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Pitting corrosion and corrosion fatigue crack growth behavior of oil-grade alloy 718 in sodium chloride solution

Ting Chen

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**PITTING CORROSION AND CORROSION FATIGUE CRACK
GROWTH BEHAVIOR OF OIL-GRADE ALLOY 718 IN SODIUM
CHLORIDE SOLUTION**

by

Ting Chen

**Dissertation submitted to the
Benjamin M. Statler College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Doctor of Philosophy
in
Mechanical Engineering**

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2014**

**Keywords: Nickel-Base Alloy; Pitting Corrosion; Passivation, Corrosion
Fatigue Crack Growth; Aging Treatment; Surface Treatment
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ABSTRACT

Pitting Corrosion and Corrosion Fatigue Crack Growth Behavior of Oil-Grade Alloy 718 in NaCl Solution

by Ting Chen

Oil-grade nickel-base alloy 718 has been recently used in the oil and gas industry for downhole drilling components especially for the parts of the bottom hole assembly (BHA) due to its superior mechanical properties, good corrosion resistance, non-magnetic properties and ability to be heat treated to various strength levels. As the modern oil and gas industry explored into coastal and marine locations, deeper and deeper wells have been drilled with high pressure high temperature, making the demand for increased strength and good toughness super critical for alloys used in ultra-deep wells drilling. Moreover, the existence of high concentrations of chloride salts in the aqueous drilling fluids and high mechanical loading will lead to corrosion problems such as pitting corrosion and corrosion fatigue for alloys applied in BHA.

The goal of this research is to achieve ideal microstructure and to improve the strength of oil-grade alloy 718 through an optimized heat treatment and a novel mechanical surface treatment, while maintaining good pitting corrosion resistance and corrosion fatigue resistance of the alloy, to better serve ultra-deep well drilling.

In this study, a new two-step aging treatment is successfully applied to modify the microstructure and to increase the yield strength of oil-grade alloy 718. Based on the microstructure analysis, isolated platelet δ phases were precipitated at some of the grain boundaries in both one-step aged and two-step aged specimens. The one-step aged specimen shows a uniform distribution of fine spherical γ' and elongated γ'' precipitates in the grains. On the contrary, the two-step aged sample shows much finer precipitates.

The effect of aging treatment on the pitting corrosion resistance and corrosion fatigue crack growth (CFCG) rates of oil-grade alloy 718 in different NaCl solutions is investigated and compared. The electrochemical measurements results show that the pitting corrosion resistance of oil-grade alloy 718, regardless of aging treatment, is nearly the same, indicated by the similar corrosion current density and pitting potential. The influencing factors including solution temperature and NaCl concentration on the pitting corrosion resistance of oil-grade alloy 718 are also studied, and the results indicate that the pitting corrosion resistance is decreased with increasing the solution temperature and NaCl concentration. The CFCG results show that there is no obvious effect of 3.5 wt.% NaCl solution on the CFCG rates of oil-grade alloy 718 samples with different aging

treatments. Nevertheless, the CFCG rates of oil-grade alloy 718 in 21 wt.% NaCl solution are increased in comparison with the ones tested in laboratory air and in 3.5 wt.% NaCl solution. Furthermore, aging treatments lead to lower CFCG rates of oil-grade alloy 718 in all tested environments. However, no visible difference of CFCG rates in NaCl solution is observed between one-step aged and two-step aged specimens.

The effect of surface modifications induced by machine hammer peening (MHP) surface treatment on the pitting corrosion behavior of oil-grade alloy 718 in 3.5 wt.% NaCl solution is also investigated. Severe work hardening and high compressive residual stress are generated with surface smoothing and microstructure evolution in terms of the formation of nano-grains and nano-twins in the near surface region after MHP. The electrochemical tests results show that MHP has a beneficial influence on the corrosion resistance, indicated by a significant increase of the critical pitting potential (+134 mV) accompanied with lower corrosion current density and higher polarization resistance. The two-step aging treatment is applied to oil-grade alloy 718 that has been previously surface-treated by mill finishing (MF) and MHP. As a result, a Cr-enriched oxide layer is formed along with a nano-precipitates layer that consists of high precipitate fractions of γ'/γ'' on the top surface. Surface hardness increases after aging but the compressive residual stress is almost relaxed. The synergistic effects of MHP and aging treatment on the pitting corrosion behavior are also studied. The results show that the corrosion resistance of the MHP specimens decreases after aging, although the corrosion resistance is still higher than the MF condition.

DEDICATION

To my parents, Muhua Chen (陈睦华) and Xiaoyun Zhu (朱晓云).

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Chapter 1: Introduction

1.1 Background

While nickel-base alloy 718 was originally developed for use in aircraft gas turbines and rotating parts in the aerospace industry, its combination of superior mechanical properties, good corrosion resistance and ability to be heat treated to various strength levels made it a corrosion resistant alloy that has been extensively used in the oil and gas industry for a variety of applications such as wellhead distribution equipments, completion components and drill tools [1-8]. It has been recently utilized in bottom hole assembly (BHA) components for example drill collars, where a non-magnetic alloy with high corrosion resistance and high fatigue strength is needed [3, 5,9-13]. The environment in which BHA must serve is the severe corrosive environments in the oil wells and the quite corrosive drilling fluids which contain very high content of chloride salts. As a result, concern has been directed towards controlling or reducing failures from pitting corrosion, crevice corrosion, erosion, environmental assisted cracking including stress corrosion cracking, sulfide stress cracking and hydrogen embrittlement, as well as corrosion fatigue in metallic materials applied in BHA [5, 7, 8, 14-20]. The wide range of corrosion problems has been exacerbated by recent industry trends towards ultra-deep well drilling into coastal and marine locations with high pressure high temperature. Furthermore, the demand for increased strength and toughness is super critical for alloys used in high pressure high temperature ultra-deep well drilling. Therefore, the development of nickel-base alloy 718 to optimize both mechanical properties and corrosion performance becomes very important in the oilfield drilling industry.

Oil-grade alloy 718 has been defined by API Specification 6A 718 for nickel-base alloy 718 used in oil and gas drilling and production equipment in terms of composition, microstructure, heat treatment and mechanical properties [21]. It is well known that alloy 718 is an age-hardened superalloy that can be heat-treated properly to achieve the optimum microstructure and the required properties [1-6]. The oil-grade alloy 718 is solution treated at the temperature of 1021°C–1052°C for one hour minimum to two and a half hours maximum, followed by single-step aging treatment at 774°C–802°C for six to eight hours [1, 2, 6, 21]. The single-step aging treatment is specified to increase stress corrosion cracking resistance and sulfide stress cracking resistance by sacrificing some strength and hardness in the mechanical properties. Since the demand of strength and toughness is increasing in ultra-deep well drilling, the two-step aging

treatment, i.e., at 760 °C and then 650 °C, which is used to maximize the yield strength of alloy 718 for aerospace components, has been adopted and modified for oil-grade alloy 718 in recent years. However, the aging time for oil-grade heat treatment is decreased to four to five hours for each step as compared to the ten hours for aerospace-grade. Thus, it is important to investigate whether the modified two-step aging treatment will affect the corrosion resistance and corrosion fatigue resistance of oil-grade alloy 718 in drilling fluids environments.

In recent decades, mechanical surface treatments such as shot peening, hammer peening and roller burnishing have been commonly applied to a wide variety of corrosion resistant alloys used in drill collars to improve strength, stress corrosion cracking resistance and fatigue/ corrosion fatigue strength by introducing a compressive residual stress layer in the near surface region through the work hardening from the surface treatment [12, 13, 22-33]. In the meantime, the surface modifications, in terms of surface roughness, surface morphology, near surface microstructure, residual stresses as well as surface passive film and oxidation layer changes induced by surface treatments, can affect the corrosion resistance of the alloys [12, 34-38]. Numerous studies have been focused on the influence of peening treatments such as shot peening, laser peening, hammer peening and ultrasonic peening on the pitting corrosion resistance of aluminium alloys and stainless steels [39-50], regardless of their applications be it oilfield drilling or otherwise. Machine hammer peening (MHP) is a mechanical surface treatment which can induce deep penetration of compressive residual stresses and a strain hardened layer below the surface as well as a strong reduction of surface roughness on work pieces with complex shape [51-57]. During MHP processes, the metal work piece is hammered with a tungsten carbide ball, which is moved by a machine tool or robot along the surface, thereby creating a uniformly smooth surface by well-directed impacts with a controlled distance between each impact. However, this method is not well covered in the literature since it is relatively novel. Recent research has focused attention on how deep machine hammer peening can smooth machined surfaces and thus achieve compressive residual stresses by adjusting hammer peening parameters. Therefore, it is logical to expect that MHP would result in an increase in corrosion resistance. Nevertheless, published data on MHP is limited, focusing on the effect of surface modifications on the corrosion behavior of alloy 718. Moreover, the effect of the aforementioned two-step aging treatment on the corrosion behavior of alloy 718 has not been extensively investigated to date, especially with respect to changes in surface-treated components. Thus, it is meaningful to

determine whether the MHP surface treatment can improve corrosion resistance, and whether the corrosion resistance of surface-treated alloy 718 can be maintained after aging treatment.

1.2 Project Goal and Research Objective

The goal of this project is to achieve ideal microstructure and to improve the strength of oil-grade alloy 718 through optimizing heat treatment and applying mechanical surface treatment, while maintaining good corrosion resistance and corrosion fatigue resistance of the alloy, to better serve as in ultra-deep well drilling.

The overall objectives of this research are:

- (1) Study the effect of temperature on pitting corrosion behavior and passive film properties of oil-grade alloy 718 in NaCl solution by using electrochemical measurements and chemical composition analysis.
- (2) Determine the pitting corrosion and passivation mechanisms of oil-grade alloy 718 in NaCl solution.
- (3) Investigate the influence of aging treatment on microstructure of oil-grade alloy 718 by morphological observation and chemical composition analysis.
- (4) Explore the influencing factors on corrosion fatigue crack growth behavior of oil-grade alloy 718 in NaCl solution by means of corrosion fatigue crack growth rate tests, electrochemical measurements and fractography examination.
- (5) Develop the corrosion fatigue crack growth mechanism of oil-grade alloy 718 in NaCl solutions.
- (6) Find the effect of surface modifications induced by machine hammer peening and aging treatment on microstructure, mechanical properties and corrosion resistance of oil-grade alloy 718 by means of morphological observation, chemical composition analysis, microhardness tests, residual stress measurement, and electrochemical testing.
- (7) Propose the deformation mechanism and pitting corrosion mechanism of surface-treated oil-grade alloy 718 in NaCl solution.

1.3 Organization of the Research

Chapter 1 has presented the background, goals and objectives of this research. Chapter 2, which gives an extensive view of the literature related to this study, begins with an introduction on

metallic materials used in BHA components, followed by the detailed information to oil-grade alloy 718 and the requirements for the oil and gas drilling industry. Up to date references on pitting corrosion, passive properties, corrosion fatigue, as well as mechanical surface treatment are also reviewed in this chapter. Experimental methodologies and procedures, as well as research results and analyses are explained and discussed in Chapters 3–5. In Chapter 3, the pitting corrosion behavior and passive film properties of alloy 718 in 3.5 wt.% NaCl solution at different temperatures including room temperature, 50°C, and 80°C are described. Chapter 4 covers the investigation on the influencing factors on corrosion fatigue crack growth behavior of oil-grade alloy 718 in NaCl solution. The effects of solution temperature, aging treatment and NaCl concentration are discussed in detail. In Chapter 5, the surface modifications induced by machine hammer peening treatment are presented, as well as the synergetic effect of aging treatment on the pitting corrosion resistance of oil-grade alloy 718 in 3.5 wt.% NaCl solution at room temperature. At last, conclusions drawn from this research are listed in Chapter 6.

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Chapter 2: Literature Review

2.1 Metallic Materials Selection for Bottom Hole Assembly

For many years, the drilling industry has been using traditional materials for bottom hole assembly (BHA) components which were developed several decades ago. However, drilling high pressure high temperature (HPHT) ultra-deep wells, i.e. those with bottom hole temperatures higher than about 400°F (200°C) and wellhead pressures greater than about 20 ksi (138 MPa), places significant requirements on the materials utilized in BHA [1-3]. Moreover, in addition to large amounts of natural gas and crude oil, many of the sour wells produce significant concentrations of hydrogen sulfide (H₂S), carbon dioxide (CO₂), chlorides, and free sulfur, which make the oil and gas conditions become more corrosive [1, 4, 5]. Thus new materials have to be designed and developed in order to satisfy the need for BHA products in harsh HPHT sour service conditions [4, 6-9]. In selecting materials for components of BHA in ultra-deep drilling, all the influencing parameters such as drilling environment, well geometry, cost and safety have to be considered. Most importantly, materials have to meet criteria for both mechanical properties and corrosion resistance in service environments for the required service life. Age-hardened nickel-base alloys and cold-worked solid solution nickel-base alloys offer many advantages such as high strength, toughness, low magnetic permeability and good corrosion resistance. Due to their location immediately above the drill bit and in the lower portion of the drillstring, BHA tools are mostly running in compression and in particular feature thick walls. Cold-worked nickel-base alloys are not suitable for thick sections and the microstructure in construction parts is not homogeneous [10-13]. Age-hardened nickel-base alloys such as MONEL alloy K-500, INCOLOY alloy 925, INCONEL alloys 718, 725, 725HS, and X-750 are commonly used to obtain the needed strength in heavier cross-sections with excellent corrosion resistance [11, 13-17]. As compared with other age-hardened nickel-base alloys, alloy 718 is specifically selected for drilling applications for components of BHA due to the high strength properties, the relatively good corrosion resistance, the cost-effectiveness and the good availability [18].

2.1.1 Bottom Hole Assembly

BHA is the lower portion of the drillstring, consisting of the bit, stabilizers, subs, a mud motor (in motor assemblies), drill collars, heavy-weight drillpipe and jarring devices connected to the bottom of the drillpipe. Figure 2.1 shows the sketch of a drillstring [19-21].

Figure 2.1 Drillstring

Drill collars are similar to drillpipe but heavier, with thicker walls and stronger connections, which used to apply weight to the drill bit. Usually one to three of nonmagnetic drill collars, which are constructed from nonmagnetic materials, will be applied in each BHA. They serve the same purpose as regular drill collars but tools like measurement while drilling (MWD) inside them can be generally capable of measuring the parameters of drilling such as inclination and azimuth of the wellbore at the location with respect to the earth's magnetic field, and immediately transmitting that information to the surface during directional drilling [10]. BHAs are divided into rotary and motor classifications. Rotary bottom hole assemblies are turned with a rotary or top drive, while the bit on motor assemblies is turned with a turbine or positive displacement motor in the lower

drill collar assembly but the drillstring remains stationary. The typical BHAs are shown in Figure 2.2.

Figure 2.2 Bottom hole assembly

2.1.2 Requirements for BHA Materials

Choosing the appropriate metallic materials is still a principal challenge in the exploration of oil and gas industry due to the more aggressive conditions in today's ultra-deep wells with HPHT. A large number of influencing factors such as mechanical properties, corrosion resistance, magnetic properties, availability and cost-effectiveness are very important for making the right choice. In this part, we are focused on the two most important requirements including mechanical properties and corrosion resistance.

2.1.3.1 Mechanical Properties

Strength is one of the most critical mechanical properties of a selected material. The desired strength levels of alloys are depending on the applications, however, the yield strength of corrosion resistant alloy (CRA) required for the oil and gas industry ranges from 65 to 160 ksi (450 to 1100 MPa) [12]. API Specification 7 requires a minimum yield strength of 110 ksi (758 MPa) and a minimum tensile strength of 140 ksi (965 MPa) for rotary drill collars below 7-inch in outside diameter (OD) [22]. For the ones with sizes of 7-inch in OD and above, the minimum yield strength and tensile strength are 100 ksi (689 MPa) and 135ksi (931 MPa), respectively [22]. Even though high strength can be produced by cold working or age hardening treatments, materials selection for BHA components requires age-hardenable alloys to achieve necessary and uniform strength through thick walled cross-sections, which cannot be obtained by cold working. Table 2.1 shows the typical mechanical properties of some nickel-base alloys used in oilfield applications [11].

Table 2.1 Typical room temperature mechanical properties

Alloy	Material Condition	Yield Strength		Tensile Strength		Elongation %	Hardness HRC
		ksi	MPa	ksi	MPa		
Inconel Alloy 625	Cold Worked	125.7	867	150.4	1037	30	33
Inconel Alloy 718	Solution Annealed & Aged	134.0	924	191.5	1320	20	39
Inconel Alloy 725	Solution Annealed & Aged	132.9	916	183.3	1264	28	36
Inconel Alloy 725HS	Solution Annealed & Aged	151.3	1043	199.4	1375	25	42
Incoloy Alloy 825	Cold Worked	114.0	786	130.5	900	15	28
Incoloy Alloy 925	Cold Worked	129.0	889	140.0	965	17	32
	Solution Annealed & Aged	113.0	779	176.0	1214	26	36
Inconel Alloy X-750	Aged	132.8	916	188.0	1296	27	34
Inconel Alloy C-276	Cold Worked	156.9	1082	172.5	1189	17	35

Increasing strength affects the stress corrosion behavior such as stress corrosion cracking (SCC) and sulfide stress cracking (SSC) of a material. Therefore, hardness limits of metallic materials have been specified in NACE standard MR0175 to control SCC and SSC in sour oilfield environments [23]. The hardness requirements of CRA with particular essential chemical compositions, manufacturing processes and finished conditions used in specific corrosive oilfield environments have been stipulated.

Toughness is also extremely important because materials with poor toughness are prone to failure at any time during the drilling processes. A charpy v-notch toughness of 20 to 40 foot-pounds for CRA is often specified [12]. However, higher toughness limits the maximum

strength of the alloys. Thus, optimization the necessary strength and good toughness through processing and heat treatment is critical important.

2.1.3.2 Corrosion Resistance

Because of the severe corrosive environment, alloys used for HPHT ultra-deep drilling have to be corrosion resistant. Properly selected CRA is either fully resistant to general corrosion or its general corrosion rates is sufficiently low in the environment of interest that significant corrosion cannot occur over the intended service life. However, in order to justify the cost and to keep the probability of unexpected failures acceptably low, CRA is also required to be resistant to pitting corrosion, crevice corrosion, environmental assisted cracking (EAC) including SCC, SSC and hydrogen embrittlement (HE), as well as corrosion fatigue [1, 8, 10, 11, 13]. Chlorides in drilling fluids and oil and gas environment such as seawater may cause pitting corrosion, crevice corrosion and SCC by a breakdown of the protective passive layer formed on the surface of alloys.

To estimate the resistance of a stainless steel or a nickel alloy against pitting corrosion or crevice corrosion the pitting resistance equivalent number (PREN) is frequently used. The PREN value is calculated using the following formula: $PREN = 1 \times \%Cr + 3.3 \times \%Mo + 16 \times \%N$ [24]. In general, the higher PREN value is the more corrosion resistant the steel or alloy is. The critical crevice temperature (CCT) and critical pitting temperature (CPT) for an alloy are determined by exposing samples in acidified 6% ferric chloride solutions, according to ASTM G48 standard, Method C& D [25]. The tests are only valid up to 85°C because the test solution becomes unstable at higher temperatures. The CCT and CPT values of typical corrosion resistant alloys are shown in Table 2.2 [11].

The corrosion effects SSC and HE in sour gas environment is caused by the presence of H₂S. In general, resistance to SCC, SSC and HE increases with increasing content of nickel, chromium, molybdenum, tungsten and niobium in an alloy. It should be pointed out that alloy strength is an influence factor in EAC susceptibility. Materials become more prone to EAC as their strength and hardness increase. Thus it is very important to explore the optimum strategy to obtain both high strength and good EAC resistance of a material.

Being run in compression and rotated in the borehole, BHA tools would be exposed to cyclic bending. The resulted stress in combination with corrosive media will lead to corrosion fatigue [19, 20, 26].

Table 2.2 CCT and CPT for corrosion resistant alloys, determined per ASTM G48, Methods C & D

Alloy	CCT (°C)	CPT (°C)	PREN
Inconel Alloy 625	35	> 85	41
Inconel Alloy 725	35	> 85	41
Incoloy Alloy 825	5	30	26
Incoloy Alloy 925	5	30	26
Inconel Alloy C-276	50	> 85	45

2.2 Oil-Grade Nickel-Base Alloy 718

Nickel-base alloy 718 is widely used in various industry applications such as aerospace, chemical processing, marine engineering, and nuclear reactors, and is utilized for wellhead components, auxiliary and downhole drilling tools in oil and gas environments starting in the early 1980s, due to its superior mechanical properties and excellent corrosion resistance[10, 12, 16, 18, 27, 28]. In this part, the metallurgy of nickel-base alloy 718 including phases and strengthening mechanisms will be firstly reviewed, and then the applications and requirements of alloy 718 in the oil and gas industry will be fully addressed.

2.2.1 Metallurgy of Nickel-Base Alloy 718

2.2.1.1 Phases in Nickel-Base Alloy 718

Nickel-base alloy 718 can form numbers of phases due to its composition and the large variety of imposed heat treatment. The major phases in nickel-base alloy 718 are as follows:

(1) Alloy matrix (γ)

The matrix is an fcc nickel-base austenitic phase, which is capable of dissolving high percentages of solid solution elements, such as Fe, Cr, Mo, Al and Ti.

(2) Gamma prime (γ')

Al and Ti are added to form one of the most important precipitates in nickel-base alloy 718, γ' , which is ordered face centered cubic (FCC, $L1_2$) in the form of $Ni_3(Al, Ti)$. The γ' phase is based on the ordered $Ni_3(Al, Ti)$ structure with nickel atoms at face centers and Al/Ti atoms at cube centers. Normally the γ' phase appears as a fine dispersion of spherical particles in nickel-base alloy 718.

(3) Gamma double prime (γ'')

Nickel-base alloy 718 that contains 4.75~5.5% Nb is mainly strengthened by γ'' precipitates, which have an ordered body centered tetragonal (BCT, DO_{22}) crystal structure based on the

Ni₃Nb compound. These γ'' precipitates contribute to a higher degree of strength of the alloy due to the higher volume fraction in comparison to γ' . The γ'' phase appears as disc-shaped particles with the following orientation relationship to the matrix: $[100] \gamma'' \parallel \{100\} \gamma$; $[001] \gamma'' \parallel \langle 001 \rangle \gamma$.

(4) Delta (δ)

If the alloy is used above about 650°C (1200°F), the γ'' coarsens very fast and some of the γ'' may convert to δ phase, which is an ordered Ni₃Nb phase having an orthorhombic crystal structure and generally a needle-shape morphology. The δ phase is found mostly growing on the (111) planes or nucleating on the grain boundaries and is associated with loss of toughness in the alloy.

(5) Carbide and nitride

The primary MC and TiN phases in alloy 718 are stable and will not change with thermal cycles at lower temperatures [29].

2.2.1.2 Strengthening Mechanisms in Nickel-Base Alloy 718

Nickel-base alloy 718 is basically strengthened by solid solution and precipitation hardening.

