 250W-25J/mm sample is 8.13 g/cm³. And the relative density is 95.53% which is relatively high comparing to previous results.

Figure 5-22. A schematic (a) and images (b) of as-printed ODS part: 250W-25J/mm

Figure 5-23. SEM micrographs showing the characteristic microstructures of the cross-section of as-printed ODS part (250W-25J/mm): (a). The interface of the substrate and deposited part; (b). Mid-layer of the deposited part; (c). Top-layer of the deposited part.

Figure 5-23 shows the characteristic microstructures of the cross-section of the as-printed ODS part. No obvious cracks and pores were found in the microstructure as a low magnification. In order to examine the characteristic microstructure clearly, higher magnifications on the specific locations (as indicated in the red blocks in Figure 5-23) were investigated and shown in Figure 5-24.

SEM images at a high magnification clearly show that the γ' phase precipitated during the printing process but it did not grow due to the rapid cooling in the early stage of printing. In the near-interface area shown in Figure 5-24 (a), spherical and tiny γ' phase started precipitated from the matrix. More γ' phase was found in the mid-layer and top-layer, as shown in Figure 5-24 (b) and (c), most of the γ' phase in the mid-layer became cuboid from spherical. However, the γ' phase displayed as stretched cuboid in the top-layer, meaning the γ' phase tended to mismatch as the building direction forwarded. Furthermore, more amount of precipitated γ' phase was observed as the building direction forwarded, suggesting a reheating and remelting occurred by the heat transmitted from previously deposited layers and the substrate.

Figure 5-24. High-magnification of SEM micrographs showing the characteristic microstructures of the as-printed ODS part in: (a). Figure 5-23 (a); (b). Figure 5-23 (b); (c). Figure 5-23 (c).

In order to confirm the precipitated phase is the γ' phase instead of pores, EDS point analysis, and XRD were conducted to examine the chemical composition and the crystal structure. Figure 5-26 shows the EDS point analysis of the specific locations in the microstructure. EDS spot 1 pinpointed the cuboid γ' phase in the mid-layer, and it shows Ni and Al are the major compositions at this location. C and Cr were also found in the EDS spectrum. EDS spot 2 pinpointed a stretched cuboid γ' phase in the top layer. It shows C, Ni and Cr are the major compositions at this locations. Published results have shown that C could form carbides with Cr. It indicates that carbides might form at the location.

Figure 5-26 shows the XRD pattern of the cross-section of the as-printed ODS part and the signals from the substrate has been removed. The XRD shows the peaks of γ matrix and the γ' phase. But two types of crystal structure existed in the γ' phase which is FCC and BCT. The major crystal structure of this γ' phase in this as-printed sample is FCC. However, the intensity of the BCT γ' phase is higher than the γ matrix, meaning the γ' phase precipitated during the printing process, but it was under stretched or compression. The thermal driving force for the γ' precipitation was not sufficient. The cuboid and upright γ' phase observed in Figure

5-23 (b) confirms the existence of the FCC γ' phase. And the stretched/mismatched γ' phase found in Figure 5-23 (c) confirms the BCT γ' phase due to the rapid cooling in top-layers.

Figure 5-25. EDS point analysis of as-printed ODS part (250W-25J/mm): (a). mid-layer; (b). top-layer.

In summary, as the laser scanning speed decreased considerably, the speed of the heat and energy loss and transmission within the melt pool was decreased because of a longer residence of the laser beam at the melt pool. Thus, the cooling rate of the deposited parts was decreased. Therefore, the cooling time was increased comparatively, and it provided more strengthened kinetics for the nucleation and grain growth [56]. So more γ' phase was found in this second batch as-printed sample than the first batch of as-printed samples.

Figure 5-26. XRD pattern of the cross-section of the as-printed ODS part: 250W-25J/mm

5.2.2 The Laser Cladding As-printed Sample

A laser cladding experiment was conducted in Siemens Company, Pittsburgh. The LENS experiments have shown that increasing the input linear energy is helpful for the precipitation of the γ' phase, but the crystal structure of the γ' phase is a mixture of FCC and BCT, meaning the driving force for the grain growth of the γ' phase was not adequate. In order to achieve the typical γ' phase in the as-printed microstructures, a 5kW laser power was selected in this laser cladding experiment to provide sufficient input energy. And the influence of the input energy on the as-printed microstructures was investigated.

Figure 5-27 shows the as-printed ODS part on a MAR-M247A flat plate as the substrate. The thickness of the deposited part is 7 mm which is much thicker than the LENS as-printed sample. Warps were found around the edge and on the top of the deposited layers. In order to avoid the warps, the sample was cut cross-sectionally and analyzed in the middle of the cross-section. The measured density laser cladding as-printed sample is 8.07 g/cm³ and the relative density is 94.83%.

Figure 5-27. Images of laser cladding as-printed samples.

Figure 5-28. SEM micrographs showing the characteristic microstructures of the cross-section of as-printed ODS part (5kW): (a). The interface of the substrate and deposited part; (b). Mid-layer of the deposited part.

Figure 5-28 shows the characteristic microstructures of the cross section of the laser cladding as-printed ODS part. No obvious cracks and pores were found in the microstructure as a low magnification, except for the area near the interface. In order to examine the characteristic microstructure clearly, higher magnifications on the specific locations (as indicated in the red blocks in Figure 5-28) were investigated and shown in Figure 5-29.