2.2.1.2.1 Solid Solution Strengthening

The solid solution strengthening is associated with inhibiting dislocation motion. The introduction of the solute atom into the matrix created elastic strain in the crystal lattice to accommodate solute atom. The solute atoms cause lattice distortions that impede dislocation motion, increasing the yield stress of the material. Solute atoms have stress fields around them which can interact with those around dislocations. The presence of solute atoms imparts compressive or tensile stress to the lattice, depending on solute size, which interfere with nearby dislocations, causing the solute atoms to act as potential barriers to dislocation propagation and multiplication.

2.2.1.2.2 Precipitation Strengthening

The dominant strengthening mechanism in nickel-base alloy 718 is considered as precipitation hardening by γ' and γ'' due to their prevention of dislocation motion [30-32]. Most of nickel-base alloys are hardened by precipitation of an L1₂ γ' phase, and the principal source of strengthening in these alloys is due to the anti-phase boundary hardening arising from the coherent, ordered γ'

particles. However, alloy 718 is one of a few nickel-base alloys which are hardened by precipitation of coherent, ordered particles of a metastable $\text{DO}_{22}\gamma''$ phase. Three variants of the γ'' phase are possible in an fcc matrix, lying on the $\{100\}$ plane. Since the precipitates form coherently, their tetragonal distortion results in considerable coherent strain. Thus the same potential contributions to strengthening are present in alloys containing γ'' phase as in those containing γ' phase.

The γ'' precipitates are usually considerably finer than the γ' precipitates. When the alloy is heat treated for maximum strength, deformation occurs as a result of dislocations interacting with the coherent strain fields and eventually shearing the precipitate.

2.2.2 Oilfield Applications of Nickel-Base Alloy 718

In the 1970s alloy 718 was firstly used for valve stems, gates, seats, fasteners and shafts in service which is slightly corrosive [12, 27]. New applications of alloy 718 were found in extremely corrosive wells using only CRA equipment. In the early 1980s alloy 718 began to be utilized for oil and gas completion and production components such as tubing hangers, subsurface safety valves, down-hole packers, side-pocket mandrels, chemical injection valves and extension seals [10, 12, 27]. These components must be able to endure long time operation in corrosive drilling fluids under high temperatures and high pressures. However, the aerospace-grade alloy 718 in high strength condition was not desirable for high SCC resistance and HE resistance in severe corrosive environments. Thus the redesign of alloy 718 to maximize the SCC resistance and HE resistance while balancing strength and toughness in order to better serve oilfield industry was needed at that time. API Specification 6A 718 defines nickel base alloy 718 for oil and gas drilling and production equipment in terms of composition, microstructure, heat treatment and mechanical properties. Finally, alloy 718 has been directly used in BHA components especially drilling measurement tools like LWD and MWD, where a nonmagnetic alloy is needed with high fatigue strength and good corrosion resistance.

2.2.3 Evolution of Nickel-Base Alloy 718 from Aerospace-Grade to Oil-Grade

Initially aerospace-grade alloy 718 was directly applied in the oil and gas industry, however, due to the presence of a significant amount of δ phase and a distribution of γ'/γ'' designed for maximum strength and creep resistance, the aerospace-grade alloy 718 is not optimum for

corrosion resistance and environmental induced cracking resistance in extremely corrosive sour wells. The NACE specification MR0175 limits the maximum hardness of alloy 718 used in sour conditions to HRC 40 because of SCC and SSC. Moreover, good toughness which also limits the maximum strength of alloy 718 is extremely important for pressure containment boundary components due to the “leak before burst” failure criteria [10, 12,27]. Thus the redesign of alloy 718 to improve the corrosion resistance and environmental induced cracking resistance while balancing strength and toughness was needed in order to better serve the oil and gas industry. The properties of oil-grade nickel-base alloy 718 have been slightly modified in chemical composition, thermo-mechanical processing and heat treatment procedure including solution annealing and aging temperatures and times for the needs of specific environmental applications. The specification requirements encompassing chemical composition limits, microstructure, and mechanical properties such as strength, toughness and hardness of alloy 718 for oil and gas drilling and production equipment are addressed by API 6A 718 standard [22].

The chemical composition shall conform to the weight percent requirements of nickel-base alloy 718 as modified below represented in Table 2.3.

Table 2.3 Chemical composition requirements

Ni	Cr	Fe	Nb + Ta	Mo	Ti	Al	C	Co	Mn
50.0–55.0	17.0–21.0	Bal.	4.87–5.20	2.80–3.30	0.80–1.15	0.40–0.60	< 0.045	< 1.00	< 0.35
Si	P	S	B	Cu	Pb	Se	Bi	Ca	Mg
< 0.35	< 0.010	< 0.010	< 0.0060	< 0.23	< 0.0010	< 0.0005	< 0.00005	< 0.0030	< 0.0060

The composition of oil-grade alloy 718 is limited to lower carbon grades (0.045% max), and ppb levels of P, S, Pb, Se and Bi compared to the aerospace used alloy 718. Ti, Al, and Nb levels are firmly controlled as well.

The standard heat treatments used to maximize the strength of alloy 718 applied in the aerospace industry is not required and suitable in oil and gas drilling applications. The oil-grade alloy 718 is solution treated at the temperature of 1870°F–1925°F (1021°C–1052°C) for one hour minimum to two and a half hours maximum, followed by the single-step aging treatment at 1425°F–1475°F (774°C–802°C) for six to eight hours [10, 22, 27]. A low annealing temperature is not sufficient to homogenize the microstructure from prior processing history, while a high annealing temperature can lead to coarse grain structure. A higher solution treatment temperature is employed for oil-grade alloy 718 as compared with the aerospace-grade one in order to maximize fracture

toughness. Single aging treatments rather than conventional double aging treatments can be used to achieve both high tensile strength and high fracture toughness. This choice of specific heat treatment can provide an optimum combination of fracture toughness $\geq 200 \text{ ksi } \sqrt{\text{in}}$ ($220 \text{ MPa } \sqrt{\text{m}}$), yield strength $\geq 120 \text{ ksi}$ (827 MPa) and hardness $\leq \text{HRC } 40$ [12, 33].

The ASTM average grain size shall be predominantly No. 3 or finer for $\leq 10 \text{ in.}$ (25.4 cm) cross section and No. 2 or finer for $> 10 \text{ in.}$ (25.4 cm) cross section. No topological duplex grain size as defined and measured per ASTM E 1181 is allowed. The microstructure should be free from continuous networks of secondary phases along grain boundaries or other unusual microstructural features, except for individual, isolated grains that are not representative of the bulk of the microstructure. The presence of discrete, isolated particles of delta phase or carbides is acceptable. The microstructure should be free from acicular delta phase except in individual, isolated grains that are not representative of the bulk of the microstructure. No laves phase should exist in the alloy.

Table 2.4 compares typical requirements for oil-grade alloy 718 (API 6A718) and aerospace-grade alloy 718 (AMS 5662).

Requirement	Aerospace AMS 5662	Oilfield API 6A718
Carbon	$< 0.080\%$	$< 0.045\%$
Niobium	$< 5.50\%$	$< 5.20\%$
Aluminum	$> 0.2\%$	$> 0.4\%$
Titanium	$> 0.65\%$	$> 0.8\%$
Phosphorus	$< 0.015\%$	$< 0.010\%$
Copper	$< 0.30\%$	$< 0.23\%$
Solution Annealing	$941\text{--}1010^\circ\text{C}$ ($1725\text{--}1850^\circ\text{F}$)	$1021\text{--}1052^\circ\text{C}$ ($1870\text{--}1925^\circ\text{F}$)
Age Hardening	718°C (1325°F) + 621°C (1150°F)	$774\text{--}802^\circ\text{C}$ ($1425\text{--}1475^\circ\text{F}$)
Grain Size	ASTM 4 or 5	ASTM 2 or 3
Second Phase	No Laves, delta banding per customer requirement	No Laves, no acicular delta, no continuous grain boundary network
Yield Strength	$> 1034 \text{ MPa}$ (150 ksi)	$> 827 \text{ MPa}$ (120 ksi)
Tensile Strength	$> 1276 \text{ MPa}$ (185 ksi)	$> 1034 \text{ MPa}$ (150 ksi)
Elongation	$> 12\%$	$> 20\%$
Reduction of Area	$> 15\%$	$25\text{--}35\%$
Hardness	$> 331 \text{ HB}$	$< 363 \text{ HB}$

2.3 Corrosion Fatigue Crack Growth

The fatigue life of a structural component may be divided into four stages: (1) cyclic plastic deformation, (2) fatigue crack initiation, (3) fatigue crack propagation/growth, and (4) fracture. Once a fatigue crack is initiated, the fatigue life of the material is dependent on the fatigue crack

growth rate. As soon as the crack grows to a critical length where the stress intensity factor reaches to the value of the fracture toughness of the material, the structure component will go to failure by fracture. Corrosion fatigue is the result of the combined synergistic actions of cyclic loading and a corrosive environment. The environment plays an important role in the fatigue behavior of a structural material during its service life. The effect of corrosive environments on the fatigue behavior of metallic materials has been widely studied and several models have been proposed for the mechanism of corrosion fatigue initiation and growth [34-40]. The initiation stage is not within the scope of the interest of this study, so the following discussion will focus on corrosion fatigue crack growth (CFCG) only.

2.3.1 Electrochemistry of Corrosion Fatigue Cracks

To understand the mechanisms of CFCG requires knowledge of the electrochemistry in cracks. Once a crack has initiated in a corrosive environment, the CFCG rate is determined and strongly influenced by the local electrochemical kinetics as well as the nature and stability of surface films at the crack tip. The electrochemistry in crack tip solution is very different in nature from that in the bulk solution [41-44]. Figure 2.3 shows the possible chemical and electrochemical processes which typically occur in the corrosion fatigue crack. Following are these electrochemical reactions taking place at the crack tip and on the crack walls.

Anodic reaction: $M \rightarrow M^{n+} + ne^{-}$

Cation hydrolysis reaction: $M^{n+} + nH_2O \rightarrow M(OH)_n + nH^{+}$

Cathodic reaction on the crack walls: $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$

Cathodic reaction at the crack tip: $H^{+} + e^{-} \rightarrow H$

$H_2O + e^{-} \rightarrow H + OH^{-}$

Figure 2.3 Possible chemical and electrochemical processes in a corrosion fatigue crack

Anodic dissolution occurs at the crack tip and on the crack walls producing M^{n+} ions. The dissolution kinetics on the crack walls will depend on the protectiveness and stability of the passive film. At the crack tip, the localized mechanical strain or the crack advance process will rupture or break the passive film leading to exposure of bare metal to the crack tip solution. Within the crack solution, the M^{n+} ions concentration will build up. The positive charge generated by dissolution will be balanced by anions such as Cl^- ions which diffuse from the bulk to maintain electrical neutrality. Hydrolysis of metal cations will take place tending to lower the pH of the solution. Thus, an aggressive, low pH electrolyte concentrated in M^{n+} and Cl^- is produced near the crack tip. Restricted mass transport helps maintain the local occluded chemistry. However, internal cathodic reactions in the crack including reduction of H^+ and water will counterbalance the decrease of pH to some extent at the crack tip.

2.3.2 Corrosion Fatigue Crack Growth Mechanisms

Understanding of the CFCG mechanism is essential to service life prediction and fracture control. The general mechanism for CFCG involves the single occurrence or complex combinations of HE (hydrogen induced cracking) or anodic dissolution at the crack tip.

2.3.2.1 Hydrogen Embrittlement

In corrosion fatigue, hydrogen is generated by the electrochemical reduction of H^+ ions or water or the reaction of environmental species such as H_2 , H_2O , and H_2S with the newly cracked metal at the crack tip. This hydrogen is absorbed at the metal surface and then transported by diffusion into the highly stressed plastic zone at the crack tip, where it causes localized damage and increases the fatigue crack growth rate. Figure 2.4 illustrates various processes that might be involved in corrosion fatigue crack growth by HE mechanism.

The mechanism which leads to HE is not well understood, however, several HE mechanisms such as lattice bond decohesion, grain or dislocation cell boundary decohesion, enhanced localized plasticity, or metal hydride formation have been proposed to explain how hydrogen enhances corrosion fatigue crack growth rates. The results of fracture due to HE may appear as cleavage cracking, intergranular cracking or ductile failure.

Figure 2.4 Various processes occurred in corrosion fatigue crack growth by HE mechanism

2.3.2.2 Anodic Dissolution

Anodic dissolution is commonly referred to as active path dissolution, slip dissolution, strain/stress enhanced dissolution, and surface film rupture dissolution. In corrosion fatigue cracking, the anodic dissolution mechanism depends on the rupture of the protective film at the crack tip and the subsequent repassivation of the newly exposed fresh metal surface. The anodic dissolution mechanism explains the accelerated crack growth of corrosion fatigue by the localized anodic dissolution of the periodically exposed fresh crack tips. The process starts when the metal or alloy

which is susceptible to corrosion is exposed to a corrosive environment. During corrosion, some of the dissolved metal ions tend to form oxides and hydroxides that precipitate on the surface, forming a thin protective film. Due to the locally concentrated plastic strain, the protective films at the crack tips are easily broken by the emerging slip steps. On the other hand, the unstrained crack walls remain passivated and cathodic relative to the crack tips. Under conditions of localized straining sufficient to rupture protective or partially protective film at the crack tip, oxidation of bared surface will occur and the crack will advance because of the localized metal loss. At the same time, a repassivation of the bared surface occurs during the unloading reversal until the next generation of film rupture. The film rupture mechanisms contain the rupture-dissolution-repassivation sequence, which must be followed in order to maintain the process of crack growth. Corrosion fatigue crack growth rates will be controlled by the bare surface anodic dissolution rate, the rate of repassivation, the rate of oxide film rupture, mass transport rate of reactant to the dissolving surface.

2.4 Mechanical Surface Treatment

As discussed earlier in this chapter, failures such as wear, corrosion, stress corrosion cracking, and fatigue/corrosion fatigue may occur in metallic materials applied in BHA due to the combination of corrosive drilling fluids and high mechanical loading. In most cases, materials failures may initiate or grow on the surface or the near-surface region of a component. Therefore, optimization of surface microstructure and properties of materials may effectively enhance the performance and play an important role in failure control. It is well known that mechanical surface treatments, such as shot peening, laser peening, ultrasonic peening, hammer peening, roller burnishing and deep rolling, can significantly improve resistance to failure, and in particular enhance fatigue strength by inducing a compressive residual stress in the surface layers of the material, making the nucleation and propagation of fatigue cracks more difficult, thus ultimately increasing the service life of the component [45-49]. This approach has proved to be efficient in a variety of materials, such as stainless steels, magnesium alloys, aluminum alloy, titanium alloys and nickel alloys. In the following, the current status of research and development on mechanical surface treatments of metal alloys will be reviewed.

2.4.1 Peening Methods

Peening is normally a cold working process which plastically deforms the surface by impacting it with a tool or small balls, thereby inducing compressive residual stresses as well as work hardening in the surface and near surface region, in order to improve yield strength, stress cracking resistance, wear resistance and fatigue life of the component. Several peening methods including shot peening, laser peening and hammer peening have been developed for years which are briefly described below.

2.4.1.1 Shot Peening

Shot peening (SP) is a widely used mechanical surface treatment in which peening media with the spherical shape and sufficiently high degrees of hardness are accelerated in peening devices of various kinds and impact with the surface of the treated workpiece, to produce near surface plastic deformation leading to the creation of high compressive residual stresses and the development of work hardening. The major advantages of SP are that it is relatively inexpensive, and can be used on components of almost any shape, particularly on those possessing complex geometries due to its flexibility. A large number of researches have successfully shown that SP is able to improve the mechanical properties of materials, although it has its limitations [50-56]. First of all, the compressive residual stresses produced by conventional SP are limited in depth. Moreover, the SP process results in a roughened surface. However, the increase in surface roughness with its accompanying local stress concentration is considered to be deleterious to the fatigue strength of shot-peened materials because it tends to accelerate the crack nucleation stage. Thus, SP parameters such as peening intensity, peening coverage, saturation, shot material, shot size, shot velocity, shot hardness and time of peening should be widely investigated to optimize the compressive residual stress and surface roughening.

Air blast shot peening is a SP process through which the shots are propelled by compressed air. The schematic of the equipment is illustrated in Figure 2.5 [57].

Figure 2.5 Schematic illustration showing the air blast shot peening equipment

Recent researches have shown that newly developed SP treatments such as ultrasonic SP (other name is II-type surface mechanical attrition treatment [58], as illustrated in Figure 2.6 [57]) and high energy SP are able to introduce a nanocrystalline surface layer while maintaining coarse grained interior by using ultrasonic equipments to give desired kinetic energy to the shots. The mechanical properties and corrosion resistance of materials treated with these methods have been significantly improved because of the refined microstructures [59-61]. The main difference between ultrasonic SP and conventional SP is the use of ultrasonic excitation to impact the shots. Because of the high frequency of the system, the surface of the sample to be treated is peened with a high number of multi-directional impacts in a short period of time. Its main benefit compared to conventional SP is the better surface quality with low roughness due to a better quality of the shots and lower impact velocity.

Figure 2.6 Schematic illustration of the surface mechanical attrition treatment equipment

High energy SP is another effective processing method for the fabrication of various ultrafine-grained structures by imposing severe plastic deformation into metals and alloys. The

principle of the high energy SP treatment is similar to that of the ultrasonic SP method, but with lower frequency. The entire surface of the sample is peened by the flying shots with high energy under different processing times.

2.4.1.2 Laser Peening

Laser peening, or laser shock peening (LSP), has been developed as an alternative novel surface process in order to achieve deeper compressive residual stress using high-power, laser pulse, and to avoid the deleterious influence of surface roughening induced by conventional SP [55, 62-67]. In LSP, the substrate is often covered with thin insulating or absorbing layer, as shown in Figure 2.7. A transparent material like water is then placed over the absorbing coating. When the high intensity laser beam is irradiated on the surface, it will be absorbed by the absorbing layer to form a plasma cloud. The plastic deformation was imparted to the surface of material through the plasma formation that is generated by a laser pulse and travels into the workpiece as a shock wave. The plastic deformation caused by the shock wave while propagating into the metal can result in compressive residual stresses.

Figure 2.7 Schematic representation of the laser peening treatment

LSP has been used for improving fatigue life of alloys by imparting deep compressive residual stresses from the surface of components. It has also been shown to reduce stress corrosion cracking in components subjected to corrosion environments. Moreover, smaller surface stress gradients are found after LSP, which is beneficial because it is known to be important in reducing or eliminating cyclic stress relaxation. LSP has also been applied to enhance the surface properties such as corrosion resistance and wear resistance of metallic materials.

2.4.1.3 Hammer Peening

Hammer peening (HP) is a cold working method by repeatedly pounding the surface with a blunt nosed chisel. The operation may be carried out manually with a ball-peen hammer or with various shafted punches and a hammer; or by a pneumatic, electromagnetic, or piezoelectric hammer operating at several thousands, impacting ratio per minute. SP and LSP surface treatments have gained acceptance in various industries to improve part performance and fatigue life. However, even if the HP technique has been available for several decades, it has not been widely used and only some applications were found to tremendously improve the fatigue resistance and stress corrosion behavior in welded components because it is a noisy and tedious process.

Recent research has been initiated and developed on fatigue improvement effects of two high frequency HP processes including impact treatment (HiFIT) and ultrasonic impact treatment (UIT) [68-74]. HiFIT process is carried out using pneumatic equipment while the pins of the UIT device are accelerated by ultrasonic vibrations, driving several thousands of impacting ratios per minute by repeatedly hammering with blunt-nosed chisel. The ordinary HP methods feature hammer frequencies of 10–80 Hz, while the HiFIT and UIT methods cold work the weld toe with a frequency of 100–200 Hz. Also, the metal pin is changed to cylindrical pins with a size of 2–5 mm diameter, and rounded tips with a radius of 1.5 mm. Figure 2.8 shows the two high frequency HP equipments of HiFIT and UIT.

Figure 2.8 HiFIT and UIT equipments

Because the manual HP processes cannot give a good repeatability, two automated HP methods including robotized (RHP) and machine hammer peening (MHP) have been recently developed. The RHP technique has been developed by the research institute of Hydro-Québec in the last few years [75, 76]. It has been demonstrated that RHP may relax tensile residual stresses due to welding and reduce distortions of welded samples. It has also been proved that RHP is the best technique among surface treatment methods to relax tensile residual stresses. Moreover, it is able to induce compressive residual stresses nearly 10 mm below the surface on initially stress free samples. Hacini et al. [76] have proposed the optimal number of HP layers to be applied to reach a maximum of intensity of compressive residual stresses induced in initial free or stressed samples. They have pointed out that HP is more effective on samples that have tensile residual stresses as it generates at the same time surface compressive residual stresses and deep strain hardening.

MHP is a novel surface treatment technology that was developed by Konstruktion and Werkzeugbau Löcker in Germany, in order to replace the manual polishing process for free form workpiece surfaces by an automated method [77-84]. During the treatment, the workpiece surface is hammered by a peening tool with a spherical tungsten carbide tip through well-directed impacts (Figure 2.9 [80]). The tool performs an oscillating movement produced by an actuator that can be moved by a machine tool or a robot, and the tool path can be programmed using CAM software [78,79,81]. The hammer frequency and force can be varied using a dedicated control system, and the hammer tip can be changed with different ball diameters. Usually the frequency of the tool tip movement can be chosen between 100 and 500 Hz [84].

Figure 2.9 Schematic illustration of machine hammer peening technology

2.4.2 Compressive Residual Stresses Induced by Peening Treatments

In most applications for mechanical surface treatments, the benefit obtained is the direct result of the compressive residual stresses produced. The depth profile of residual stresses in the near surface region is illustrated in Figure 2.10 [85]. The maximum compressive residual stresses are produced just below the surface of materials.

Figure 2.10 Scheme of residual stress depth profile for surface-treated materials

The actual depth and value of induced residual stresses vary depending on surface treatment methods, processing conditions and material properties. The compressive residual stresses depth of the SP treatment is usually in the range of 0.2–0.4 mm [56, 85-95]. The compressive residual stress depth of laser-peened specimens widely ranges from 0.1 to over 3 mm [55, 65, 96-105]. As compared with the SP and LSP surface treatments, HP can produce much deeper compressive residual stress layers varies from 1 mm to nearly 10 mm [48, 75, 106-109]. This compressively stressed layer is extremely effective in preventing premature failure under cyclic loading conditions. Also crack growth is slowed significantly in a compressive layer, and the crack resistance is increased with increasing the depth of the compressive layer.

2.4.3 Modifications in Surface Topography and Microstructure

Surface topography such as surface roughness and surface morphology needs to be carefully considered because they are closely related to the corrosion resistance and fatigue properties of metals and alloys in application. Numerous investigations on the surface topography after surface

treatments have been performed by using optical microscopy (OM), scanning electron microscopy (SEM) and roughness measurements. Moreover, mechanical surface treatments which may induce plastic deformation in near surface region lead to severe microstructure evolution such as generation of high density dislocations and nano-twins, nanocrystallization and phase transformation. The microstructure change has been investigated by means of OM, SEM, transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques. In this section we will go through the details of the obtained results on modifications in surface topography and microstructure produced by different peening treatments.

2.4.3.1 Surface Topography

The conventional SP treatments usually generate a rough surface with large increase in the value of the mean and peak roughness. Detailed studies have demonstrated that surface roughening by SP can be explained by the indentation process of impacting balls, and the surface roughness evolution can be divided into three stages: the roughness increase stage, the roughness decrease stage, and the steady-state stage [52]. These three stages are related to different stages of the surface coverage of indents generated by impacting balls. The steady-state stage corresponds to the impact coverage of the entire surface multiple times, and the surface roughness at the steady-state increases with the shot size. Azar et al. [52] have investigated the effect of SP time on surface morphology of 316L stainless steel by means of surface roughness measurement and SEM. Their results have shown that surface roughness is increased until 10 min due to local deformation of surface by SP; however, it is decreased after this time with increasing the SP time because of over peening effect. Sandá et al. [110] have investigated the surface state of Inconel 718 after ultrasonic SP with different processing time, material and quantity of shot balls and distance from radiating surface to specimen. Their results have shown that a higher density of impact marks was generated by higher processing times, lower distances between booster and sample, as well as using WC/Co balls instead of steel balls.

When there is no protective laser absorbent coating applied on the substrate, the LSP process will cause severe surface melting and ablation of alloys during laser irradiation [64, 104, 111, 112]. This can result in very rough surfaces with resolidified droplets, cracks and craters. A large number of researches have pointed out that LSP without absorbing coatings could result in higher surface roughness, and the surface roughness increases nonlinearly with the laser power and pulse density

[101, 102, 113]. However, surface melting issues can be solved with laser energy absorbent coatings as discussed in previous sections. Chu et al. [102] have studied the effect of LSP with various laser energies on surface microstructure of low carbon steel and their results have indicated that no surface melting but uneven indentations were found on the surface at 31 J laser pulse energy. As the laser energy was increased, the surface indentation became more pronounced and deeper. The study on the effect of LSP using lower energy laser on precipitation hardened aluminum alloy 6061-T6 by Sathyajith and Kalainathan [114] have also confirmed that there was no melting observed on the surface. The laser-peened surface showed large number of indentations [115], and the indentations became wider and deeper as the laser pulse density increased [99].

Even though one of the disadvantages for the traditional HP treatment is the relatively high degree of surface roughness produced by this treatment, newly developed MHP technology has been proven as a surface treatment which could greatly smoothen the surface of a work piece [77, 79-84]. It has been reported that the MHP treatment could be a plausible substitute for manual polishing in pressing die because the workpiece surface was significant smoothened and the lead time can be reduced by 75% [79, 83]. Figure 2.11 [80] shows an example of the surface topography difference between machine hammer-peened and an unpeened (original milled) surfaces. It can be observed that the surface roughness in peening direction is shapely reduced from about 10 μm to about 50 nm.

Figure 2.11 Surface topography of the machine hammer-peened and unpeened surfaces.

2.4.3.2 Microstructure

Investigations have shown that severe plastic deformation produced by mechanical surface treatments is very effective in inducing grain refinement and phase transformation in some materials.

2.4.3.2.1 Nanocrystallization

Surface nanocrystallization can be obtained with the application of mechanical surface treatments such as shot peening, surface mechanical attrition treatment, cold rolling, ultrasonic peening and laser shock peening by inducing localized severe plastic deformation in the surface layer of the metals and alloys, resulting better surface properties such as fatigue strength, wear resistance, hardness, corrosion resistance and cracking resistance [58-61, 116-130].

Lu et al. [117] have suggested that under contact loading deformation localized in specific shear bands is created on the surface of the material, which consists of an array of dislocations with high density. The second contact loading in a different direction may activate deformation in other shear band systems. When the action is repeated multiple times, the initial crystallite might be divided into a large number of subgrains or domains separated by small angle grain boundaries that result from annihilation and recombination of the dislocation arrays. Further mechanical treatments may lead to a change of orientation on the part of subgrains with respect to their neighboring grains, eventually becoming completely random, thus developing a metastable nanocrystalline layer on the surface of the material.

Umemoto et al. [118] and Liu et al. [119] have illustrated that air blast SP may induce a nanocrystalline surface layer on the top of the work hardening area of Fe-3.29Si and Fe-0.03C steels. When using small shot sizes, the nano-area can be formed in very short treatment times, and the thickness and continuity of the nanolayer is enhanced. On the contrary, the nanocrystalline region is more difficult to synthesize when using large shot particles, even though the deformed area is much thicker. Lee et al. [122] have found nano-sized grains on the surface of AISI 304SS specimens after ultrasonic peening and SP. It has been reported by Liu et al. [60] that surface nanocrystallization on a 316L SS was introduced by means of ultrasonic SP treatment. Sandá et al. [110] have pointed out that surface nanocrystallization may not be induced by ultrasonic SP on the surface of precipitated state Inconel 718 if the impact energy of the balls is not large enough. Reduce the quantity of balls, increase the process time or reduce distance from radiating surface

to the sample can produce more impact energy to achieve grain refinement. Todaka et al. [120] have compared air blast SP and ultrasonic SP in similar peening conditions, and found that the produced volume of nanocrystalline region in air blast SP is larger than that in ultrasonic SP. Wang et al. [125] have reported that high energy SP can cause surface nanocrystallization with an average grain size of about 18 nm nanocrystalline microstructure in the surface layer of 1Cr18Ni9Ti stainless steel. Ni et al. [126] have demonstrated that a nanostructured surface layer of 304 SS could be obtained by high energy SP treatment.

Some researchers have reported the grain refinement of steels and aluminum alloys induced by ultra-high plastic strain during LSP [64, 131-138]. Lu et al. [131] have found that the grain in the surface layer of LY2 aluminum alloy subjected to multiple LSP impacts was refined to 100–200 nm at the top surface. Based on their microstructure observation, a grain refinement mechanism has been developed and it involves the formation and development of dislocation lines in original grains, the pile-up of dislocation lines contributing to dislocation tangles and dense dislocation walls, the transformation of dislocation tangles and dense dislocation walls into subgrain boundaries, and the evolution of the continuous dynamic recrystallization in subgrain boundaries to refined grain boundaries. Lu et al. [135, 136] have also observed that the grain size in the surface layer of AISI 8620 steel was decreased from several hundred nanometers to micrometers, to about tens nanometers after LSP. They have proposed a microstructural strengthening mechanism due to multiple LSP impact, as described as follows: (1) the parallel lamellar pearlites are broken into bitty pearlites, and dislocation activities simultaneously led to the formation of dislocation lines (DLs) and dislocation pile-ups in original grains; (2) bitty pearlites were all broken into Fe_3C granules, and dislocation movement made Fe_3C granules disperse near subgrain boundaries and led to subgrain boundaries separating individual cells, and (3) subgrain boundaries were refined to grain boundaries. Lu et al. [133, 134, 138] have also investigated the microstructure evolution and grain refinement in ANSI 304 stainless steels subjected to multiple LSP impacts. The grain size in the top surface was refined to about 50–200 nm due to the ultra-high plastic strain. They have suggested an as followed mechanism to describe the grain refinement process during multiple LSP: (1) formation of planar dislocation arrays and stacking faults along multiple directions due to the pile up of dislocation lines; (2) formation of submicron triangular blocks or irregularly shaped blocks by the intersection of mechanical twins–mechanical twins or mechanical twins–planar dislocation arrays or planar dislocation arrays–planar dislocation arrays along multiple directions;

(3) transformation of mechanical twins into subgrain boundaries; (4) evolution by continuous dynamic recrystallization of subgrain boundaries to refined grain boundaries.

2.4.2.2.2 Phase Transformation

Difference of strain-induced phase transformation behavior at the deformation layer depends on both surface treatment methods and materials. For some stainless steels and Fe alloys, the process of severe plastic deformation is always associated with martensitic phase transformation [112, 125, 126, 137, 139-143].

Todaka et al. [120, 144] have reported that the deformation-induced layer consists of very fine martensite phase was formed on by SP for Fe-C alloy due to severe plastic deformation. Sato et al. [142] have also found strain-induced martensitic transformation on the shot-peened surface for Fe-33mass%Ni specimen with γ single structure. Some researchers have reported that martensitic phase transformations took place during the severe plastic deformation in the nanocrystalline surface layers of 316L stainless steel and 304 stainless steel after the SP treatment [126, 139, 141, 143, 144]. In general, the relative fraction of martensitic phase increases with the increment of the SP treatment time, while the increasing rate is remarkably greater in the initial stage. According to Ni et al. [126, 141], two types of martensite phase different magnetic hyperfine field were formed in a nanostructured surface layer of 304 stainless steel by the high energy SP treatment. The amount of martensite phase increases extremely with increasing high energy SP treatment time until a maximum value is reached then decreases slightly. Wang et al. [125] have reported that shot peening can induce α -martensite of about 15% in volume fraction in the surface of 1Cr18Ni9Ti stainless steel.

It has been published that the LSP treatment can lead to the formation of metastable phases [112, 137, 139, 143]. Banaś et al. [140] reported that after laser peening the austenite weld phase reverted to martensite, and Ni_3Ti and Ni_3Mo precipitates are visible in the matrix of 18Ni (250) maraging steel. Also the dislocation density qualitatively increased in the martensite matrix. Laser peening of Hadfield manganese steel was found to induce extensive formation of ϵ martensite and high density dislocations in the γ austenite matrix. Numerous twins as well as α -phase embryos located at the twin intersections were found in laser-peened 316L stainless steel and 304 stainless steel.

2.4.4 Effect on Pitting Corrosion Behavior

A variety of factors, such as surface roughness, surface morphology, surface passive/oxide film, surface nanocrystallization, phase transformation and residual stress induced by surface treatments, can affect the corrosion behavior. Each one of these factors has its own influence on corrosion resistance and they are highly interdependent with each other. Thus, it would be difficult to interpret the corrosion performance to a single contribute. Numerous studies have been focused on the influence of surface modifications induced by peening treatments on the pitting corrosion resistance of the metals and alloys. However, whether it may improve or decrease pitting corrosion resistance depends on the surface treatment method and conditions.

2.4.4.1 Surface Roughness

Surface roughness has a greater influence on corrosion resistance. In general, a smoother surface is believed to offer a better corrosion resistance. Increase in the surface roughness has been shown to increase the pitting susceptibility of alloys. It has been reported by Azar et al. [52] that surface roughening, which was considered to be deleterious to the corrosion resistance by increasing the corrosion current density and decreasing the break-down potential, could be produced by the shot peening treatment. According to Lee et al. [122], ultrasonically peened AISI 304 stainless steel showed better general and localized corrosion resistance than the shot-peened specimen due to the rendering of a smoother surface and the creation of strain-induced martensite. Peyre et al. [143] have pointed out that the deleterious roughened surface state produced by shot peening could counterbalance the beneficial effect of compressive residual stress on the pitting corrosion resistance of 316L steel.

2.4.4.2 Surface Nanocrystallization

Nanocrystallization can change the composition of the passive film. The increase in density of grain boundaries due to nanocrystallization could promote diffusion of Cr to the surface and enable rapid formation of homogenous passive film rich in Cr than could offer a better corrosion resistance. Wang et al. [125] have reported that the surface nanocrystallization by shot peening can improve the potentiodynamic polarization behavior of 1Cr18Ni9Ti stainless steel in 3.5% NaCl solution, and the passive film is easier to form and more stable compared to the as-received coarse crystalline counterpart. The corrosion resistance in 6% FeCl₃ solution is also markedly

enhanced by shot-peening-induced nanocrystallization. Mordyuk et al. [139] addressed that the corrosion performance of AISI-321 stainless steel in 3.5% NaCl solution can be enhanced by the ultrasonic peening due to the grain refinement and increase in the volume fraction of strain-induced α martensite.

2.4.4.3 Phase Transformation

Phase transformation is an important factor that influences the corrosion resistance of steels. The influence of martensite phase on the corrosion resistance of stainless steels has been addressed by many researchers. It has been reported that phase transformation could lead to a decrease or increase or cause an insignificant effect on the corrosion resistance of stainless steels. Mordyuk et al. [139] have pointed out that an increase in volume fraction of strain-induced martensite produced during peening induced a galvanic effect between the austenite and martensite phases. A similar phenomenon was also reported by Ningshen and Kamachi Mudali[145]. The detrimental influence of strain-induced martensite on the corrosion resistance of stainless steels has also been observed by Elayaperumal et al. [146] and Barbucci et al.[147].

2.4.4.4 Compressive Residual Stress

It has been reported by Peyre et al. [111] that a significant improvement in pitting potential (+0.1 V) was observed in 0.05 M NaCl solution after a pure mechanical laser peening treatment. Based on their findings, Peyre et al. have suggested that the increase in critical pitting potential is most likely due to the combined effects of compressive residual stress and work hardening. The anodic shift of the pitting potential was also detected for aluminium alloy after laser shock peening, which was attributed to high compressive residual stresses due to the shockwave effect of the laser shock peening process [148]. Liu et al. [149] have confirmed the beneficial effects of compression on localized corrosion, indicated by the significantly increased breakdown and repassivation potentials, and a decrease in passive current density for samples under compression or with compressive residual stress. Krawiec et al. [150] have also reported a big increase of charge transfer and oxide film resistance of AA2050–T8 aluminium alloy as a consequence of the compressive residual stress developed through laser shock peening process. Omar et al.[151] have addressed that the resistance to pitting corrosion can be greatly increased by a shot peening and polishing. The objective of using shot peening and polishing together is to induce compressive

stress on the metal surface at the same time make the surface very smooth and soft and that may induce the compressive stresses on the metal surface and eliminate the microscopic scratches during manufacturing process. The results showed that shot peening and polishing can be beneficial in decreasing the pitting corrosion on stainless steel 304L in nitric acid and NaCl environments.

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Chapter 3: Effect of Temperature on Pitting Corrosion Resistance and Passivation Properties of Oil-Grade Alloy 718 in 3.5 wt.% NaCl Solution

3.1 Introduction

Nickel-base alloy 718 is widely used in various industry applications such as aerospace, chemical processing, marine engineering, and nuclear reactors due to its superior mechanical properties and oxidation resistance at high temperatures [1-4]. Recently it is also proposed for downhole drilling components in oil and gas industry [5-10]. However, corrosion environments encountered in oil and gas industry are rather aggressive. Most of the water based drilling muds contain very high content of chloride salts and significant levels of hydrogen sulfide and carbon dioxide which make the oil field conditions become more corrosive [6, 9-11]. Therefore, localized corrosion properties such as pitting corrosion resistance of nickel-base alloy 718 became a very important issue for its use in such conditions.

Pitting corrosion resistance is strongly related to protective properties of passive films formed on alloy surface [12-14]. A considerable number of investigations have been devoted to the study of passive films on nickel and nickel-base alloys. In aqueous solutions a $\text{Ni}(\text{OH})_2$ film is first formed by dissolution/ precipitation on the nickel surface, and then gradually changes to NiO oxide [15-17]. The passive film on nickel-base alloy surface behaves as a duplex structure formed by an inner layer of p-type Cr_2O_3 and an outer layer consisted of n-type Cr/Ni hydroxides and Fe oxides [18-21]. In chloride solution, the passive film may be damaged by forming soluble CrCl_3 , or be oxidized to soluble CrO_4^{2-} if the applied anodic potential is higher than $0.4 V_{\text{SCE}}$ [22-25]. Also, Cl^- incorporation into the Cr_2O_3 passive film may induce the high corrosion resistant p-type Cr_2O_3 oxide film to be transformed to the n-type oxide film [26].

The effect of temperature on the properties of passivation film on alloy 33 in sodium sulphate solutions containing or not sodium chloride have shown that the previously air formed film was a n-type semiconductor due to the presence of point defects of donor species, such as oxygen vacancies and interstitial metallic cations [25]. The passive film became more porous and less protective at higher temperatures mainly in the presence of chloride. It has been reported that the passive film formed on Alloy 625 in a lithium borate buffer solution in the temperature range of 25 and 150°C was a single layer mixed of Cr_2O_3 and $\text{Cr}(\text{OH})_3$, while it changed to double layer contained $\text{Ni}(\text{OH})_2$ in addition to Cr_2O_3 and $\text{Cr}(\text{OH})_3$ at 250 and 300°C [27]. Passive films formed

on Alloy 690 in alkaline environments have been investigated in the temperature range of 25 to 300°C. It has been claimed that the passive current density and donor density of the films increased with temperature due to increased diffusion rates of metallic ions and dehydration of hydroxides, and the passive film showed a duplex structure including an inner layer of Cr oxide or spinel oxide and an outer layer of Ni-Fe spinel oxide and Ni hydroxide [28, 29].

The investigation about the composition, electronic structure and protective properties of the passive film is needed in order to fully understand the pitting corrosion behavior of nickel-base oil-grade alloy 718. However, the electrochemical investigations are lacking for nickel-base alloy 718, especially for oil-grade alloy 718 which is newly designed and used in oil field industry. Thus, it's important to understand the electrochemical behaviors and clarify the corrosion mechanisms of oil-grade alloy 718 in chloride-containing environment by using electrochemical techniques. Also, temperature is one of the influencing variables in determining the capability of metals to resist corrosion. The objective of this study is to investigate the effect of temperature on the passivation behavior and pitting corrosion resistance of oil-grade nickel-based alloy 718 in 3.5 wt% NaCl solution at three different temperatures using electrochemical measurement and surface analysis. The passive film growth mechanism of oil-grade alloy 718 in 3.5 wt% NaCl solution is also addressed.

3.2 Experimental

3.2.1 Materials

The oil-grade alloy 718 used in this study was provided by ThyssenKruppVDM and its chemical composition is shown in Table 3.1. The as-received alloy was solution annealed at 1026°C for 1.5 h then water quenched (WQ). The microstructure with an average grain size of 46 μm is shown in Figure 3. 1. It can be seen that there are amounts of carbides and nitrides inside grains or on grain boundaries.

Table 3.1 Chemical composition of oil-grade alloy 718

Ni	Cr	Fe	Nb	Mo	Ti	Al	Co	Si	Mn	C	Cu	Ta
52.88	18.34	19.00	4.98	3.02	0.96	0.49	0.13	0.04	0.04	0.03	0.03	0.01
P	B	S	Pb	Se	Bi							
0.005	0.002	0.002	0.0002	<0.0003	<0.00003

Figure 3.1 Typical microstructure of oil-grade alloy 718

3.2.2 Surface Chemistry Analysis

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI 5000 VersaProbe System, utilizing monochromatic $AlK\alpha$ radiation to examine the passive film formed on the surface of specimens in 3.5 wt.% sodium chloride (NaCl) solution. For detecting the passive films formed in 3.5 wt.% NaCl solution, the samples were rinsed with deionised water after being taken out from the solution and dried before being transferred into the ultra-high vacuum XPS chamber environment. The $C1s$ peak from carbon contamination at 284.8 eV was used as a reference to correct for charging shifts. The thickness of the passive film was determined by argon-ion sputtering with an ion energy of 2 kV for different time intervals over an area of $2\text{ mm} \times 2\text{ mm}$. The reference sputtering rate was 18.5 nm/min, and this was calculated relative to the Ta_2O_5 layer as the intensity of the oxygen signal decreased to a half. After a background subtraction according to Shirley, the quantification of the species in the passive film was processed with XPSpeak 4.1 peak fitting software.

3.2.3 Electrochemical Measurements

1.0 cm × 1.0 cm × 2.0 mm specimens were cut from the alloys by using electrical discharge machining (EDM). All electrochemical measurements were performed at different temperatures using an aerated 3.5 wt.% NaCl solution, prepared with deionized water. All specimens were mounted using epoxy, ground with silicon carbide (SiC) papers starting from 120 grit and finishing with 800 grit, rinsed with distilled water, dried in air at room temperature and then transferred to the test solution. These experiments were set up according to ASTM standard G5–94 with a three electrode cell in a 1.5 L glass container. The three electrode cell setup consisting of a pair of graphite counter electrodes (CE), an Ag/AgCl reference electrode (RE) immersed in a saturated potassium chloride (KCl) solution and the specimen as the working electrode (WE) was employed. Potentials cited in this chapter are all referred to Ag/AgCl. Experiments for each specimen condition were conducted at least five times with the results averaged. At the beginning of each experiment, the working electrode was first cathodically polarized at $-1\text{ V}_{(\text{Ag}/\text{AgCl})}$ for 10 min to remove the air-formed surface oxides because it has been proved that the reproducibility of electrochemical measurements performed on passive films was improved after cathodic polarization.

3.2.3.1 Open-Circuit Potential

The open-circuit potential (OCP) was monitored for up to 1 h after cathodic polarization treatment. The OCP values were obtained from the average value of the last 300 s of the OCP measurement.

3.2.3.2 Potentiodynamic polarization

Potentiodynamic polarization curves were performed using a Solartron SI 1287. For this series of tests, the specimens were immersed in the solution for 1 h prior to the measurement in order to stabilize the surface at OCP after cathodic pretreatment. The test was performed at a scanning rate of 0.5 mV/s starting from $-0.5\text{ V}_{(\text{Ag}/\text{AgCl})}$ towards the anodic direction until the transpassive region was reached.

3.2.3.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were carried out with a Solartron SI 1287 electrochemical interface and a SI 1260 impedance analyzer. EIS measurements were

conducted at OCP after the specimens had been immersed in the solution for 1 h. The EIS testing frequency ranged from 10 kHz to 10 mHz while the AC amplitudes were 10 mV (rms–root mean square). The resulting impedance spectra obtained during testing were then fitted using ZSimpWin software.

3.2.3.4 Mott-Schottky Plots

Mott-Schottky (MS) plots tests were also carried out with a Solartron SI 1287 electrochemical interface and a SI 1260 Impedance analyzer. To obtain MS plots, the samples were immersed at OCP for 1 h for the formation of passive films, then the measurement was scanned from $-0.5 V_{(Ag/AgCl)}$ to $1.3 V_{SCE(Ag/AgCl)}$ at the rate of 50 mV/s in the anodic direction. An AC signal with amplitude of 10 mV and a frequency of 1000 Hz was superimposed on the scanning signal.

3.3 Results

3.3.1 Electrochemical Measurements

3.3.1.1 Open-Circuit Potential Curves

Figure 3.2 gives the dependent of corrosion potential (OCP) on the time of alloy 718 exposure to a 3.5 wt.% NaCl solution at three different temperatures. Initially the OCP values increases soon after cathodic polarization pretreatment at all temperatures, indicating a spontaneous passivation of oil-grade alloy 718 due to the self-formation of an oxide film in 3.5 wt.% NaCl solution. The OCP values are summarized in Table 3.2. It can be seen that OCP shifts to more positive direction with increasing temperature for oil-grade alloy 718, which indicates that the corrosion potentials are decreased with temperature.