SEM images at a high magnification clearly show that the γ' phase precipitated during the printing process. In the near-interface area shown in Figure 5-29 (a), upright γ' phase is obviously round in the substrate and the near-interface area. The phase of the γ' phase in the near-interface area is similar to the γ' phase in the substrate, indicating the laser power for the precipitation and the epitaxial grain growth of the γ' phase. But the size of the γ' phase in the near-interface area is slightly smaller than γ' phase in the substrate. Figure 5-29 (c) and (d) show the morphology and size of the γ' phase in the mid-layer of the deposited part. The γ' phase became stretched and less as the building direction forwarded which is contrary to the LENS as-printed samples.

Figure 5-29. High-magnification of SEM micrographs showing the characteristic microstructures of the laser cladding as-printed ODS part in: (a). Figure 5-29 (a) block 1; (b). Figure 5-28 (a) block 2; (c). Figure 5-28 (b) block 1; (d). Figure 5-28 (b) block 2.

This contrary of the γ' phase in the LENS as-printed sample and the laser cladding as-printed sample suggests that the laser cladding provided greatly enough power such that the γ' phase precipitated and grew in the first stage. The γ' phase precipitated faster than the LENS as-printed in such high input energy. And once the γ' phase was saturated under the high input energy, less and less γ' phase would precipitate along the building direction. However, for the LENS as-printed sample, the input energy was only enough for the precipitation of the γ' phase. The growth of the γ' phase required more energy and thermal driving force. As the building direction forwarded, the reheating and remelting from the previous layers and the substrate would boost the γ' phase to precipitate along the building direction.

In order to confirm the precipitated phase is the γ' phase instead of pores, XRD was conducted to examine the crystal structure. Figure 5-30 shows the XRD

pattern of the cross section of the laser cladding as-printed ODS part and the signals from the substrate has been removed. The XRD shows the peaks of γ matrix and the γ' phase. Unlike the LENS as-printed samples, only very few BCT γ' phase is shown in the XRD pattern. Most of the γ' phase is in FCC structure, Ni_3Al (111). This is a confirmation that the laser cladding provided sufficient energy for the γ' phase to precipitate from the matrix and grow during the process. And the γ' phase was almost saturated in the matrix. In summary, much higher input energy would cause a densified microstructure, the precipitate of the γ' phase and the grain growth of the γ' phase.

Figure 5-30. XRD pattern of the cross section of the laser cladding as-printed ODS part

CHAPTER 6: CONCLUSIONS

I). Powder Fabrication

In this study, an MCB technique and its combined technique were employed to fabricate homogeneous ODS Ni-based superalloy powders with Y_2O_3 uniformly distributed in the powders. Initially, the powders were processed by the MCB process and the BM process and then characterized by using XRD and SEM/EDS. The results imply that:

- During the MCB process, the Y_2O_3 particles were bonded and coated onto the surface of hosting particles such as Ni and Cr to form a nanosize amorphous thin film. This caused the disappearance of Y_2O_3 peak in the XRD spectrum.
- The soft Al particles were subjected to mixing, break-down, and coating under shearing force and were randomly bonded to the hosting particles or existed as elemental particles in the powder mixture.
- The MCB process was capable of generating pre-alloyed powders with γ' matrix existing in the powders. And the milling time of the MCB process was successfully decreased to 11 hours which is much more effective than the conventional BM process.
- The MCB processed powders were further processed by utilizing a BM machine to improve the MA effect of the powder. And the γ' phase formed after the BM process. It could also introduce the lattice strain and defects.
- The particle size of the powders increased significantly after the MCB+BM process.
- As a benchmark and reference experiment, BM-only processed powder was subjected generated much similar crystal structures in powders to the MCB-only process, but no γ' phase has been formed during the process.
- Powders processed by MCB+BM generated larger micro-strain and smaller crystal size than BM-only and MCB-only.
- MCB is a potential alternative to produce ODS superalloy powders for AM applications.

II). Additive Manufacturing

The MCB+BM processed powders were applied on LENS 450 system into densified bulks. The MCB-only processed powders were applied on LENS 450 system and deposited by laser cladding. The as-printed samples were characterized by XRD, SEM/EDS. And the results suggest that:

- The density is affected by the input linear energy. The higher the input linear energy, the densifier microstructure.
- The microstructure is also influenced by the input linear energy. The first batch of the LENS as-printed samples showed very little γ' phase. While as the input linear energy increased in the second batch LENS experiment, the γ' phase precipitated in the microstructure.

- The laser power of the laser cladding was the highest, and the γ' phase near completely precipitated in the microstructure.
- Higher laser power will generate higher melt pool temperature, and thus provide sufficient driving force to form γ' phase.

CHAPTER 7: RECOMMENDATIONS FOR FUTURE WORKS

This work showed explanatory research was done on MCB+BM processed and the MCB-only processed ODS superalloy on their processing. One of the next work that can be performed on this ODS superalloy system is investigating their performance in a thermo-chemical environment for understanding their combined corrosive and oxidation behaviors.

Moreover, in this work, it was investigated the possibility of applying ODS superalloy in the field of AM. The recommended future work is that the as-printed ODS superalloy needs to be tested regarding the mechanical properties, corrosion resistance, and oxidation resistance. The following outline could be a recommended method for achieving this goal:

- The composition of designed ODS super alloy should be adjusted to investigate the effect of the content of oxide dispersoid on powder properties and as-printed microstructures.
- The fabrication method by utilizing MCB-only process should be modified for ODS superalloy powder production.
- The MCB-only processed powders should be applied on EOS M290 which is the standard, and commercialized powder bed AM technique to investigate the powder performance and as-printed microstructures.
- The processing parameters and melt pool geometry should be adjusted, conducted and refined to investigate the effect of parameters and melt pool on microstructures.
- Mechanics performance testing should be carried out to test the mechanical properties of as-printed samples, i.e., Tensile strength, Young's modulus, and fracture strength, etc.

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