Figure 3.2 OCP curves of oil-grade alloy 718 in 3.5 wt.% NaCl at three different temperatures

3.3.1.2 Potentiodynamic Polarization Curves

Figure 3.3 shows the potentiodynamic polarization curves for the oil-grade alloy 718 specimen in 3.5 wt.% NaCl solution at three different temperatures. Table 3.2 lists the characteristic parameters values for all the curves. The corrosion potential E_{corr} of oil-grade alloy 718 shifts towards more positive value with increasing temperature. According to Figure 3.3, two stages of the passive process can be distinguished in the curve obtained at RT. The low potential passive region (Region 1) lies between 100 $\text{mV}_{(\text{Ag}/\text{AgCl})}$ to 800 $\text{mV}_{(\text{Ag}/\text{AgCl})}$, which can be characterized by a steady-state current density. In region 2, the comparatively slow increase of the current in the potential range 800–1000 $\text{mV}_{(\text{Ag}/\text{AgCl})}$ could be ascribed to the formation of high valency Cr in the passive film prior to transpassive dissolution. The steeper increase in the range from 1000 $\text{mV}_{(\text{Ag}/\text{AgCl})}$ to 1150 $\text{mV}_{(\text{Ag}/\text{AgCl})}$ (region 3) is most probably related to the onset of transpassive dissolution. The corrosion current density i_{corr} is increased as the temperature increased, indicating a decreased corrosion resistance. It is evident that the pitting corrosion resistance of oil-grade alloy 718 is significantly reduced with temperature, confirmed by the marked decrease in the pitting potential E_p from 1150 $\text{mV}_{(\text{Ag}/\text{AgCl})}$ at room temperature to 436 $\text{mV}_{(\text{Ag}/\text{AgCl})}$ at 50°C and 434 $\text{mV}_{(\text{Ag}/\text{AgCl})}$ at 80°C. It is clear from the cyclic potentiodynamic polarization curves that the higher the temperature, the lower the potential required for the film breakdown and pitting formation. Thus the rise in temperature made it easier for the film breakdown and pits formation by applying an anodic potential in 3.5 wt% NaCl solution. The above results concerning effect of temperature on

the pitting behaviors of oil-grade alloy 718 are in agreement with results reported by other authors for various nickel based alloys in halide containing solutions [30, 31].

Figure 3.3 Potentiodynamic polarization curves of oil-grade alloy 718 in 3.5 wt.% NaCl at three different temperatures.

Table 3.2 Electrochemical parameters of oil-grade alloy 718 in 3.5 wt% NaCl solution at three different temperatures obtained from OCP and potentiodynamic polarization curves.

Temperature	OCP(mV _{Ag/AgCl})	E_{corr} (mV _{Ag/AgCl})	E_p (mV _{Ag/AgCl})	i_{corr} (μ A/cm ²)
RT	-190	-225	1150	0.21
50°C	-140	-165	436	0.40
80°C	-110	-125	434	0.45

3.3.1.3 Electrochemical Impedance Spectroscopy

In order to investigate and compared the protectivity and stability of the passive films formed on oil-grade alloy 718 in 3.5 wt.% NaCl solution at different temperatures, EIS measurements were carried out at OCP after passive films were generated on the surface.

The EIS results recorded for oil-grade alloy 718 at OCP after 1 h immersion in 3.5 wt % NaCl solution at three different temperatures are presented in Figure 3.4, in the form of Nyquist plots and Bode plots. At all temperatures, the Nyquist plots show one depressed semicircle that does not end at low frequency. The Bode diagram has two capacitive time constants related to dielectric properties of the double layer passive film. The impedance plots show a great decrease of impedance values with the increase in temperature to 50°C, and there is no big difference of impedance between 50°C and 80°C.

Figure 3.4 EIS plots measured at OCP for 1h immersion in 3.5 wt.% NaCl at three different temperatures.

The two time constants feature is often considered as the response from an inhomogeneous passive film, which consists of a compact inner layer and a porous outer layer. It has been demonstrated that the passive films on nickel-base alloys can be more accurately described as a double layer structure composed of an n-type outer region containing Ni/Fe oxide and hydroxide and a p-type inner region containing Cr oxide [15, 18].

The low frequency time constant has been related to the inner barrier layer, and the time constant at high frequency range has been associated to the porous outer layer. The equivalent electrical circuit that has been usually used to interpret the EIS spectra displaying two time constants for the passive film is illustrated in Figure 3.5. In this model, R_s is the solution resistance. R_1 and Q_1 correspond to the resistance and capacitance of the porous layer which is responsible for the dissolution/precipitation processes through the passive film. R_2 and Q_2 represent the resistance and capacitance of the barrier layer that is responsible for the good resistance of the alloy.

Figure 3.5 Equivalent electrical circuit for EIS results fitting.

The fitted impedance parameters obtained from ZSimpWin software are summarized in Table 3.3.

Table 3.3 Fitted parameters for EIS data measured at OCP in 3.5 wt.% NaCl solution at three different temperatures.

Temperature	$R_s (\Omega \text{ cm}^2)$	$R_1 (\Omega \text{ cm}^2)$	$Q_1 (\text{F cm}^{-2})$	n_1	$R_2 (\Omega \text{ cm}^2)$	$Q_2 (\text{F cm}^{-2})$	n_2
RT	6.2	160.6	4.0×10^{-4}	0.99	1.4×10^5	5.2×10^{-5}	0.90
50°C	4.1	4206	1.1×10^{-4}	0.92	6.7×10^4	8.2×10^{-5}	0.92
80°C	1.9	4825	9.3×10^{-5}	0.93	6.5×10^4	8.6×10^{-5}	0.92

It can be seen that the R_1 values are greatly increased and R_2 values are decreased by almost one time with increasing in temperature. Also, the Q_1 values decrease and Q_2 values increase, which means the thickness of the porous outer layer is increased, however, the thickness of the barrier inner layer is decreased with temperature. The polarization resistance ($R_p = R_1 + R_2$) of the passive film decreases with temperature, indicating the corrosion resistance of oil-grade alloy 718 in 3.5 wt.% NaCl solution decreases with temperature. This may be due to the less stability of passive film formed on the surface of oil-grade alloy 718 at higher temperatures.

3.3.1.4 Mott-Schottky Plots

Oxide films formed on the metallic surface when the metal is exposed to air or immersed in aqueous solutions under OCP or under polarization conditions are extrinsic semiconductors, because the oxide does not present perfect crystallography but rather donor defects or acceptor defects. The space charge region developed in the passive film and the Helmholtz layer can be considered as two conductors in series. The electronic properties of the oxide film formed on the surface of oil-grade alloy 718 in 3.5 wt% NaCl solution at three different temperatures after passivation at OCP were investigated by Mott-Schottky plots based on measurements of the electrode capacitance as a function of electrode potential, assuming that the capacitance of the space charge layer C_{SC} was much less than that of the Helmholtz layer when the capacitance measurement frequency was high enough (1–3 kHz). The electrochemical behavior of passive oxide films can be expressed using the Mott-Schottky relationship as follows [32, 33]:

$$C^{-2} = C_H^{-2} + C_{SC}^{-2} + 2C_H^{-1}C_{SC}^{-1} = C_H^{-2} + (2/e\epsilon\epsilon_0N)(E - E_{FB} - k_B T / e) \quad \text{Equation 3.1}$$

where e is the electron charge (1.60×10^{-19} C), ϵ is the dielectric constant of the oxide film, ϵ_0 is the vacuum permmissivity constant (8.85×10^{-14} F/cm), N is the doping density which represents the donor N_d or acceptor N_a densities for an n-type or p-type semiconductor, respectively, E is applied potential, E_{FB} is the flat band potential, k_B is the Boltzmann constant ($1.38 \times 10^{-23} \text{ JK}^{-1}$), and T is the absolute temperature. It is well known that these oxide films present an extrinsic semiconductive n-type or p-type. For an n-type semiconductor, C^{-2} vs E should be linear with a

positive slope that is inversely proportional to the donor density. On the other hand, a p-type semiconductor introduces a negative slope which is inversely proportional to the acceptor density.

The doping species density can be calculated by:

$$N = 2 / e\epsilon\epsilon_0\alpha \quad \text{Equation 3.2}$$

Where α is the slope obtained for the straight line C^{-2} vs E .

The flat band potential E_{FB} can be obtained from the extrapolation of $1/C^{-2}$ to $1/C^{-2} = 0$.

To study the electronic structure of the passive film, the electrode capacitance was measured after the specimen had been previously immersed at OCP for 1 h at three different temperatures. Figure 3.6 shows the C^{-2} vs E plots for passive films formed on the oil-grade alloy 718 specimens in 3.5 wt% NaCl solution at three different temperatures. All the graphs presented a straight line with a positive slope at a low applied potentials range which changed to a negative slope at higher applied potentials. This result indicated that the passive film formed on oil-grade alloy 718 at open-circuit potential conditions presented an n-type semiconductor which transformed to a p-type as the anodic potential increased. However, the capacitances formed at higher temperatures were higher than the ones formed at lower temperatures. It can be seen that the Mott-Schottky plots measured after passivation at different temperatures presented similar features, which means that the electronic structure of the passive films seems to be independent of temperature. But it evidently shows that the slopes decreased with increasing temperature, indicating an increment of point defect in the passive film, which lies in the variation of the film composition with temperature. From the MS plots, the positive slopes can be used to calculate the donor concentration and the negative slopes can be applied to calculate the acceptor density, respectively. Considering Cr_2O_3 as a passive oxide, the donor species are interstitial Cr^{3+} cations and O^{2-} anion vacancies, and the acceptor species are Cr^{3+} cation vacancies [26, 31]. The ϵ of 15.6 was assumed in the above calculations as in literatures [26, 28].

Figure 3.6 MS plots for oil-grade alloy 718 measured after 1 h immersion at OCP in 3.5 wt.% NaCl solution at three different temperatures.

According to Equation 3.2, the values of N_d and N_a were calculated and shown in Table 3.4. The decrease in positive slopes with increase in temperature indicates that the donor concentration of the passive film increases with increase in temperature. It was observed that the values of donor densities at all temperatures were very high and increased with increasing temperature. Acceptor and donor density have been reported to increase with increase in conductivity of passive film, which implies that high acceptor or donor density will lead to high values of the passive current density [25, 28]. However, the difference of acceptor density between three different temperatures is less pronounced than donor density, which means the p-type film is less influenced by the temperature than the n-type film.

Table 3.4 Mott-Schottky calculated results for the passivation films formed on oil-grade alloy 718 after immersion at OCP for 1 h in 3.5 wt.% NaCl solution at three different temperatures.

Temperature	Positive Slope ($F^{-2}cm^4V_{SCE}^{-1}$)	$N_d (cm^{-3})$	Negative Slope ($F^{-2}cm^4V_{SCE}^{-1}$)	$N_a (cm^{-3})$
RT	1.0×10^{10}	8.7×10^{26}	-1.0×10^{10}	8.7×10^{26}
50°C	7.4×10^9	1.2×10^{27}	-8.8×10^9	1.0×10^{27}
80°C	6.2×10^9	1.5×10^{27}	-8.5×10^9	1.1×10^{27}

3.3.2 XPS Analysis

The passive films were formed on the surface of oil-grade alloy 718 samples by immersion at OCP for 1 h in 3.5 wt% NaCl solution at three different temperatures. XPS depth profiling results of surface films are shown in Figure 3.7 for the oxide films prepared at three different temperatures. At all temperatures, Cr-rich oxide compared to substrate was formed in the outer layer. It is notable that in the outer layer the content of Cr was increased with temperature. Both Ni and Fe concentrations were slightly low in the outer layer and increased with increasing sputtering time at all temperatures because of the selective dissolution. The difference in thickness of the passive films at three different temperatures were hardly to tell due to the films were very thin.

Figure 3.7 XPS depth profiling for passive films formed on oil-grade alloy 718 after immersion at OCP for 1 h in 3.5 wt.% NaCl solution at three different temperatures: (a) room temperature, (b) 50°C, (c) 80°C.

In order to understand the composition changes of passivation films, the fitted XPS detailed peaks of Cr2p, Ni2p, Fe2p, Nb3d and Mo3d for passive film formed at room temperature with different sputtering time are represented in Figure 3.8 (a)~(e), respectively. It shows that Ni and Cr contained hydroxides, and small amounts of Nb₂O₅ and MoO₃ oxides existed in the external surface of the passive film.

Figure 3.8 XPS detailed peaks for passive films formed on oil-grade alloy 718 after immersion at OCP for 1 h in 3.5 wt.% NaCl solution at RT: (a) Cr2p, (b) Ni2p, (c) Fe2p, (d) Nb3d, (e) Mo3d.

Before sputtering, Cr was initially observed in a completely oxidized state as Cr^{3+} , since the binding energy of Cr2p_{3/2} was found to be around 577.1 eV. For Cr^{3+} , the exact identification of the compound was difficult because the peak positions of $\text{Cr}(\text{OH})_3$ and Cr_2O_3 are very close [34, 35]. After 0.05 min sputtering, the new peak which was located at the binding energy of 574.4 eV, corresponding to metallic Cr was shown in the Cr2p spectra. Further sputtering to 0.15 min, the intensity of Cr oxide component was abruptly decreased.

At the beginning of sputtering, one major peak which was located at the binding energy of 853.0 eV and an associated satellite at about 858.8 eV were detected in Ni2p spectrum. Besides, an

additional low intensity peak at about 856.2 eV with an associated satellite at about 862.0 eV was clearly visible on the higher binding energy side of peak 853.0 eV. According to the literature data, these two features originated from metallic Ni and Ni(OH)₂, respectively. The metallic Ni peaks gained high intensity after removing the Ni(OH)₂ and became the dominant peak after 0.05 min sputtering, also another Ni oxide (NiO) at the binding energy of 854.4 eV was appeared. The spectra collected after longer sputtering times have similar features, indicating no further change of the chemical states.

In this study, the identification of iron chemical states relied on the peak position of Fe2p_{1/2}, since iron may exist in different valence states as well as in mixed valence, with the chemical shifts close to each other. Also nickel, as the major alloy element in alloy 718, has a strong Auger peak (711.7 eV) in the vicinity of Fe2p_{3/2} when using Al anode in XPS. Before sputtering, no obvious signals of Fe peak can be seen in the spectrum, indicating that Fe was dissolved during the electrochemical process. After sputtering 0.05 min, only one peak at about 720.4 eV, which is assigned to metallic Fe was found and remained all the same with increasing sputtering time.

It was found that Nb occurred in two oxidized states, as Nb⁵⁺ in Nb₂O₅ and Nb²⁺ in NbO, since the peak positions of Nb3d_{5/2} were at 207.3 eV and 203.3 eV, respectively. After 0.10 min sputtering time, the peak intensity of Nb₂O₅ is gradually becoming lower than the NbO component in the spectra.

From the Mo spectra it was observed that the oxidized state corresponding to MoO₃ was shown at the peak positions of 232.6.3 eV (Mo3d_{5/2}) and 235.6 eV (Mo3d_{3/2}), respectively. After 0.05 min sputtering, the MoO₃ was completely removed and the character peaks of metallic Mo at 228.0 eV (Mo3d_{5/2}) and 231.0 eV (Mo3d_{3/2}), respectively, were the only peaks showed up in the Mo3d spectrum, and became stronger with sputtering time. Therefore, Mo is present in the sample surface only with the metallic chemical state, and a very thin MoO₃ layer on the top of the surface.

The XPS detailed peaks of passive films formed at 50°C and 80°C were also shown similar trend with sputtering time, which illustrates that the chemical compositions of passive films were independent with investigated temperature. However, temperature affected the concentrations and distribution of Ni, Fe, Cr, Nb and Mo in the oxide films. This is reflected by the change of doped semiconductor properties of the passive film, which agrees with the M-S plots results. Table 3.5 shows the atomic concentration profiles of chemical species in the passive films according to the fitted XPS detailed peaks. It can be seen that Cr³⁺ hydroxide and oxide were the dominant

component in the passive films, and the atomic concentration of Cr^{3+} was increased with increasing temperature. The concentrations of other species in the oxide film did not change much with temperature.

Table 3.5 Atomic concentration profiles for chemical species of passivation films formed on oil-grade alloy 718 after immersion at OCP for 1 h in 3.5 wt.% NaCl solution at three different temperatures with sputtering time.

Temperature	Sputtering time (min)	Atomic concentration (%)									
		Cr^{3+}	Cr	$\text{Ni}(\text{OH})_2$	NiO	Ni	Fe	Nb_2O_5	NbO	MoO_3	Mo
RT	0	48.4	0	13.8	0	22.7	0	8.6	1.8	1.5	3.1
	0.05	10.5	14.6	0	14.9	41.9	11.3	2.6	2.0	0	2.2
	0.10	10.1	13.3	0	16.1	42.2	11.8	0.8	2.7	0	2.9
	0.15	5.5	16.9	0	14.2	41.8	13.9	0.9	3.4	0	3.4
50°C	0	54.7	0	11.6	0	16.5	0	11.1	1.0	2.7	2.3
	0.05	19.1	14.6	0	14.6	35.2	9.9	2.7	2.0	0	1.9
	0.10	6.4	15.2	0	20.2	39.7	12.1	1.3	2.8	0	2.4
	0.15	5.6	18.4	0	14.4	40.0	13.8	1.7	3.0	0	3.0
80°C	0	69.1	0	11.8	0	9.1	0	6.7	0	1.5	1.8
	0.05	22.7	15.9	0	12.9	33.1	8.9	3.1	1.4	0	2.0
	0.10	5.8	17.9	0	18.6	38.7	12.6	1.0	2.7	0	2.7
	0.15	4.3	18.5	0	15.8	41.4	12.3	0.9	3.5	0	3.2

The O1s spectra for the passive films formed at three different temperatures with sputtering time are shown in Figure 3.9. It was observed that there were two components, which were ascribed to oxides O^{2-} around 530.8 eV and hydroxides OH^- around 531.7 eV, indicating two layers of passive film formed at OCP for 1 h at all temperatures which consists of outer hydroxides and inner oxides. However, before sputtering the intensity of hydroxide was much higher than the oxides especially at 80°C, which means that the passive films formed at higher temperatures was more porous. It can be seen that the intensity of oxides was increased after 0.05 min sputtering, and when the sputtering time increased up to 0.10 min the hydroxides were completely removed.

Figure 3.9 O1s spectra for passive films formed on oil-grade alloy 718 after immersion at OCP for 1 h in 3.5wt.% NaCl solution at three different temperature with sputtering time: (a) room temperature, (b) 50°C, (c) 80°C.

The proportions of OH^- and O^{2-} in the O1s spectra of the passive films formed on oil-grade alloy 718 in 3.5 wt.% NaCl solution at three different temperatures are represented in Table 3.6.

Table 3.6 The proportion of OH^- and O^{2-} in O1s spectra of passive films formed on oil-grade alloy 718 after immersion at OCP for 1 h in 3.5 wt.% NaCl solution at three different temperatures with sputtering time.

Sputtering time (min)	Proportion (%)					
	RT		50°C		80°C	
	OH^-	O^{2-}	OH^-	O^{2-}	OH^-	O^{2-}
0	56.3	43.7	64.0	36.0	83.0	17.0
0.05	26.5	73.5	31.1	68.9	37.3	62.7
0.10	0	100	0	100	0	100

The concentration of OH^- of the outer layer was much higher than that of the inner layer. Moreover, the OH^- proportion was increased with temperature in both external and internal oxide layers, which means the passive films formed at high temperatures were more porous than the one formed at room temperature.

According to XPS results, a mixture of $\text{Cr}(\text{OH})_3$ and $\text{Ni}(\text{OH})_2$ hydroxides mainly concentrated on the top surface of the oxide film, while Cr_2O_3 and NiO oxides were enriched in the inner layer at all temperatures.

3.4 Discussion

It is well known that temperature has a significant effect on the rate of electrochemical corrosion of alloys.

Figure 3.10 shows the Arrhenius plots of the exchange current density vs. reciprocal temperature.

Figure 3.10 Arrhenius plots of the exchange current density for oil-grade alloy 718 in 3.5 wt.% NaCl solution at three different temperatures.

It is the linearity relationship in the Arrhenius plots, indicating that the passivation on oil-grade alloy 718 in 3.5 wt% NaCl solution can be considered as a thermally activated process, which is in accordance with the Arrhenius equation [26, 30]:

$$i = A \cdot \exp\left(\frac{-E_a}{RT}\right) \quad \text{Equation 3.3}$$

Where i is the current density, A is the pre-exponential factor, E_a represents the activation energy of the electrochemical reaction, R is the molar gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$), and T is the absolute temperature. The activation energy for passivation at OCP for oil-grade alloy 718 in 3.5 wt% NaCl solution is 8.96 KJmol^{-1} , which is in the region of the activation energy for liquid phase diffusion (below a value of 41.84 KJmol^{-1}) [27, 31]. Therefore, the passivation process of oil-grade alloy 718 in 3.5 wt% NaCl solution is controlled by ion diffusion in the liquid phase.

The effect of temperature on structure and composition of the passive film can be discussed on the basis of the formation mechanism of the double-layer oxide film. The activation energy obtained from Arrhenius plots was so low that the electrochemical process can be considered using

Castle-Masterson model, which believed that the corrosion process was limited by the solution phase transport of metallic ions through pores in the oxide film. The inner layer grows by access of OH^- to the oxide/alloy interface through the micropores in the oxide film, while the outer layer forms by the diffusion of metallic ions through micropores in the oxide film. XPS results showed that $\text{Cr}(\text{OH})_3$ -enriched passive film grew on the surface of oil-grade alloy 718 in 3.5 wt% NaCl solution by the selective dissolution of the other two major elements Fe and Ni, and the film formation rate was higher than the dissolution rate. The OH^- diffused inward through the oxide film and reacted with the Cr in the alloy at the metal/film interface.

With increasing passive time, the $\text{Cr}(\text{OH})_3$ will convert into Cr_2O_3 on the alloy surface and then further growth of Cr_2O_3 will happen to form a continuous Cr_2O_3 layer, which could resist the dissolution of the alloy as a barrier layer.

Then, the transport of Cr will slow down by the growth of Cr_2O_3 layer. However, the faster diffusing component like Ni will transport through the Cr_2O_3 layer, forming $\text{Ni}(\text{OH})_2$ in the outside layer and then dehydrating into NiO oxide .

$\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni}(\text{OH})_2$ $\text{Ni}(\text{OH})_2 \rightarrow \text{NiO} + \text{H}_2\text{O}$ Also, the new $\text{Cr}(\text{OH})_3$ could be formed by the reaction as follows:

Based on the above analysis, it was believed that the effect of temperature on the protective properties of passive film on oil-grade alloy 718 could be mainly attributed to the temperature dependent variation of the composition of the double layers.

3.5 Summary

(1) Solution temperature is an influencing factor on the pitting corrosion resistance of oil-grade alloy 718 in 3.5 wt% NaCl solution. The corrosion current density was increased by one time and the polarization resistance was decreased by one time as the temperature increased to 50°C. The pitting potential sharply dropped from 1150 mV_(Ag/AgCl) at room temperature to 436mV_(Ag/AgCl) at 50°C. Moreover, there was a small decrease of pitting corrosion resistance when the temperature was increased from 50°C to 80°C.

(2) The passive films formed on oil-grade alloy 718 in 3.5 wt% NaCl solution at three different temperatures exhibited n-type double-layer structure. The outer layer was composed of Cr and Ni hydroxides and small amounts of Nb_2O_5 and MoO_3 oxides, while the inner layer consisted of Cr_2O_3 , NiO and NbO oxides.

(3) The passive film became more porous as the temperature increased to 50°C and 80°C. The thickness of the outer layer was increased but the one of the inner layer was decreased with increasing temperature. The OH^- proportion was increased with temperature in both external and internal oxide layers.

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Chapter 4: Corrosion Fatigue Crack Growth Behavior of Oil-Grade Alloy 718 in NaCl Solution

4.1 Introduction

Nickel-base alloy 718 was originally developed for use in aircraft gas turbine engines in aerospace industry, but recently has been extensively used by the oil and gas industry for a variety of applications due to its high strength, good corrosion resistance and ability to be heat treated to various strength levels [1-7]. Nevertheless, due to the presence of a significant amount of δ phase and a distribution of γ'/γ'' designed for maximum strength and creep resistance, the aerospace-grade alloy 718 is not desirable for maximum resistance to corrosion and environmental induced cracking in extremely corrosive wells. Thus alloy 718 has been redesigned and developed to improve the corrosion resistance and environmental induced cracking resistance at the same time to maintain desired mechanical properties.

Oil-grade alloy 718 has been specified by API Specification 6A 718 for nickel-base alloy 718 used in oil and gas drilling and production equipment in terms of composition, microstructure, heat treatment and mechanical properties [8]. It is well known that alloy 718 can be properly heat-treated to achieve the optimum microstructure and the required properties [2-7]. The oil-grade alloy 718 is solution treated at the temperature of 1021°C–1052°C for one hour minimum to two and a half hours maximum, followed by single-step aging treatment at 774°C–802°C for six to eight hours [3-5]. This choice of specific heat treatment can provide an optimum combination of fracture toughness ≥ 220 MPa $\sqrt{\text{m}}$, yield strength ≥ 827 MPa and hardness $\leq$ HRC 40 [3, 5]. However, as the modern oil and gas industry explored into coastal and marine locations, deeper wells have been drilled with high pressure high temperature, making the demand for increased strength and toughness super critical in high pressure high temperature ultra-deep well drilling [9, 10]. As a result, the two-step aging treatment, i.e., at 760 °C for 4–5 hours and then at 650 °C for 4–5 hours, which is used to maximize the yield strength of aerospace-grade alloy 718, has been used and modified for oil-grade alloy 718 in recent years [7].

Oil-grade alloy has been now directly utilized in bottom hole assembly components such as drill collars and measurement while drilling tools, where it applies a combination of high fatigue strength, good corrosion resistance and non-magnetism in high concentration chloride solution environment [6, 7]. The fatigue strength of alloy 718 has been widely studied [11-24], however,

corrosion fatigue behaviors in aqueous solution have previously received little investigation, especially in NaCl solution. Moreover, it has been reported in our previous research that the pitting corrosion behavior of oil-grade alloy 718 in high chloride solution at room temperature did not change in spite of different heat treatments, however, the fatigue strength was significantly increased by the two-step aging treatment [7]. Thus, it is meaningful to determine whether this two-step aging treatment can also lead to much higher corrosion fatigue strength in different chloride solutions.

The first aim of this study is to investigate the effect of aging treatment on the microstructure of oil-grade alloy 718. The second aim is to study the corrosion fatigue crack growth behavior of oil-grade alloy 718 with different aging treatments in several aerated NaCl solutions with variations in temperature and NaCl concentrations.

4.2 Experimental

4.2.1 Materials

The oil-grade alloy 718 used in this study was manufactured by ThyssenKruppVDM and the chemical composition is listed in Table 4.1.

Table 4.1 Chemical composition of oil-grade alloy 718

Ni	Cr	Fe	Nb	Mo	Ti	Al	Co	Si	Mn	C	Cu	Ta
52.66	18.34	19.18	4.96	3.00	0.95	0.49	0.16	0.06	0.05	0.03	0.04	0.01
P	B	S	Pb	Se	Bi							
0.006	0.003	0.001	0.0002	<0.0003	<0.00003							

The alloy was solution-annealed (SA) at 1026°C for 1.5 h then water quenched (WQ). In order to study the aging effect, the solution-annealed alloy was aging treated by one-step aging and two-step aging, respectively in the materials laboratory at Baker Hughes. The alloy 718 referred to as Alloy 718–TSA was age hardened according to the two-step aging treatment procedure in Baker Hughes. The samples referred to as Alloy 718–OSA was age hardened according to the API 6A 718 specification. The detailed information of the samples with different heat treatment is listed in Table 4.2.

Table 4.2 Sample information with different heat treatment conditions

Sample	Solution Annealing	Age Hardening
Alloy 718-SA	1026 °C/1.5h, WQ	None
Alloy 718-OSA	1026 °C/1.5h, WQ	780 °C $\pm$ 8 °C/8 h, AC
Alloy 718-TSA	1026 °C/1.5h, WQ	760 °C $\pm$ 8 °C/4.5 h, 650 °C $\pm$ 8 °C/5 h, FC

The mechanical properties of three different oil-grade alloy 718 samples addressed in the material specifications are shown in Table 4.3. It is observed that the yield strength of Alloy 718-SA increases about 1 time as compared with Alloy 718-OSA and Alloy 718-TSA. However, there is only small difference of the strength between two different age treated alloy 718 samples.

Table 4.3 Mechanical properties of oil-grade alloy 718 with different heat treatment conditions

Sample	Tensile Strength	Yield Strength	Elongation	Reduction of Area	Impact Strength	Hardness
Alloy 718-SA	> 965 MPa	> 520 MPa	> 30%	—	—	> 260 HB
Alloy 718-OSA	> 1150 MPa	> 965 MPa	> 20%	> 30%	>90 J	> 325 HB
Alloy 718-TSA	> 1250 MPa	> 1100 MPa	> 18%	> 30%	>80 J	> 365 HB

4.2.2 Microstructure Observation

The microstructure of all three alloys was examined by means of optical microscope (OM), scanning electron microscope (SEM) and transmission electron microscope (TEM), respectively. The specimens mounted in epoxy were mechanical ground by 120–1200 grit silicon carbide waterproof papers and polished with 3 μ m and 1 μ m diamond suspension, followed by 4 min chemical etching with Kalling's solution which was consisted of 200 ml methanol, 200 ml hydrochloric acid and 10 g CuCl₂. A JEOL JSM-7600F SEM equipped with an Oxford Inca energy-dispersive X-ray spectrometry (EDS) system was used to examine the microstructure and phases in these alloys. For TEM analysis, specimens were first ground to about 50 μ m in thickness then finally thinned by twin-jet electrolytic polishing using a solution containing 10% perchloric acid and 90% ethanol at a current of 90 mA at –20 °C. The TEM foils were observed in the JEOL 2010 TEM at 200 kV.

4.2.3 Potentiodynamic Polarization

1.0 cm $\times$ 1.0 cm $\times$ 2.0 mm specimens were cut from the alloys by using electrical discharge machining (EDM). All electrochemical measurements were performed by using an aerated NaCl solution, prepared with deionized water. All specimens were mounted using epoxy, ground with silicon carbide (SiC) papers starting from 120 grit and finishing with 800 grit, rinsed with distilled water, dried in air at room temperature and then transferred to the test solution. These experiments

were set up according to ASTM standard G5–94 with a three electrode cell in a 1.5 L glass container. The three electrode cell setup consisting of a pair of graphite counter electrodes (CE), an Ag/AgCl reference electrode (RE) immersed in a saturated potassium chloride (KCl) solution and the specimen as the working electrode (WE) was employed. Potentials cited in this chapter are all referred to Ag/AgCl. Experiments for each specimen condition were conducted at least five times with the results averaged. At the beginning of each experiment, the working electrode was first cathodically polarized at $-1 \text{ V}_{(\text{Ag/AgCl})}$ for 10 min to remove the air-formed surface oxides because it has been proved that the reproducibility of electrochemical measurements performed on passive films was improved after cathodic polarization. Potentiodynamic polarization curves were performed using a Solartron SI 1287. For this series of tests, the specimens were immersed in the solution for 1 h prior to the measurement in order to stabilize the surface at OCP after cathodic pretreatment. The test was performed at a scanning rate of 0.5 mV/s starting from $-0.5 \text{ V}_{(\text{Ag/AgCl})}$ towards the anodic direction until the 10^{-4} A/cm^2 of current density was reached.

4.2.4 Fatigue Test Sample Preparation

The as-received alloy 718 specimen supplied by Baker Hughes was machined into single-edge-notched (SEN) plate with special designed dimensions for corrosion fatigue crack growth rate testing, as shown in Figure 4.1 (a). All these specimens were polished to a grit of 600 finish, as seen in Figure 4.1 (b). For the CFCG tests in NaCl solution, specimen surface was covered with vinyl tape and silicone rubber except for a narrow region near each side of the notch.

Figure 4.1 (a) Scheme of CFCG testing specimen (unit: mm), (b) Image of the polished specimen.

Figure 4.2 gives an example of how to prepare the CFCG sample before placing it into the testing container.

Figure 4.2 An example showing how to prepare the CFCG sample before placing it into the testing container: (a) covering specimen with 2 mm² exposed area, (b) connecting wires for potential drop and electrochemical measurements, (c) protecting wires tip with silicone rubber.

4.2.5 Fatigue Test Setup

FCG experiments were carried out on a material test system (MTS) with a computer controlled data acquisition system. The crack propagation was continuously monitored by using a direct current (DC) potential drop technique. A power supply was used to provide constant current to the specimen. As the crack length of the specimen increased, the resistance of the specimen increased resulting in an increase of potential drop across the crack. The change in the voltage was detected by the multimeter, which would send the message to the computer. The AutoLab electrochemical station was used to monitor the open-circuit potential during corrosion fatigue testing. All the potentials were measured with respect to a silver chloride reference electrode, and a platinum plate was used as counter electrode. The solution container was built by the material of aluminum 5052 which has relative good corrosion resistance and low weight. The corrosive solution was heated up using a single resistant heating rope that wrapped around the container and controlled by a temperature controller. The solution temperature was monitored by a T-type thermocouple during the test. The overall CFCG testing setup in the laboratory and aluminum container are shown in Figure 4.3.

Figure 4.3 (a) Overall CFCG testing setup and (b) aluminum container used for this study.

4.2.6 Fatigue Test Procedure

FCG tests were carried out in laboratory air and four different aerated NaCl solutions. The information details of each test are listed in Table 4.4.

Table 4.4 Fatigue crack growth rate test matrix

No.	Sample	Testing Environment
1	Alloy 718-SA	Laboratory air, RT
2	Alloy 718-OSA	Laboratory air, RT
3	Alloy 718-TSA	Laboratory air, RT
4	Alloy 718-SA	3.5 wt.% NaCl, RT
5	Alloy 718-OSA	3.5 wt.% NaCl, RT
6	Alloy 718-TSA	3.5 wt.% NaCl, RT
7	Alloy 718-SA	3.5 wt.% NaCl, 50°C
8	Alloy 718-OSA	3.5 wt.% NaCl, 50°C
9	Alloy 718-TSA	3.5 wt.% NaCl, 50°C
10	Alloy 718-SA	3.5 wt.% NaCl, 80°C
11	Alloy 718-OSA	3.5 wt.% NaCl, 80°C
12	Alloy 718-TSA	3.5 wt.% NaCl, 80°C
13	Alloy 718-SA	21 wt.% NaCl, 80°C
14	Alloy 718-OSA	21 wt.% NaCl, 80°C
15	Alloy 718-TSA	21 wt.% NaCl, 80°C

Prior to FCG tests, all specimens were pre-cracked in laboratory air by using a triangle waveform loading cycle at a frequency of 10 Hz. In the CFCG tests, the corrosive solution was poured into

the container and heated up to the desired temperatures, then stabilized for 1h before testing. Each specimen was loaded with triangular waveform at a load ratio ($R = \text{minimum load}/\text{maximum load}$) of 0.1 with a loading frequency of 1 Hz. In both pre-crack and crack growth testing, the same constant loading of a minimum of 890 N and a maximum of 8896 N was applied. However, the actual applied loads by the hydraulics were 1333 N minimum and 8452 N maximum resulting in $R = 1.58$. The crack length was measured using the direct current potential drop technique with an applied current of 10 A. The voltage was measured and recorded by a strain gage input channel connected to the MTS controller with a resolution of 1 mV. After the test, each specimen was pulled apart, and the fractured surface was examined by using a JEOL JSM-7600F SEM.

4.2.7 Data Processing

A MATLAB program was written to remove the noise and calculate the change in crack length and stress intensity factor K from the recorded voltage data.

The new crack length would be calculated according to Johnson's equation:

$$A = \frac{2W}{\pi} \times \cos^{-1} \left[\frac{\cosh(\pi Y / 2W)}{\cosh\{(U / U_0) \cosh^{-1}[\cosh(\pi Y / 2W) / \cos(\pi A_0 / 2W)]\}} \right] \quad \text{Equation 4.1}$$

Where A is the actual crack length, A_0 is the initial crack length, Y is one half of the potential prove span, W is the width of the specimen, U_0 is the initial measured potential drop, U is the updated measured potential drop. The Johnson's equation is valid only for SEN type of specimens.

Tada's equation was used to evaluate the K with the obtained new crack length.

$$K = \frac{P}{B\sqrt{w}} \frac{\sqrt{2 \tan \theta}}{\cos \theta} \left[0.752 + 2.02 \left(\frac{A}{W} \right) + 0.37(1 - \sin \theta)^3 \right] \quad \text{Equation 4.2}$$

Where P is the applied load, B is the plate thickness, and $\theta = \frac{\pi A}{2W}$.

4.3 Results

4.3.1 Microstructure

Figures 4.4 and 4.5 show the typical microstructure of three alloys obtained from optical microscopy (OM) and SEM, respectively. Based on the criteria in API specification 6A718, both aged specimens were judged to be acceptable for oil-grade alloy 718. After solid solution treatment, the average grain size of Alloy 718-SA is about 46 μm . The average grain sizes of Alloy

718–OSA and Alloy 718–TSA have grown to 52 μm and 60 μm , respectively. Neither Laves phases nor acicular delta phases are present in the matrix. The amount of globular delta phases is within the acceptable levels.

Figure 4.4 Optical micrographs of three alloys: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

Figure 4.5 SEM images of three alloys: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

SEM image of Alloy 718-SA is shown in Figure 4.6 (a), where carbides and nitrides are both distributed along the grain boundaries and within the grains. EDS analysis in Figures 4.6 (b) and (c) have verified that the big globular particles are (Nb,Ti)C carbides and the rectangular shaped inclusions are (Ti,Nb)N nitrides.

Figure 4.6 (a) Higher magnification SEM image showing carbides and nitrides, EDS spectrum from (b) (Nb, Ti)C and (c) (Ti, Nb)N.

Thin foil TEM analysis shown in Figures 4.7–4.9 found inclusions, annealing twins and planar type dislocations in this specimen.

Figure 4.7 (a) shows the bright field (BF) image recorded from the alloy matrix and the corresponding diffraction pattern, indicating that the matrix is a FCC nickel-base austenitic phase. Some grain boundaries shown in Figure 4.7 (b) are generally free of inclusions. Globular shaped carbides and rectangular shaped nitrides are clearly observed inside the grains, as shown in Figure 4.7 (c) and Figure 4.7 (d), respectively.

Annealing twins formed during solution annealing treatment can be observed in Figures 4.8 (a) and (b). Some carbide is also present at the twin/matrix interface, as illustrated in Figure 4.8 (c).

Figure 4.9 presents the dislocation structures found in the alloy. Dislocations at grain boundaries and twin boundaries are observed in Figure 4.9 (a). Some dislocations exist close to inclusions formed within the grains, as shown in Figure 4.9 (b).

Figure 4.7 TEM images of Alloy 718-SA: (a) BF image, (b) BF image in higher magnification showing grain boundaries, (c) carbide, (d) nitride.

Figure 4.8 TEM images showing twinning structures in Alloy 718-SA: (a) BF image, (b) BF image in higher magnification, (c) carbide at twin/matrix interface.

Figure 4.9 TEM images showing dislocations in Alloy 718-SA: (a) at grain boundaries and twin boundaries, and (b) near inclusions.

SEM images of Alloy 718–OSA are shown in Figure 4.10. As observed in Alloy 718–SA specimen, Alloy 718–OSA sample also contains (Nb, Ti)C and (Ti, Nb)N particles along the grain boundaries and within the grain matrix as shown in Figure 4.10 (a). Nevertheless, isolated platelet δ phases were precipitated at some of the grain boundaries as revealed in Figure 4.10 (b). Therefore, it can be concluded that the platelet δ particles are present in an acceptable amount in Alloy 718–OSA. A depletion of precipitates is observed surrounding grain boundaries due to the formation of δ phases and illustrated in the higher magnification SEM image (Figure 4.10 (c)). Moreover, Figure 4.10 (d) shows a uniform distribution of very fine spherical and elongated precipitates in the grains.

Figure 4.10 SEM images of Alloy 718–OSA showing: (a) carbides and nitrides, (b) δ phases, (c) δ phases in higher magnification, (d) γ' and γ'' precipitates.

TEM analysis of the specimen in Figure 4.11 shows that the fine precipitates consist of γ' and γ'' phases. Figure 4.11 (a) displays the BF image recorded from the alloy matrix. The identification of these precipitates was made from the $[001]$ electron diffraction pattern as shown in Figure 4.11 (b). It is assumed from the diffraction pattern that both γ' and γ'' phases are present in this sample. The superlattice reflections $\{100\}$, $\{010\}$ and $\{110\}$ on the selected area diffraction of $\langle 001 \rangle$ orientation are both due to γ' and γ'' phases, whereas, $\{1\ 1/2\ 0\}$ and $\{1/2\ 1\ 0\}$ type reflections only belong to γ'' phase [25-28]. However, it should be pointed out that some of the reflections from the γ'' precipitates are superimposed on all the reflections

from the γ' precipitates. Therefore, the diffraction pattern only confirms the presence of γ'' precipitates. However, the presence of γ' precipitates can be illustrated by the dark field (DF) images. Figure 4.11 (c–e) demonstrates the three variants of γ'' . Also, γ' precipitates were observed but they were not as pronounced in the DF as γ'' precipitates. Spherical γ' precipitates are approximately in 20–30 nm diameter while the γ'' disks are 5–15 nm in the c dimension and the diameter is in the range of 30–150 nm.

Figure 4.11 TEM images of Alloy 718-OSA: (a) BF micrograph; (b) [001] zone axis SAD pattern; (c) DF image of point 1; (d) DF image of point 2; (e) DF image of point 3.

SEM images of Alloy 718–TSA are shown in Figure 4.12. (Nb, Ti)C and (Ti, Nb)N inclusions can be seen in Alloy 718–TSA sample as shown in Figure 4.12 (a). Moreover, isolated platelet δ phases were formed in an acceptable amount at some of the grain boundaries in Alloy 718–TSA as illustrated in Figure 4.12 (b). A depletion of γ' and γ'' precipitates is also observed surrounding grain boundaries due to the formation of δ phases and revealed in the higher magnification SEM image in Figure 4.12 (c). Figure 4.12 (d) shows a uniform distribution of much finer γ' and γ'' precipitates in the grains.

Figure 4.12 SEM images of Alloy 718–TSA showing: (a) carbides and nitrides, (b) δ phases, (c) δ phases in higher magnification, (d) γ' and γ'' precipitates.

Figure 4.13 shows the TEM images of γ' and γ'' precipitates in Alloy 718–TSA. Figure 4.13 (a) displays the BF image recorded from the alloy matrix. The identification of these precipitates was made from the $[001]$ electron diffraction pattern as shown in Figure 4.13 (a). It is assumed from the diffraction pattern that both γ' and γ'' phases are present in this sample. The superlattice reflections $\{100\}$, $\{010\}$ and $\{110\}$ on the selected area diffraction of $\langle 001 \rangle$ orientation are both due to γ' and γ'' phases, whereas, $\{1\ 1/2\ 0\}$ and $\{1/2\ 1\ 0\}$ type reflections only belong to γ'' phase. Figure 4.13 (b–d) demonstrates the three variants of γ'' . Since the

precipitates are too small, γ' precipitates could not be clearly observed and differentiated from γ'' phases.

Figure 4.13 TEM images of Alloy 718–TSA: (a) BF micrograph and [001] zone axis SAD pattern; (b)–(d) γ' and γ'' precipitates.

Figure 4.14 illustrates the high resolution TEM images of Alloy 718–TSA. It is shown that a high amount of γ' and γ'' phases was precipitated after the two-step aging treatment. The γ' is in globular shape with a size of 5–15 nm and the γ'' is in disc shape with a diameter of 10–30 nm, which are much smaller than the ones formed during the one-step aging treatment.

Figure 4.14 TEM images of Alloy 718-TSA: (a)–(c) γ' and γ'' precipitates, (d) δ phases on the grain boundary.

4.3.2 Potentiodynamic Polarization

4.3.2.1 Effect of Aging Treatment

Figure 4.15 illustrates the effect of aging treatment on potentiodynamic polarization curves measured in four different aerated NaCl solutions. Electrochemical parameters including corrosion potential (E_{corr}), pitting potential (E_{pit}) and corrosion current density (i_{corr}) obtained from potentiodynamic polarization curves are listed in Table 4.5. E_{pit} was defined as the potential at which the current density increases significantly and rather rapidly above the passive current density. The i_{corr} values were determined by means of the Tafel extrapolation method by using the cathodic branches of the polarization curves because they display well-defined cathodic Tafel regions exist over one decade of current density. It can be observed that aging treatment has no noticeable effect on the polarization characteristics for oil-grade alloy 718 in all testing environments, indicating that alloy 718 with different aging treatments has similar susceptibility to pitting corrosion in these NaCl solutions.

Figure 4.15 Potentiodynamic polarization curves of oil-grade alloy 718 in four different NaCl solutions: (a) 3.5 wt.% NaCl at RT, (b) 3.5 wt.% NaCl at 50°C, (c) 3.5 wt.% NaCl at 80°C, (d) 21 wt.% NaCl at 80°C.

Table 4.5 Potentiodynamic polarization results of oil-grade alloy 718 in different NaCl solution environments

Sample–Environment	E_{corr} (mV _{Ag/AgCl})	E_p (mV _{Ag/AgCl})	i_{corr} ($\mu\text{A}/\text{cm}^2$)
Alloy 718–SA, 3.5 wt.% NaCl at RT	–260	1150	0.21
Alloy 718–SA, 3.5 wt.% NaCl at 50°C	–166	436	0.40
Alloy 718–SA, 3.5 wt.% NaCl at 80°C	–125	434	0.45
Alloy 718–SA, 21 wt.% NaCl at 80°C	–47	—	0.50
Alloy 718–OSA, 3.5 wt.% NaCl at RT	–247	1110	0.22
Alloy 718–OSA, 3.5 wt.% NaCl at 50°C	–139	409	0.32
Alloy 718–OSA, 3.5 wt.% NaCl at 80°C	–94	396	0.38
Alloy 718–OSA, 21 wt.% NaCl at 80°C	–8	—	0.44
Alloy 718–TSA, 3.5 wt.% NaCl at RT	–246	1109	0.21
Alloy 718–TSA, 3.5 wt.% NaCl at 50°C	–178	405	0.46
Alloy 718–TSA, 3.5 wt.% NaCl at 80°C	–94	395	0.49
Alloy 718–TSA, 21 wt.% NaCl at 80°C	–9	—	0.55

4.3.2.2 Effect of Testing Environment

Figure 4.16 compares the influence of different aerated NaCl solutions on potentiodynamic polarization curves for the three types of alloy 718 specimens. As shown in Figure 4.16, the active, passive, and transpassive regions can be seen clearly in the potentiodynamic polarization curves measured in 3.5 wt.% NaCl solution at three different temperatures, demonstrating that alloy 718 exhibits passive behavior in these corrosive environments. However, the electrochemical behavior of oil-grade alloy 718 in 21 wt.% NaCl solution at 80°C

is quite different. The anodic current is observed to continue rising with increasing potential, and there is no clear passive range can be defined in the potentiodynamic polarization curves obtained in 21 wt.% NaCl solution at 80°C for all samples, indicating that the metal dissolution behavior of the alloys in this environment is active corrosion. By using the results of 3.5 wt.% NaCl solution at RT as the baseline data for comparison, it is clear observed from Figure 4.13 and Table 4.5 that E_{pit} is decreased with an increase in temperature of 3.5 wt.% NaCl solution from RT to 50°C. Further increase solution temperature to 80°C results in similar E_{pit} values. It can also be seen that i_{corr} values are increased with an increase in solution temperature. These comparisons clearly demonstrate that alloy 718 is more susceptible to pitting corrosion in 3.5 wt.% NaCl solution with a higher temperature, indicated by the decreased E_{pit} and increased i_{corr} values. In addition, with an increase in the NaCl concentration in the corrosive solution at 80°C, the passive region was eliminated. This might be ascribed to the presence of high Cl^- concentration, leading to break down the porous passive films more easily.

Figure 4.16 Potentiodynamic polarization curves of oil-grade alloy 718 in four different NaCl solutions: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

4.3.3 Corrosion Fatigue Crack Growth Rate

4.3.3.1 Effect of Aging Treatment

Figure 4.17 shows the effect of aging treatment on the CFCG rates of oil-grade alloy 718 samples in different test conditions. It is clearly seen that the CFCG rates of Alloy 718-OSA and Alloy 718-TSA specimens are significant lower than the rates of Alloy 718-SA specimen in all conditions in the ΔK range of 25–60 MPa $\sqrt{m}$, which is in accordance with the published results on the effect of heat treatment on the FCG rate of alloy 718 [18-21, 29]. James et al. [18] have reported that the FCG rate of IN718 in annealed condition is generally higher than that in

heat-treated one, except at the low ΔK region where a sharp transition to lower growth rates is observed. This illustrates that the big difference of mechanical properties and formation of strengthening precipitates induced by aging treatment have noteworthy influence on the CFCG rates of oil-grade alloy 718 in all testing environments. The difference of CFCG rates between the solution annealed and two aged samples are higher at high ΔK range than the low ΔK range. Compared with the aged specimens, the FCG rate of solution annealed alloy 718 in laboratory air and NaCl solution are about 0.8 to 1 time larger at $\Delta K = 25 \text{ MPa}\sqrt{\text{m}}$, and are about 1.3 to 2 times larger at $\Delta K = 50 \text{ MPa}\sqrt{\text{m}}$. In addition, there is no visible difference of CFCG rates between Alloy 718–OSA and Alloy 718–TSA specimens in all testing conditions. These results indicate that the metallurgical difference between Alloy 718–OSA and Alloy 718–TSA specimens in terms of different amount and size of precipitates has no effect on the CFCG rates of oil-grade alloy 718 in all testing conditions.

Figure 4.17 Effect of aging treatment on the CFCG rates of oil-grade alloy 718 specimens in (a) air, (b) 3.5 wt.% NaCl solution at RT, (c) 3.5 wt.% NaCl solution at 50°C, (d) 3.5 wt.% NaCl solution at 80°C, (e) 21 wt.% NaCl solution at 80°C.

4.3.3.2 Effect of Testing Environment

The CFCG tests results of three different oil-grade alloy 718 specimens tested in all the given environments are plotted as (da/dN) vs (ΔK) in Figure 4.18. For all samples, the crack growth rate generally increases as the ΔK value increased. The CFCG rates of alloy 718 indicated by the results are independent of the test environments, except for 21 wt.% NaCl solution with a temperature of 80°C at the lower ΔK region. It can be seen that the 3.5 wt.% NaCl solution, regardless of solution temperature, has little or no obvious effect on the CFCG rates of oil-grade alloy 718 in three different conditions. It is indicated that the environmental enhancement effect of 3.5 wt.% NaCl solution on the CGCG behavior of alloy 718 is not observed in this research, and the mechanical rather than environmental factors predominates in the FCG process in this particular material-environment system. It is observed that 21 wt.% NaCl solution with a temperature of 80°C produces a deleterious effect on the CFCG behavior of alloy 718 indicated by the increased CFCG rates as compared with the ones in 3.5 wt.% NaCl and in air in the lower ΔK range, however, the effect seems to be diminishing at higher ΔK levels indicating that the CFCG mode changes from corrosion-mechanical driven to pure mechanical driven. In comparison to laboratory air, 21 wt.% NaCl solution increases the CFCG rates by about 60% to 120% in the lower ΔK range of 20–30 MPa $\sqrt{m}$ for Alloy 718–SA. As the ΔK increases, the CFCG rates in 21 wt.% NaCl solution at 80°C are almost similar to the rates

in air. For Alloy 718–OSA, the CFCG rates in 21 wt.% NaCl solution at 80°C are about 40% to 80% larger than the rates in air in the ΔK range of 25–50 MPa $\sqrt{\text{m}}$ and are almost equal to the rates in air in the ΔK range of 50–65 MPa $\sqrt{\text{m}}$. For Alloy 718–TSA, the CFCG rates in 21 wt.% NaCl solution at 80°C are about 30% to 90% faster than the rates in air in the ΔK range of 25–55 MPa $\sqrt{\text{m}}$ and are similar to the rates in air in the ΔK range of 55–65 MPa $\sqrt{\text{m}}$.

Figure 4.18 Effect of testing environment on the CFCG rates of oil-grade alloy 718 specimens in different NaCl solutions: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

4.3.4 Fractography

The fracture surfaces of oil-grade alloy 718 after CFCG tests in air and four different NaCl solution environments are shown Figures 4.19–4.23. The fatigue cracks propagate in the transgranular mode in oil-grade alloy 718 in all tested conditions, regardless of solution temperature and NaCl concentration. Mixed brittle cleavage and ductile striations are easily observed on the fracture surfaces for all situations, as illustrated in Figure 4.24 (a) and (b), respectively. Some secondary cracks are also observed on the fracture surface, as shown in Figure 4.24 (c). Corrosion products are found on the fracture surfaces tested in NaCl solution, but not observed on the ones tested in air (Figure 4.24 (d)).

In comparison with the fractographs in air, the fractographs in NaCl solution show the same fracture mode and the difference is only the corrosion products covering the fracture surface. The corrosion products are much easier found in the low ΔK range than in the high ΔK range for the samples tested in 3.5 wt.% NaCl solution. The reason may be because the corrosion products found on the fracture surface in the low ΔK levels are due to the corrosion occurred on the fracture surface rather than the crack tip region, resulting the fracture surface in the low ΔK region exposed to the NaCl solution for a longer time than the area in the high ΔK region.

Figure 4.19 The fractographs of oil-grade alloy 718 specimens after CFCG rate testing in air: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

Figure 4.20 The fractographs of oil-grade alloy 718 specimens after CFCG rate testing in 3.5 wt.% NaCl at RT: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

Figure 4.21 The fractographs of oil-grade alloy 718 specimens after CFCG rate testing in 3.5 wt.% NaCl at 50°C: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

Figure 4.22 The fractographs of oil-grade alloy 718 specimens after CFCG rate testing in 3.5 wt.% NaCl at 80°C: (a) Alloy 718–SA, (b) Alloy 718–OSA, (c) Alloy 718–TSA.

Figure 4.23 The fractographs of oil-grade alloy 718 specimens after CFCG rate testing in 21 wt.% NaCl at 80°C: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

Figure 4.24 SEM images showing typical fracture surface characteristics: (a) and (b) mixed brittle cleavage and ductile striations in low and high magnifications, (c) secondary cracks, and (d) corrosion products.

Figure 4.25 compares varied features of fracture surfaces of oil-grade alloy 718 samples with three different aging treatments. As shown in Figure 4.25 (a), the mode of fracture of Alloy 718–SA appears to be transgranular, faceted, crystallographic fracture mode, as can be observed by the sharp, big, and angular facets in the fracture surfaces. Moreover, very fine fatigue striations and

river-shape cleavage can be seen on some of the facets. However, the extent of crystallographic facets failure decreases for Alloy 718–OSA and Alloy 718–TSA fracture surfaces.

Figure 4.25 SEM images showing different features of fracture surfaces for oil-grade alloy 718 samples with various aging treatments: (a) Alloy 718-SA, (b) Alloy 718-OSA, (c) Alloy 718-TSA.

4.4 Discussion

4.4.1 Effect of Aging Treatment on Corrosion Fatigue Crack Growth Rate

On the basis of our previous microstructure analysis, aged oil-grade alloy 718 specimens reveal relatively larger grain size, isolated platelet δ phases along some of the grain boundaries, and fine γ'/γ'' precipitates formed within the grains compared to the solution-annealed one. Meanwhile, the two-step aged specimen showed much finer γ'/γ'' precipitates in comparison with the one-step aged one. These different heat treatment processes resulted in various mechanical properties of oil-grade alloy 718. It should be pointed out that the two aged samples have much higher strength and hardness than the only solution-annealed one because of the γ'/γ'' precipitation, however, there is no big discrepancy in the mechanical properties between those two age-treated alloy 718 although they exhibit different precipitates morphologies. The effect of heat treatment in terms of microstructure and mechanical properties on FCG rates in alloy 718 has been extensively studied [7, 18-21, 30-35]. Tsay et al. [29] have investigated the FCG behavior of IN 718 plate and laser annealed specimens in air. Their results have indicated that both solution-annealed and aged IN 718 specimens showed similar fatigue properties in air in the low ΔK range, even though they had

significant differences in tensile strength and impact toughness. They have suggested that those fine precipitates formed during aging treatment did not resist dislocation shearing, thereby had little influence on the retardation of crack growth. Moreover, the solution-annealed sample had higher FCG rates than the aged one at the $\Delta K > 30 \text{ MPa}\sqrt{\text{m}}$, while the laser-annealed specimen had higher FCG resistance than the bulk. Ghonem has pointed out that microstructure factors including precipitate size, grain size, and morphology cause the degree of homogeneity of plastic deformation and associated slip density become the influencing parameters at the crack tip, thus in turn greatly had an effect on the FCG rates. Published TEM results have shown that fine γ'' precipitates were sheared by dislocations, slip and twinning, which could hamper fatigue crack propagation [24, 36-38]. According to Pedron and Pineau [39], the coarsening of γ'' particles would alter the mechanism of dislocation motion from shearing to bypassing them through Orowan process, which could cause a homogeneous slip process thus leading to an increase in the intergranular crack tip resistance. The results of the present study confirms the advantage of γ'/γ'' precipitates microstructure formed during both one-step and two-step aging treatments when compared to the purely γ austenitic phase in terms of FCG rates in air. It is deduced that the shearing mechanism of γ'/γ'' precipitates results in the lower FCG rate of oil-grade alloy 718 in air. Our potentiodynamic polarization results show that three types of alloy 718 have similar corrosion performance in 3.5 wt. % NaCl solution at different temperatures, however, three specimens still display the similar difference of CFCG rates in 3.5 wt. % NaCl solution as the one in air. This may be due to the predominant mechanism of mechanical loading rather than corrosion controlling mechanism.

4.4.2 Effect of Testing Environment on Corrosion Fatigue Crack Growth Rate

The CFCG behavior of stainless steels and nickel-base alloy in NaCl solution has been determined in a large number of studies [40-47]. On one hand, Lin et al. [44] have indicated that all the given NaCl solutions produced essentially detrimental effects on the CFCG rates of UNS S45000

martensitic stainless steel from the air values. Masuda et al. [46] have investigated the influence of corrosion in fatigue crack propagation of 304 stainless steel under various frequencies in 3% NaCl solution. Their results have shown that the contributions of corrosion to the CFCG rates are dependent on testing frequency. On the other hand, Krishnan [48] has observed that the crack growth rates in air and 3.5% NaCl solution are the same at low ΔK levels, while with an increase in ΔK the crack growth rate in NaCl solution is higher than the one in air. Mohamed [47] has reported that the fatigue lives of nickel based alloys including IN600, IN601 and C22 alloys in 3.5% NaCl solution at pH = 6.8 are essentially the same as for the ones tested in air. The work done by Ho et al. [42] has shown that the environmental enhancement on the FCG rates of Alloy 600 is no significant in the NaCl solution.

Our test results show that the FCG rates of oil-grade alloy 718 in air and in 3.5 wt.% NaCl solution at three different temperatures have no significant discrepancy with each other. It has been reported that the presence of Cl^- in solution may result in a localized acidification of the crack tip caused by the metal dissolution and subsequent hydrolytic reactions, which could result in a higher crack growth rate of the alloy in NaCl solution. However, the CFCG rates of alloy 718 in 3.5 wt.% NaCl solution at RT are similar to the rates in laboratory air. The probable reason may be that the anodic dissolution rate of alloy 718 in 3.5 wt.% NaCl solution at RT at the crack tip is much lower than the rate of mechanical damage at the crack tip due to cyclic loading. It is seen from the potentiodynamic polarization curves obtained in 3.5 wt.% NaCl solution at RT that alloy 718 is in passive state. Thus, it is assume that t the CFCG rates are similar in air and 3.5 wt.% NaCl solution at RT because the repassivation kinetics is fast enough to alleviate any acceleration in crack growth rates caused by film rupture. It has been confirmed in Chapter 3 that the very dense and stable Cr_2O_3 oxide film can be formed on the surface of oil-grade alloy 718 in 3.5 wt.% NaCl solution. Thus, the Cr_2O_3 passive film repassivated at the crack tip can suppress metal dissolution, thereby reducing CFCG rate. Lin et al. [44] have pointed out that solution temperature had an important effect on the crack propagation rate of UNS S45000 martensitic stainless steel in NaCl solutions

because higher temperature of 80°C could provide higher activation energy for electrochemical reactions thus accelerate CFCG rates as compared with the NaCl solutions at RT. On the contrary, our results have shown that solution temperature has no detectable influence on the CFCG rates of alloy 718 in 3.5 wt.% NaCl solution even though it is clearly observed from potentiodynamic polarization results that the pitting corrosion behavior of alloy 718 in 3.5 wt.% NaCl solution at three varied temperatures are different. It is well known that temperature has complicated influence on the electrochemical reactions in corrosive aqueous solutions. On one hand, increase in temperature could lead to an increased corrosion rate because higher temperature accelerates both anodic and cathodic reactions. On the other hand, with increasing temperature the dissolved oxygen in the solution decreases, resulting in lower corrosion rate if the cathodic reaction is controlled by oxygen reduction. Thus, the exact effect of temperature on the CFCG rate depends on the specific conditions such as temperature range and the changes of mechanical properties of the material and environment factors resulted from the temperature. In the current testing system, the influence of the temperature of 3.5 wt.% NaCl solution is not visible on the CFCG rate of alloy 718, even though some change in pitting corrosion behavior of alloy 718 was observed. This is indicated by higher corrosion current density and lower pitting potential, due to the increased solution temperature. The reason might be that the anodic dissolution rates at the crack tip in 3.5 wt.% NaCl solution at 50°C and 80°C are increased, but still not comparable to the rate of mechanical damage during loading. These results may be attributed to a possible mechanism that the CFCG rates of alloy 718 in 3.5 wt.% NaCl solution at RT, 50°C and 80°C are all mainly controlled by mechanical loading rather than corrosive conditions. On the basis of above analysis, it is reasonable to conclude that 3.5 wt.% NaCl solution is not aggressive enough to accelerate the CFCG rate of oil-grade alloy 718 that is predominated by the mechanical variables.

Nevertheless, 21 wt.% NaCl solution at 80°C show a deleterious effect on the CFCG rates of alloy 718 as compared with those in air at low and medium ΔK region. The difference between the CFCG rates of alloy 718 in 3.5 wt.% NaCl solution and 21 wt.% NaCl solution at 80°C could be

related to the difference of their electrochemical behaviors. It is observed that alloy 718 demonstrates a typical passive behavior in 3.5 wt.% NaCl solution but does not in 21 wt.% NaCl solution at 80°C. These facts suggest that the anodic dissolution of the crack tip is greatly increased to some extent that could lead to obvious CFCG rate of alloy 718 in this solution because the crack tip continuously remains unprotected by the porous passivation film due to absorbing very high concentration of Cl^- . It is also likely that the repassivation kinetics is extremely slow and the repassivation film formed on the crack tip surface is not protective enough during unloading conditions. On the other hand, the solution-annealed specimen still shows higher CFCG rate than the ones of aged specimens in 21 wt.% NaCl solution at 80°C, indicating that the mechanism of CFCG of oil-grade alloy 718 in 21 wt.% NaCl solution at 80°C is also dominated by mechanical loading.

4.4.3 Corrosion Fatigue Crack Growth Mechanism

When a corrosion fatigue crack propagates, a great amount of stress will be concentrated at the crack tip, where local plastic deformation will occur. The deformation facilitates the rupture of passivation film at the crack tip, leading to exposure of bare metal to the crack tip solution. Thus the electrochemical potential of the crack tip drops and it acts as an anode relative to the crack walls, resulting in the anodic dissolution of the alloy at the crack tip and crack advance. M^{n+} ions produced from anodic dissolution do not easily diffuse outside the crack, therefore, they will be balanced by anions such as Cl^- ions which diffuse from the bulk to maintain electrical neutrality. Hydrolysis of M^{n+} with increased Cl^- will take place tending to lower the pH of the solution. Thus, an aggressive, low pH electrolyte concentrated in M^{n+} and Cl^- is produced near the crack tip. Cathodic reactions such as hydrogen evolution and oxygen reduction will then occur on the crack walls and metal surface outside the crack. As described above, interaction between oil-grade alloy 718 and aerated NaCl solution in free corrosion potential conditions during CFCG tests can involve a series of electrochemical reactions as shown below:

Anodic reaction at the crack tip: $M \rightarrow M^{n+} + ne^-$

Cation hydrolysis reaction: $M^{n+} + nH_2O \rightarrow M(OH)_n + nH^+$

Cathodic reaction on the crack walls: $H^+ + e^- \rightarrow H$

Cathodic reaction on metal surface outside the crack: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

At the same time, a repassivation of the bared surface occurs during the unloading reversal until the next generation of film rupture. Some of the produced hydrogen are absorbed on the crack surface and then transported by diffusion into the highly stressed plastic zone at the crack tip, where it causes localized damage and increases the CFCG rate. As a result, the CFCG of oil-grade alloy 718 may be caused by both anodic dissolution and hydrogen embrittlement.

In our study, the CFCG mechanism of oil-grade alloy 718 in NaCl solution at free corrosion potential should be anodic dissolution control. It has been reported that the CFCG rate controlled by anodic dissolution mechanism is determined by the bare surface anodic dissolution rate, the rate of repassivation, the rate of oxide film rupture, mass transport rate of reactant to the dissolving surface. Our CFCG testing results show that 3.5 wt.% NaCl solution has little influence on the CFCG rates of oil-grade alloy 718 as compared with the one in air. While 21 wt.% NaCl solution at 80°C increase the CFCG rate by about 60%–130% for Alloy 718–SA in the lower ΔK range of 20–30 MPa $\sqrt{m}$, and by about 40%–80% for Alloy 718–OSA in the ΔK range of 25–50 MPa $\sqrt{m}$, and by about 30%–90% for Alloy 718–TSA in the ΔK range of 25–55 MPa $\sqrt{m}$ in comparison with the ones in air. It is suggested that the higher concentration of Cl^- retards the rate of repassivation and accelerates the higher dissolution rate in 21 wt.% NaCl solution at the crack tip, contributing obvious CFCG rate enhancement than the ones in 21 wt.% NaCl solution.

4.5 Summary

The influence of aging treatment on microstructure, pitting corrosion resistance and corrosion fatigue crack growth behavior of oil-grade alloy 718 in NaCl solution were studied. Some meaningful conclusions are summarized below:

(1) Based on the microstructure analysis, the average grain sizes of oil-grade alloy 718 increased from 46 μm (solution-annealed) to 52 μm (one-step aged) and 60 μm (two-step aged). Isolated platelet δ phases were precipitated at some of the grain boundaries in both one-step aged and two-step aged specimens. The one-step aged specimen showed a uniform distribution of fine spherical (γ' , in 20-30 nm diameters) and elongated (γ'' , 5-15 nm in the c dimension and 30-150 nm in diameters) precipitates in the grains. On the contrary, the two-step aged sample showed much finer precipitates (γ' , in 2-10 nm diameters; γ'' , 2-12 nm in the c dimension and 5-35 nm in diameters).

(2) Electrochemical results showed that aging treatment has no obvious influence on pitting corrosion resistance of oil-grade alloy 718 in all tested NaCl solutions, indicated by the similar corrosion current density and pitting potential. However, various NaCl solution conditions in terms of solution temperature and NaCl concentration lead to different susceptibility to pitting corrosion of oil-grade alloy 718, regardless of aging treatment. Oil-grade alloy 718 exhibited passive behavior in 3.5 wt.% NaCl solution at RT, 50°C and 80°C, and the pitting corrosion resistance was decreased with increasing solution temperature indicated by decreased pitting potential and increased corrosion current density. Nevertheless, oil-grade alloy 718 showed an active corrosion behavior in 21wt.% NaCl solution at 80°C.

(3) CFCG results demonstrated that there is no obvious effect of 3.5 wt.% NaCl solution on the CFCG rates of three types of oil-grade alloy 718 samples with different aging treatments, regardless of solution temperature. Nevertheless, the CFCG rates of oil-grade alloy 718 in 21 wt.% NaCl solution were increased in comparison with the ones tested in laboratory air and in 3.5 wt.% NaCl solution. Furthermore, aging treatments led to lower CFCG rates of oil-grade alloy 718 in all tested environments. However, no visible difference of CFCG rates in NaCl solution is observed between one-step aged and two-step aged specimens.

(4) Fractographic examination of the fractured surfaces indicated that the fatigue cracks propagate in the transgranular mode in oil-grade alloy 718 in all tested conditions, in spite of solution temperature and NaCl concentration.

(5) The CFCG mechanism of oil-grade alloy 718 in 3.5 wt.% NaCl solution at different temperatures was predominated by mechanical variables due to the very small dissolution rate and fast repassivation kinetics at the crack tip, while both anodic dissolution and mechanical loading were controlling mechanisms for the CFCG of oil-grade alloy 718 in 21 wt.% NaCl solution at 80°C because the higher concentration of Cl^- retarded the rate of repassivation and preserved the higher dissolution rate at the crack tip, resulting in obvious increase in CFCG rate.

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Chapter 5: Effects of Machine Hammer Peening and Aging Treatment on Pitting Corrosion Resistance of Oil-Grade Alloy 718

5.1 Introduction

Peening surface treatments such as shot peening, ultrasonic peening, hammer peening, laser shock peening and roller peening [1-5] have been widely used for improving the mechanical properties, fatigue life and corrosion fatigue resistance by introducing a compressive residual stress layer in the near surface region through the work hardening from the surface treatments [6-9]. In the meantime, the surface modifications, in terms of surface roughness, surface morphology, surface passive/oxide film, near surface microstructure and residual stress induced by surface finishing processes, can affect the corrosion properties, especially pitting corrosion which is usually considered to be a precursor to stress corrosion cracking and corrosion fatigue crack initiation in chloride solutions [10-13]. Numerous studies have been focused on the influence of peening treatments on the corrosion resistance of alloys [14-24], regardless of their applications be it oilfield drilling or otherwise. It has been reported by Azar et al. [15] that surface roughening, which was considered to be deleterious to the corrosion resistance by increasing the corrosion current density and decreasing the break-down potential, could be produced by the shot peening treatment. According to Lee et al. [14], ultrasonically peened AISI 304 stainless steel showed better general and localized corrosion resistance than the as-received and shot-peened specimens due to the rendering of a smoother surface and the creation of strain-induced martensite. Peyre et al. [12, 21] have pointed out that the deleterious roughened surface state produced by shot peening could counterbalance the beneficial effect of compressive residual stress on the pitting corrosion resistance of 316L steel. However, Wang et al. [19] have reported that surface nanocrystallization induced by shot peening can markedly enhance the corrosion resistance of 1Cr18Ni9Ti stainless steels in NaCl solution. The effect of laser shock peening on pitting corrosion resistance of aluminium alloys in NaCl solution has also been studied by Trdan et al. [16] and Amar et al. [22]. Their results showed that laser shock peening could improve the pitting corrosion resistance by

increasing pitting potential and polarization resistance due to the induced compressive residual stress and modified surface film. Klapper [25] has also reported the investigation of surface treatments on the pitting corrosion resistance of non-magnetic stainless steel surfaces. He has found that hammer-peened surfaces exhibited higher pitting potentials than mechanical ground surfaces and shot-peened surfaces by +90 mV and +165 mV, respectively.

Machine hammer peening (MHP) is a mechanical surface treatment which can induce deep penetration of compressive residual stress and a strain hardened layer below the surface as well as a strong reduction of surface roughness on work pieces with complex shapes [26-33]. During MHP processes, the metal work piece is hammered with a tungsten carbide ball, which is moved by a machine tool or robot along the surface, thereby creating a uniformly smooth surface by well-directed impacts with a controlled distance between each impact. However, this method is not well covered in the literature since it is relatively novel. Recent research has focused attention on how deep machine hammer peening can smooth machined surfaces and thus achieve compressive residual stress by adjusting hammer peening parameters [27, 29,31-33]. Therefore, it is logical to expect that MHP would result in an increase in corrosion resistance. Nevertheless, published data on MHP is limited, focusing on the effect of surface modifications on the corrosion behavior of alloy 718. Thus, it is meaningful to determine whether the MHP surface treatment can improve corrosion resistance. Although there have been some reports concerning corrosion behaviors of alloy 718 [34-49], the effect of heat treatment on the corrosion resistance of alloy 718 has not been extensively investigated to date, especially with respect to changes in surface-treated components. Hereby, it is important to study the effect of aging treatment on surface-treated alloy 718 to determine whether the pitting corrosion resistance of the MF and MHP specimens can be maintained after heat treatment.

The objective of this research is to study the effect of MHP on surface modified properties including microhardness, residual stress, surface chemistry, surface morphology, surface roughness and the near surface microstructure of oil-grade alloy 718. The research goal will relate surface

modifications induced by MHP on the pitting corrosion behavior of alloy 718 in a 3.5 wt.% NaCl solution at room temperature. The other aim of the present work is to determine how the surface conditions and pitting corrosion behavior of MF and MHP alloy 718 specimens change due to aging treatment.

5.2 Experimental

5.2.1 Materials and Specimen Preparation

The chemical composition of oil-grade alloy 718 used in this study is listed in Table 5.1. The as-received alloy was solution annealed at 1032 °C for 2 h. Before MHP the specimen surface was prepared by mill finishing (MF). During MHP, a tungsten carbide ball with a diameter of 8 mm was used to treat one side of the milled surface at a frequency of 140 Hz and feed rates of 2 m/min (MHP1) and 4 m/min (MHP2), respectively. The MF and MHP specimens were then cut in half. One half of each specimen was unaged and the other half was double aged at the 760°C for 4.5 h followed by 650°C for 5 h. Details on the surface treatments, heat treatments and specimen designations are found in Table 5.2.

Table 5.1 Chemical composition of oil-grade alloy 718

Ni	Cr	Fe	Nb	Mo	Ti	Al	Co	Si	Mn	C	Cu
52.55	18.47	19.11	5.09	3.00	0.97	0.49	0.08	0.08	0.05	0.019	0.02
Ta	P	B	Ca	S	Mg	Se	Pb	Bi			
0.01	0.003	0.002	0.001	<0.002	<0.001	<0.0003	0.0002	<0.00003			

Table 5.2 Sample information in detail

Sample	Surface Treatment and Heat Treatment Conditions
MFU	1032 °C/2 h, WQ + milling
MFA	1032 °C/2 h, WQ + milling + 760 °C ± 8 °C/4.5 h, 650 °C ± 8 °C/5 h, FC
MHP1U	1032 °C/2 h, WQ + milling + machine hammer peening (2 m/min)
MHP1A	1032 °C/2 h, WQ + milling + machine hammer peening (2 m/min) + 760 °C ± 8 °C/4.5 h, 650 °C ± 8 °C/5 h, FC
MHP2U	1032 °C/2 h, WQ + milling + machine hammer peening (4 m/min)
MHP2A	1032 °C/2 h, WQ + milling + machine hammer peening (4 m/min) + 760 °C ± 8 °C/4.5 h, 650 °C ± 8 °C/5 h, FC

5.2.2 Specimen Characterization

Vickers micro-hardness tests conforming to the ASTM E384-05 standard [50] were carried out using 0.3 N (300g) load with an indentation cycle time of 15s on cross-sections of the MF and MHP specimens. An average of ten indentation measurements was used to determine each data point.

Surface and near surface residual stress induced on the MF and MHP samples was obtained according to the $\sin^2\Psi$ method [51] by using X-ray Diffraction (XRD, Bruker D8 Discovery).

X-ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI 5000 VersaProbe System, utilizing monochromatic $AlK\alpha$ radiation to examine the oxide film formed on the surface of specimens before and after aging treatment. The C1s peak from carbon contamination at 284.8 eV was used as a reference to correct for charging shifts. Depth profiling of oxide films was performed over an area of $2\text{ mm} \times 2\text{ mm}$ using Argon ion bombardment with an ion energy of 2 kV. Sputtering rate was determined to be 18.5 nm/min with reference to the Ta_2O_5 layer. Therefore, it should be noted that the thickness change after the MHP treatment rather than the absolute thickness values of the oxide film was meaningful. The quantification of the species in the oxide films was performed via XPSpeak 4.1 peak fitting software.

The surface roughness and surface topography of the MF and MHP specimens before and after aging treatment were measured by using an optical profiler (Bruker Contour GT K0). The vertical scanning interferometry type was chosen based on the samples surface conditions. A $5\times$ objective lens and $1\times$ field of view multiplier were used to give a measurement area of $1.257\text{ mm} \times 0.942\text{ mm}$. The tilt was removed from the measurement during data analysis because it could alter the surface profile. R_a , R_q , R_p , R_v , R_t are arithmetic average roughness, root mean squared roughness, maximum peak height, maximum valley depth, maximum height of the profile ($R_t = R_p - R_v$). These roughness parameters of each specimen are the average values of five measurements.

The near surface microstructure of all the specimens was examined by means of optical microscopy (OM, Meiji MT 7000), scanning electron microscopy (SEM, JEOL JSM-7600F) and transmission electron microscopy (TEM, JEOL JEM-2010). Cross-sectional specimens mounted in epoxy were mechanically ground using a series of abrasive SiC grit sizes, i.e., 120–1200 grit, with final polishing using 3 μm and 1 μm diamond suspension. Chemical etching using a mixture of 200 ml methanol, 200 ml hydrochloric acid and 10 g CuCl_2 for 4 min produced the final surface for OM and SEM examination. For TEM analysis, specimens were first ground to 50 μm thickness and then thinned electrolytically using a twin jet polishing unit. The electropolishing solution was consisted of 10 % perchloric acid in 90 % ethanol. Electropolishing was performed using a current of 90 mA at -20°C .

5.2.3 Electrochemical Measurements

Electrochemical measurements were performed at room temperature using an aerated 3.5 wt.% NaCl solution, prepared with deionized water. Specimens for electrochemical testing were mounted in epoxy leaving only 0.5 cm $\times$ 0.5 cm surface area of the MF or MHP exposed. Immediately prior to each testing, the specimens were rinsed with acetone, ethanol and deionized water, and dried in air at room temperature, then transferred into the test solution. None of the specimens were ground as is usually the case in electrochemical testing because doing so might lead to information loss on corrosion behavior differences due to different surface treatment conditions. Electrochemical testing was carried out using a standard three electrode system in a 1.5 L glass cell. A three-electrode cell setup was employed that consisted of a pair of graphite counter electrodes, an Ag/AgCl reference electrode and specimen as working electrode. Experiments for each specimen condition were conducted at least three times with the results averaged. Before each measurement, the working electrode was polarized cathodically for 10 min at $-1 \text{ V}_{\text{Ag/AgCl}}$ to achieve reproducible results because it has been proved that there producibility of electrochemical measurements performed on passive films was improved after cathodic polarization[52-54].

The test specimens were then immersed in the test solution for 1 h to attain a relatively stable value of open-circuit potential (OCP) after cathodic pretreatment. Potentiodynamic polarization curves were performed using a Solartron SI 1287 after measuring OCP for 1h. For this series of tests, the test specimens were excited from $-0.5 \text{ V}_{\text{Ag/AgCl}}$ towards the anodic direction at a scanning rate of 0.5 mV/s. Electrochemical impedance spectroscopy (EIS) measurements were carried out with a Solartron SI 1287 electrochemical interface and a SI 1260 impedance analyzer. EIS measurements were conducted at OCP after the specimens had been immersed for 1, 6, 12, 24 and 48 h, respectively, in a 3.5 wt.% NaCl solution. The testing frequency ranged from 10 kHz to 10 mHz while the AC amplitudes were 10 mV (rms–root mean square). The resulting impedance spectra obtained during testing were then fitted using ZSimpWin software.

The morphology of corrosion pits formed after potentiodynamic polarization testing was observed by means of SEM.

5.3 Results

5.3.1 Effect of Machine Hammer Peening on Surface Modifications

5.3.1.1 Mechanical Modifications

5.3.1.1.1 Microhardness

Microhardness measurements were carried out on the cross-section of the MFU and MHPU specimens to determine the hardness at different layers from the treated surface in order to assess the depth of work hardening. The hardness values versus depth from the surface of specimens are presented in Figure 5.1.

Figure 5.1 Microhardness depth profiles for the MFU and MHPU specimens.

Microhardness in the MFU specimen shows decreased values with increased depth from the surface. At the surface, the hardness is about 350 HV while it decreases to about 210 HV in the bulk. This clearly shows that the microhardness is influenced by MF. After MHP at feed rates of 2 m/min and 4 m/min, the microhardness of the respective specimens in the near surface region is about 50 HV and 100 HV higher compared with the MFU specimen. This can be attributed to the increase in work hardening in this layer as a consequence of the MHP treatment and is manifested by a dramatic increase in the dislocation density. Also, it can be seen that the microhardness of the MHPU and MFU specimens decreases with distance from the surface at a sharp gradient until depths of about 1500μm and 700 μm, respectively, are reached with respect to the modified surface. Once these distances from the surface are reached, variations in hardness are minor and within the scatter of the hardness test.

5.3.1.1.2 Residual stress

The surface and near surface residual stress was measured by using XRD for the MFU and MHPU specimens, and the curves of residual stress values as a function of depth from surface are displayed in Figure 5.2.

Figure 5.2 Residual stress depth profiles for the MFU and MHPU specimens.

These results show quite clearly the extent of the compressive residual stress field produced in the near surface region due to the MF and MHP surface treatments. The surface compressive residual stress values of the MHP1U and MHP2U specimens are significantly greater than, approximately two and three times that of the MFU specimen, respectively. Thus, higher strain hardening is obtained with MHP, which is in accordance with the microhardness test results. Also, the general trend in residual stress is consistent with the results reported by Bleicher et al. [27] concerning the application of MHP on a milled C45E (1.1191) specimen. It also clearly shows that the absolute values of compressive residual stresses are firstly increased to the maximum when the depth is increased to about 50–100 μm then decrease with depth from surface. Feng et al. [55] have reported that the compressive residual stress increased with the depth to a peak value and then decreased for the shot-peened TC4–DT titanium alloy. Cai et al. [56] have found that the

maximum value of the compressive residual stress occurred about 0.1 mm below the surface of a shot-peened Inconel 718. It was suggested that the maximum compressive residual stress was located in the subsurface layer because the hertz dynamic pressure was dominant but the plastic deformation was weak at material surface, while both high shear stress and plastic deformation occurred at the subsurface [55].

5.3.1.2 Surface Oxide Film

Corrosion behavior of alloys might be influenced by chemical modifications, such as changes of oxide film, induced by surface treatments. Peyre et al. [12, 21] have reported that after shot peening treatment or pure mechanical laser peening treatment, the surface composition of 316L stainless steel was kept nearly constant. However, the thermo-mechanical laser peening modified the oxygen, aluminum and chromium profiles to a depth of 2 μm , indicating the formation of an oxide layer which resulted in a clear anodic ennoblement of rest potential and a decreased passive current density as compared with as polished specimen. Moreover, Trdan et al. [16] have confirmed that laser peening could transform amorphous Al_2O_3 oxide into more stable oxide form, probably into Al_2O_3 -sapphire, which serves as an effective barrier against corrosion attack in a chloride solution. Thus, it is meaningful to investigate and compare the surface chemistry of our surface modified samples before corrosion tests.

It was found by XPS surface analysis that a very thin and adherent oxide film was formed on the surface for all three unaged specimens. This air-formed oxide film was probably formed by exposure to the ambient environment after solution annealing treatment. The XPS survey scans for the oxide films on the surface of MFU and MHPU specimens are illustrated in Figure 5.3. C1s, O1s, Ni2p, Fe2p, Cr2p, Ti2p, Ca2p, Mo3d and Nb3d peaks can be seen for each of the surface modified conditions. It should be noticed that MHP did not alter the composition of the oxide films formed on the surface of the specimens.

Figure 5.3 XPS survey scan peaks for the oxide films formed on the surface of the MFU and MHPU specimens.

The existence of Ni, Fe, Cr, Ti, Ca, Mo and Nb oxides on the alloy surface were detected from the XPS detailed peaks as shown in Figure 5.4 (a–g). Figure 5.4 (a) shows the Ni 2p_{3/2} core level spectra and the decompositions for oxide film formed on the MF specimen. The spectrum consists of two peaks at the binding energy (BE) of 852.7 ± 0.1 eV and 855.8 ± 0.3 eV, and their associated satellite peaks at 858.7 ± 0.3 eV and 861.9 ± 0.3 eV, respectively. These features originate from metallic Ni and Ni(OH)₂. Figure 5.4 (b) displays the Cr 2p core level spectra recorded on the surface of the MF specimen. One peak was located at a binding energy of about 577.0 eV, in the Cr 2p spectrum. The signal at a BE of 577.0 ± 0.3 eV is assigned to Cr³⁺ in Cr₂O₃/ Cr(OH)₃. The exact identification of the compound was difficult because the peak positions of Cr(OH)₃ and Cr₂O₃ are very close. The identification of iron chemical states relies on the peak position of Fe2p_{1/2} as shown in Figure 5.4 (c). Since iron may exist in different valence states as well as in mixed valence, with the chemical shifts close to each other. Also nickel, as the major alloy element in alloy 718, has a strong Auger peak (711.7 eV) in the vicinity of Fe2p_{3/2} when using Al anode in XPS. The Fe 2p_{1/2} spectra should decompose into FeO, Fe₃O₄, and Fe₂O₃, at the BE of 722.6 ± 0.1 eV, 724.1 ± 0.1 eV, and 724.6 ± 0.2 eV, respectively. Figure

5.4 (d) reveals the existence of TiO_2 associated with the BE at 485.4 ± 0.3 eV. It was observed from Figure 5.4 (e) that the Ca^{2+} in $\text{CaO}/\text{Ca}(\text{OH})_2$ was detected from the signal at 347.2 ± 0.3 eV. The Ca oxide might be introduced as a contamination during previous melting, fabrication and solution treatment since there is very less concentration of Ca in nickel-base alloy 718. The XPS spectra of Mo3d shown in Figure 5.4 (f) indicated that Mo peaks decomposed into metallic Mo and MoO_3 oxide, which is assigned with the BE of 227.9 ± 0.3 eV and 232.5 ± 0.3 eV, respectively. Figure 5.4 (g) illustrates the Nb 3d core level spectra and shows the presence of NbO and Nb_2O_5 , as indicated by two peaks located at the BE of 203.2 ± 0.3 eV and 207 ± 0.3 eV, respectively.

Figure 5.4 XPS detailed peaks of the oxide films formed on the surface of the MFU and MHPU specimens: (a) Ni 2p_{3/2}, (b) Cr 2p, (c) Fe 2p_{1/2}, (d) Ti 2p, (e) Ca 2p, (f) Mo 3d, (g) Nb 3d.

The surface compositions of the specimens are summarized in Table 5.3 after fitting the XPS data. The presence of a high C content in the surface is due to environmental contamination.

Table 5.3 Chemical compositions of the oxide films formed on the surface of the MFU and MHPU specimens.

Element	C	O	Ni	Fe	Cr	Ti	Ca	Mo	Nb
At. %	51.9	41.1	1.3	1.3	2.0	0.3	1.4	0.3	0.4

Table 5.4 lists the atomic concentrations of the different oxides found in the surface films. As observed from Table 5.4, the concentration of Cr-enriched oxide is the highest compared to other oxides in the surface oxide film. Cr/Ni hydroxides and Fe oxides were observed in the oxide film. MoO₃, TiO₂, NbO and Nb₂O₅ oxides were also detected on the surface modified samples. Our XPS results are consistent with other investigations on the air-formed oxide film formed on a nickel-base alloy [57-59]. Lloyd et al. [57] have reported the presence of NiO, Cr₂O₃ and MoO₃ in the air-formed film on Inconel 625. According to Bakare et al. [58], the air-formed film on Inconel 625 consisted of a mixture of NiO, Cr₂O₃, MoO₂, MoO₃, NbO and Nb₂O₅. It has been confirmed that the passive film on nickel-based alloys surface behaved as a duplex structure formed by an inner layer of p-type Cr₂O₃ and an outer layer consisted of n-type Cr/Ni hydroxides and Fe oxides. The good corrosion resistance of nickel-base alloys is due to the spontaneous development of a Cr-rich inner passive layer.

Table 5.4 Atomic concentrations of the oxides in the surface films on the MFU and MHPU specimens.

Oxide	Ni	Fe	Cr	Ti	Ca	Mo	Nb
At. %	13.6	16.7	32.1	5.5	22.0	3.0	7.1

In order to compare the thickness of the oxide films formed on the surface of the MF and MHP specimens, XPS depth profiles for Cr-enriched oxides formed on the surface of all specimens were carried out. The results of this activity are shown in Figure 5.5 (a–c). The film exhibited a gradual transition from oxide to metal for all conditions. It was clear that the thickness of the surface oxide film did not undergo any distinguishable changes since the sputtering time is almost the same for all conditions. Thus, it was confirmed that the surface chemistry is almost unchanged after MHP.

Figure 5.5 XPS depth profiling of the oxide films formed on the surface of specimens: (a) MFU, (b) MHP1U, (c) MHP2U.

5.3.1.3 Surface Topography

It was observed that the surface of specimens was visibly smoother after MHP. This effect was quantified by using surface roughness measurement. Table 5.5 lists the surface roughness parameters of the MFU and MHPU specimens. MHPU surfaces show a significant roughness reduction compared to the initial MFU surface roughness. The arithmetic average roughness R_a and the root mean squared roughness R_q are reduced by 92 % and 94 %, respectively, for the MHP1U and MHP2U specimens. The maximum height of the profile R_t is reduced by 77 % and 83 %, respectively, for the MHP1U and MHP2U specimens. This is in accordance with the results reported by other researchers [26, 29] that even rough milling surfaces could be smoothed considerably after MHP.

Table 5.5 Surface roughness parameters of the MFU and MHPU specimens

Specimen	R_a (μm)		R_q (μm)		R_p (μm)		R_v (μm)		R_t (μm)	
	Avg.	Std. dev.	Avg.	Std. dev.	Avg.	Std. dev.	Avg.	Std. dev.	Avg.	Std. dev.
MFU	6.08	0.99	7.63	0.75	20.79	0.98	-10.96	2.13	31.75	1.67
MHP1U	0.50	0.04	0.63	0.05	3.28	0.76	-3.96	0.68	7.24	0.45
MHP2U	0.38	0.01	0.49	0.01	1.94	0.13	-3.44	0.76	5.38	0.85

The smoothening effect of MHP was also observed in the surface topography by the use of the 3D surface measurement device. The surface topographies taken from the MFU and MHPU specimens are presented in Figure 5.6. It is clearly seen that a large number of ridges and grooves are generated by the MF process (Figure 5.6 (a)), while after MHP these ridges and grooves have been flattened (Figure 5.6 (b) and (c)). It is visible that the coarse texture of the material has also been smoothened at the smaller scale. A quantity of burs and cracks caused by MF are observed on the ridges. However, it is noticeable that some surface cracks still exist on the ridges after MHP.

Figure 5.6 Surface topographies of specimens: (a) MFU, (b) MHP1U, (c) MHP2U.

5.3.1.4 Microstructure

Cross-sectional microstructure analysis was performed on the MFU and MHPU samples. Figure 5.7 consists of OM images of the cross-sectional microstructure in the near surface region for all specimens. A visible plastic deformation layer is observed in the MFU sample, which is about 100 μm thick (Figure 5.7 (a)). Some deformation twins are seen in the near surface region. After MHP, the near surface region is deeper and darker, which indicates that the MHPU specimens were severely deformed. The thickness of the rigorously deformed layer is increased to 250–300 μm for the MHP1U specimen (Figure 5.7 (b)) and to 350–400 μm for the MHP2U specimen (Figure 5.7 (c)). It is also observed that the plastic deformation is regional inhomogeneous in the MHPU specimens. It is interesting to note that a large number of globular-shaped and rectangular-shaped inclusions are distributed heterogeneously throughout the alloy all the way from the top surface into the interior in all three specimens, both in intergranular and transgranular positions. EDX results have confirmed that these inclusions are (Nb, Ti)C (globular) and (Ti, Nb)N (rectangular), respectively. It is known that primary carbides and nitrides are normally formed in nickel-base alloy 718 during solidification, and their size and volume fraction depend on the carbon or nitrogen content of the alloy and solidification history. Also, these inclusions are very stable and will not be changed drastically during forging, heat treating or thermal cycles at lower temperatures [35]. Thus, it is expected to find that there is almost no change of their density and distribution before and after MHP.

Figure 5.7 OM images of the cross-sectional microstructure of specimens: (a) MFU, (b) MHP1U, (c) MHP2U.

SEM images in Figure 5.8 illustrate more detailed information about the microstructure evolution of the near surface region of the MHPU specimens. At the very impact surface ($< 20 \mu\text{m}$ measured from the MHP surface), the original grain boundaries are unresolvable while some nanoparticles are visible, as shown in Figure 5.8 (a) and (a'), suggesting the formation of ultrafine grains at and beneath the MHPU surface. When the depth to the top surface is increased up to about $10\text{--}20 \mu\text{m}$, many deformation lines (straight or curved) start to populate in the deformed area and they are confined within individual grains, which can be clearly identified in Figure 5.8 (b) and (b'). These deformation lines have been identified as deformation twins rather than deformation bands by the TEM analysis, as will be discussed later. These deformation twins are apparent in two major ways: some of them are evident to be parallel to each other, and some of them are intersecting with each other in multiple directions. Moreover, the density of these deformation twins is decreased as the location becomes farther away from the peened surface, as can be seen in Figure 5.8 (c) and (c').

Figure 5.8 SEM images of the cross-sectional microstructure of specimens: nano-grains of (a) MHP1U and (a') MHP2U at the depth of less than 20 μm, higher density of mechanical twins of (b) MHP1U and (b') MHP2U at the

depth of less than 200 μm , lower density of mechanical twins of (c) MHP1U and (c') MHP2U at the depth of less than 500 μm .

Figures 5.9–5.12 show the TEM images of the microstructure in the near surface region of the MHPU2 specimens.

In the region of low strain and strain rate (at the depth of about 500 μm), TEM analysis indicates that the plastic deformation mode of the MHPU specimens is dislocation slip. Microstructures in this region are characterized by planar dislocation arrays formed on different $\{111\}$ slip planes, as shown in Figure 5.9 (a). The spacing between dislocation arrays is in the range of 50–250 nm, depending upon the orientation of the original grains. The extended stacking faults, planar dipolar dislocation groups and dislocation pile-ups were shown in Figure 5.9 (b). The SAD pattern illustrates the FCC crystal structure of alloy 718, as shown in Figure 5.9 (c).

Figure 5.9 TEM images showing the dislocation slips at the depth of about 500 μm from the MHPU2 specimen surface: (a) bright field (BF) micrograph; (b) BF micrograph (higher magnification); (c) [001] zone axis SAD pattern.

Figure 5.10 shows the planar dislocation arrays at the depth of about 200 μm from the MHPU2 surface. The spacing between dislocation arrays is in the range of 10–30 nm, which is smaller than the one at the depth of about 500 μm . It appears that the dislocation density has increased when the distance to the surface is decreasing.

Figure 5.10 TEM images showing the dislocation slips at the depth of about 200 μm from the MHPU2 specimen surface: (a) BF micrograph; (b) BF micrograph (higher magnification); (c) [011] zone axis SAD pattern.

Dark-field (DF) TEM images (as in Figure 5.11) show discontinuous contrast along the nano-twins (parallel bands) formed at the depth of about 50 μm from the MHPU2 surface, indicating that these lamellar structures are broken into equiaxed nanometer-sized blocks with different crystallographic orientations. Apparently, these nanometer-sized blocks originated from a continued increase in orientation deviation of nanometer-sized regimes surrounded by dislocation arrays. With

increasing strain, more dislocations are generated and form more and dense dislocation arrays that gradually subdivide the nano-twin lamellae into refined nano-structured blocks.

Figure 5.11 The DF TEM images taken from the SAD spots marked with 1, 2 and 3, showing the evolution of nano-twins into equiaxed nanometer-sized blocks.

After MHP the surface layer suffered severe plastic deformation resulting in subgrains or grains with average sizes from 10 to 30 nm (Figure 5.12 (a) and (a')). A high density of dislocations can be observed in this layer. Furthermore, multiple nano-twins are occupied the microstructure in the heavily deformed region and some intersections are evident in the micrographs (Figure 5.12 (b) and (b')). High densities of dislocations are still visible in the grains beside the deformation twins.

The accompanying SAD pattern shows well-defined diffraction spots for an incident electron beam close to $[011]$. This pattern is a superposition of two sets of $\langle 011 \rangle$ diffraction patterns that are symmetrical with each other and with respect to the $\{111\}$ plane (Figure 5.12 (b')). Thus, the entire region shown in Figure 5.12 (b') constitutes a single grain before MHP treatment and becomes a grain that consists of sets of nano-twins with intersections after MHP. A group of parallel nano-twins with high dislocation densities also can be seen in Figure 5.12 (c) and (c')). Many dislocations are trapped within these nano-twins. The SAD pattern from these parallel nano-twins exhibits long arcs and the twin diffraction spots are connected to the brighter spots by streaks, indicating that these parallel nano-twins are originated from one parent grain, but have large departures from the orientation of the parent grain (Figure 5.12 (c')). The thickness of these deformation nano-twins ranges from 10 to 70 nm for the MHP2U specimen and from 100 to 150 nm for the MHP1U specimen. The density of mechanical twins of the MHP2U specimen exhibits higher than the MHP1U specimen. It has been reported by Lee et al. [14] that the ultrasonic-peened specimen exhibited denser mechanical twins than the shot-peened specimen because it had more plastic strain energy than the shop-peened specimen. Taking together the microstructure results with microhardness and residual stress data discussed earlier, it can be suggested that with an increased feed rate, the plastic strain induced during MHP increases, resulting in higher compressive residual stress and hardness values, as well as finer nano-grains and denser nano-twins.

Figure 5.12 TEM images of the cross-sectional microstructure of the MHPU specimens: nano-grains of (a) MHP1U and (a') MHP2U, multi-directional nano-twins of (b) MHP1U and (b') MHP2U, parallel nano-twins of (c) MHP1U and (c') MHP2U.

5.3.2 Effect of Aging Treatment on Surface Modifications

5.3.2.1 Mechanical Modifications

5.3.2.1.1 Microhardness

In order to determine the effect of age hardening on the hardness and the work hardening depth, the microhardness of aged surface-treated samples at different depths was measured, and the microhardness values versus distance from the surface of the MFA and MHPA samples are also shown in Figure 5.13. It can be observed that the microhardness of the bulk material in each condition significantly increases by about 260 HV while the microhardness in the near surface region increases by about 160 HV after the two-step aging treatment due to the formation of the γ'/γ'' strengthening phases. Furthermore, the microhardness of the MHPA and MFA specimens decreases with a more moderate slope as compared with the unaged surface-treated specimens, which seems to indicate that the two-step aging treatment counteracts the effect of work hardening and decreases the near surface compressive residual stresses values.

Figure 5.12 Microhardness depth profiles for all specimens.

5.3.2.1.2 Residual stress

Figure 5.13 shows the residual stress values as a function of depth from surface of all specimens. It is expected to find that the residual compressive stresses in the MFU and MHPU specimens relaxed after aging treatment. The surface compressive residual stresses greatly relaxed by 50%, 90%

and 86% for the MFU, MHP1U and MHP2U specimens, respectively. Moreover, the compressive residual stresses in the region of 50–100 μm below the surface are very similar for all three specimens. Furthermore, after the two-step aging treatment there was no significant difference in surface compressive residual stress values between the MFA and MHPA specimens. The residual stress relaxation phenomenon has also been found in shot-peened alloy 718 and titanium alloys specimens during annealing or aging treatments [55, 56, 60]. Cai et al. [56] have reported that the compressive residual stress induced by shot peening on Inconel alloy 718 samples would partially or fully relax during aging treatment at 700°C or 740°C with different aging time. As aging time increased, the residual stress gradually decreased. After about 12 h, the compressive residual stress decreased to around -100 MPa, and the ratios of relaxation at 700°C and 740°C were 71% and 83.7%, respectively. It is also observed that after aging treatment the absolute values of residual stresses are continuously increased with increasing depth.

Figure 5.13 Residual stress depth profiles for all specimens.

5.3.2.2 Surface Oxide Film

Surface oxide films formed on both the MF and MHP specimens after the two-step aging treatment were studied by means of SEM and XPS. After aging treatment, it was visually observed that there was a thin, adherent green-black oxide film, which could not be removed by acetone and ethanol, was formed on the surface for all three specimens. The SEM images of the surfaces and the cross-sectional morphologies of the oxide films formed on the surface of aged surface-treated specimens are shown in Figure 5.14. From these images, the oxide layer consists of some large and discrete oxide particles in the size range of 200–500 nm, and small uniform oxide particles in the size range of 50–100 nm (Figure 5.14 (a) and (b)). It is also observed from Figure 5.14 (c) that the thickness of the oxide layer is about 200–300 nm. Additionally, EDX results have confirmed that the oxide film is rich in Ti, Al, Mo and Nb as compared with bulk matrix chemistry.

Figure 5.14 SEM images of oxide films formed on the surface of the MFA and MHPA specimens after aging treatment: (a) oxide particles on the surface, (b) high magnification image of surface oxide particles, (c) cross-sectional image of the oxide films.

XPS surface analyses were also performed to investigate the oxide films that pre-formed on the surface of the MFA and MHPA samples. It was revealed that the two-step aging treatment produced a distinguishable modification of the surface chemistry. Figure 5.15 shows the XPS survey scans obtained at the surface of the MFU and MFA specimens. C1s, O1s, Ni2p, Fe2p, Cr2p, Ti2p, Ca2p, Mo3d and Nb3d peaks were detected in both conditions. At the same time, the MFA

specimen revealed relative higher intensity of Cr2p, Ti2p and Ca2p peaks but lower intensity of Ni2p, Fe2p, Mo3d and Nb3d peaks.

Figure 5.15 XPS survey scan peaks for the MFU and MFA specimens.

The XPS detailed peaks of surface oxides formed on MFU and MFA specimens are shown in Figure 5.16 for better display and comparison. It is observed that the intensities of peaks corresponding to metallic Ni and Fe also decrease after aging treatment, indicating a thicker oxide layer. Additionally, the peaks ascribed to metallic Mo and NbO oxide disappear for the MFA specimen.

Figure 5.16 XPS detailed peaks of surface oxides for the MFU and MFA specimens: (a) Ni 2p, (b) Cr 2p, (c) Fe 2p, (d) Ti 2p, (e) Ca 2p, (f) Mo 3d, (g) Nb 3d.

All peaks were fitted to determine the atomic concentrations of oxides in the surface layers on the MFA specimen and the results are listed in Table 5.6. The surface films mainly consist of Cr-enriched oxide. However, the concentrations of Cr oxide, Ti oxide and Ca oxide in the surface layer of the MFA specimen are higher than in the MFU specimen.

Table 5.6 Atomic concentrations of the oxides in the surface films on the MFA specimens

Oxide	Ni	Fe	Cr	Ti	Ca	Mo	Nb
At. %	9.5	10.5	40.7	9.5	24.9	2.4	2.5

In order to compare the thickness of the oxide films formed on the surface of unaged and aged specimens, XPS depth profiles were performed looking for Cr-enriched oxides that formed on the surfaces of the MFA specimen. The results are shown in Figure 5.17. It is clear, indirectly, that the thickness of the surface oxide film increased after the two-step aging treatment since the sputtering time increased from 3.7 min to 10.3 min. Moreover, XPS data showed no significant difference in the composition and thickness of the oxide layers between the MFA and MHPA specimens.

Figure 5.17 XPS depth profiles of Cr-enriched oxides for the MFA and MHPA specimens.

5.3.2.3 Surface Topography

Table 5.7 lists the surface roughness parameters of the MFA and MHPA specimens. After aging treatment, the MHPA specimens still show lower surface roughness as compared with the MFA specimen surface roughness. The arithmetic average roughness R_a and the root mean squared roughness R_q of the MHP2A specimen are 56% and 55% less compared to the MHP1A specimen.

Table 5.7 Surface roughness parameters of the MFA and MHPA specimens.

Specimen	R_a (μm)		R_q (μm)		R_p (μm)		R_v (μm)		R_t (μm)	
	Avg.	Std. dev.	Avg.	Std. dev.	Avg.	Std. dev.	Avg.	Std. dev.	Avg.	Std. dev.
MFA	7.73	0.49	9.20	0.38	22.47	1.23	-13.01	1.57	35.48	0.61
MHP1A	0.73	0.04	0.94	0.05	4.02	0.49	-3.77	0.61	7.79	0.63
MHP2A	0.32	0.01	0.42	0.02	2.92	0.39	-3.16	0.66	6.09	0.71

The surface topographies taken from the MFA and MHPA specimens are presented in Figure 5.18.

Figure 5.18 Surface topographies of specimens: (a) MFA, (b) MHP1A, (c) MHP2A.

5.3.2.4 Microstructure

The cross-sectional microstructure of the MF and MHP samples after the two-step aging treatment was also observed using OM, SEM and TEM imaging techniques. The OM and SEM images of the near surface region for the MFA and MHPA specimens after aging treatment are shown in Figure 5.19 and Figure 5.20. After the two-step aging treatment, the thickness of the visible deformed layer is dramatically decreased to between 20 and 50 μm in the MFA specimen (Figure 5.19 (a)), 100 and 150 μm for the MHP1A specimen (Figure 5.19 (b)), and 200 and 250 μm for the MHP2A specimen (Figure 5.19 (c)), respectively. Furthermore, for the surface-treated specimens in the aged conditions, a thin layer with a high volume fraction of nano-sized precipitates is formed close to the specimen surface.

Figure 5.19 OM images of the cross-sectional microstructure of specimens: (a) MFA, (b) MHP1A, (c) MHP2A.

It can be seen from the SEM image (Figure 5. 20) that the nano-precipitates are γ'/γ'' with sizes of between 30 and 300 nm, which will be further confirmed by TEM analysis later. It is also observed that the density of γ'/γ'' precipitates increases and the thickness of the nano-precipitate layer in the MHPA specimens increases from about 1–3 μm to about 10–15 μm as compared with the MFA specimen.

Figure 5.20 SEM images of the cross-sectional microstructure of specimens: (a) MFA, (b) MHP1A, (c) MHP2A.

After aging treatment, the dislocation arrays with the width about 300–500 nm are still visible at the depth of about 500 μm from the MHP2A specimen surface, but the dislocation density seemed to have reduced considerably, as shown in Figure 5.21. Also, it was interesting to see that higher amount of precipitations were formed along the $\{111\}$ slip planes than the matrix. The SAD pattern shows that the superlattice reflections $\{100\}$, $\{010\}$ and $\{110\}$ on the $\langle 001 \rangle$ electron beam direction are both due to γ' and γ'' phases, whereas, $\{1\ 1/2\ 0\}$ and $\{1/2\ 1\ 0\}$ type reflections only belongs to γ'' phase [61-63].

Figure 5.21 The TEM images at the depth of about 500 μm from the MHPA2 specimen surface: (a) BF micrograph; (b) $[-112]$ zone axis SAD pattern corresponding to (a); (c) BF micrograph (higher magnification); (d) BF micrograph showing precipitates; (e) $[001]$ zone axis SAD pattern corresponding to (d); (f)–(h) γ'/γ'' precipitates.

Figure 2.22 shows the deformation bands at the depth of 200 μm from the MHP2Aspecimen surface. The width of the deformation bands is in the range of 30–80 nm. It appears that the dislocation density is very high and most of the dislocations are accumulated between the bands and on the grain boundaries. Moreover, the γ' and γ'' precipitates were formed near those dislocations. The corresponding SAD patterns on the beam direction of $[011]$ present the superlattice reflections $\{100\}$ and $\{110\}$ on the due to γ' and γ'' phases.

Figure 5.22 The TEM images at the depth of 200 μm from the MHPA2 specimen surface: (a) BF micrograph; (b) BF micrograph (higher magnification); (c) [011] zone axis SAD pattern corresponding to (b).

Figure 5.23 shows bright-field TEM images of the near surface microstructure of the MHPA specimens. Much of the fine detail in the microstructure is obscured due to the strain contrast from the high density of dislocations induced by the surface treatment. Nevertheless, after aging treatment γ' precipitates with a global shape and γ'' precipitates with a disc shape are generated in the very top of the surface layer of the MHPA specimens (see Figure 5.23 (a) and (b)). The selected area diffraction (SAD) pattern inserted in Figure 5.23 (b) with a beam direction of $\langle 001 \rangle$ shows the superlattice reflections due to the γ'/γ'' precipitates[61, 62, 64,65]. It is evident from the MHPA specimens that the twin intersections and parallel nano-twins still existed in the near surface region. However, it seems that after the two-step aging treatment the density of nano-twins is reduced. Also, the width of the nano-twins increases from 100–150 nm (MHP1U) and 10–70 nm (MHP2U) to between 200 and 300 nm for MHP1A and 50 and 150 nm for MHP2A (Figure 5.23 (c) and (d)). The corresponding SAD pattern in Figure 5.23 (d) illustrates the elongated spots showing clearly the twinned structure, and the very faint γ' and γ'' super-lattice reflections.

Figure 5.23 TEM images of the near surface microstructure of the MHPA specimens: (a) nano-precipitates of MHP1A, (b) nano-precipitates of MHP2A, (c) nano-twins of MHP1A, and (d) nano-twins of MHP2A.

5.3.3 Corrosion behavior

Summarizing the results discussed previously, the MHP specimens displayed higher compressive residual stress values and deeper work hardening layers. Also the surface was smoother after MHP and the near surface region showed extensive microstructure changes, including nano-grains and nano-twins. At the same time, after the two-step aging treatment the compressive residual stresses in the near surface region have mostly been released, accompanied by increased hardness due to γ'/γ'' precipitation. Also, Cr-enriched oxide films with the thickness of 200–300 nm and nano-precipitates layers with high volume fractions of γ'/γ'' were formed in the top layer of the near surface region.

It has been reported that many influencing factors such as surface treatment, surface roughness, oxide/passive film, grain size, residual stress, alloy composition, temperature, corrosion environment, heat treatment, etc., may affect the corrosion behavior of alloys [10-13]. The first aim

of the electrochemical study was to obtain some information so as to ascertain how surface modifications induced by MHP could influence the corrosion behavior of the nickel-base alloy 718 in a 3.5 wt.% NaCl solution. The second aim of the electrochemical investigation was to determine how the additional aging treatment affected the pitting corrosion behavior of the surface-treated 718 alloy in a 3.5 wt.% NaCl solution. This part was accomplished by using EIS and potentiodynamic polarization measurements.

5.3.3.1 Electrochemical Impedance Spectroscopy

The passive films developed on corrosion resistant alloy including stainless steels and chromium containing nickel-base alloys have been extensively investigated by EIS and XPS [52, 53, 66-80]. Passive films formed on corrosion resistant alloys are generally bilayer or even multilayer structure, consisting of an inner defective oxide layer (primary passive film or barrier layer) that grows directly into the metal and an outer hydroxide layer that forms from the reaction of metal cations that are ejected from the barrier layer with species in the solution or by the hydrolytic restructuring of the barrier layer at the barrier layer/outer layer interface [66-70]. On stainless steels, XPS studies have confirmed the inner layer to be a Cr^{3+} oxide, and the outer layer to comprise predominantly iron hydroxide [52, 53, 71-74]. On chromium containing nickel-base alloys, the inner layer has found to be a Cr-enriched oxide, while the outer layer is a nickel-iron hydroxide [46-53].

Thus the impedance response of the passive alloys in contact with an electrolyte is a sum of three components including impedances of the two interfaces and that of the barrier passive film:

$$Z_{\text{total}} = Z_{\text{m/f}} + Z_{\text{f}} + Z_{\text{f/e}} \quad \text{Equation 5.1}$$

The processes occurring at the metal/passive film interface, at the passive film/solution interface, and within the passive film barrier layer, have been associated to a single time constant each. The high frequency time constant has been correlated to the metal/film interface [49,59,69,70], the

medium time constant has been attributed to the response of the film/electrolyte interface [59,62,63], and the low frequency time constant has been associated to the passive film [59,62,65].

In order to investigate the electrochemical characteristics of the passive films formed on the MF and MHP specimens, EIS measurements were carried out at OCP after immersion in a 3.5 wt.% NaCl solution at room temperature with different times, i.e. 1, 6, 12, 24, and 48 h. The results are presented in the form of Nyquist and Bode plots versus immersion time for the MF, MHP1 and MHP2 specimens, respectively, as shown in Figure 5.23–25.

Figure 5.23 shows the EIS diagrams of the MF specimen in a 3.5 wt.% NaCl solution. The Nyquist plots showed one small semicircle at high frequency and a large semicircle that did not end at low frequency for all immersion times. The Bode diagrams are characterized by two well-defined time constants, as indicated by the two peaks in the high–medium frequency range and the medium–low frequency range, respectively. It can be clearly seen that the impedance modulus in the medium–low frequency range increases with increasing immersion time. For longer immersion time, the impedance diagrams are very similar, which means that the passive films become relatively stable. For the MHP specimens, the impedance diagrams display the same features in comparison with the MF specimen, as indicated in Figure 5.24 and Figure 5.25.

Figure 5.23 EIS spectra measured at OCP after immersion for different times in a 3.5 wt.% NaCl solution at room temperature for the MF specimen.

Figure 5.24 EIS spectra measured at OCP after immersion for different times in a 3.5 wt.% NaCl solution at room temperature for the MHP1U specimen.

Figure 5.25 EIS spectra measured at OCP after immersion for different times in a 3.5 wt.% NaCl solution at room temperature for the MHP2U specimen.

The two time constants feature is often considered as the response from an inhomogeneous passive film, which consists of a compact inner layer and a porous outer layer. It has been demonstrated that the passive films on nickel-base alloys can be more accurately described as a double layer structure composed of an n-type outer region containing Ni/Fe oxide and hydroxide and a p-type inner region containing Cr oxide [54, 66, 80]. The low frequency time constant has been related to the inner barrier layer, and the time constant at high frequency range has been associated to the porous outer layer. The equivalent electrical circuit that has been usually used to interpret the EIS spectra displaying two time constants for the passive film is illustrated in Figure 5.26. In this model, R_s is the solution resistance. R_1 and Q_1 correspond to the resistance and capacitance of the porous layer which is responsible for the dissolution/precipitation processes through the passive film. R_2 and Q_2 represent the resistance and capacitance of the barrier layer that is responsible for the good resistance of the alloy [54, 66, 75, 80,81].

Figure 5.26 Equivalent electrical circuit for EIS results fitting.

Macdonald and his co-workers [68, 70,82] have proposed the point-defect model, involving the growth and destruction of the passive films. This model assumes that passive films generally form as bilayers, with a highly disordered barrier layer adjacent to the metal and an outer film comprised of a precipitated phase that may incorporate anions and cations from the solution. The R_2 and Q_2 combination at low frequencies may represent a diffusion phenomenon. It has been demonstrated that the process of migration of the metal vacancies and the oxygen vacancies within the passive films would exhibit the Warburg-type impedance. The surface is expected to be non-homogeneous because of surface roughness, impurities, dislocations, etc. [66, 75]. Consequently, the capacitance is replaced with a constant phase element (CPE) instead of an ideal capacitor for a better quality fit. The impedance of the CPE is given by

$$Z_{\text{CPE}} = [Q(j\omega)^n]^{-1} \quad \text{Equation 5.2}$$

where $j^2 = -1$, ω is the angular frequency, and n is an empirical exponent between 0 and 1. When $n = 1$, Q becomes equivalent to a true capacitance associated to an ideal capacitor. When $n = 0$, Q becomes equivalent to a resistance. When $n = 0.5$, Q becomes equivalent to Warburg impedance [16].

This circuit was used to fit the presented EIS data and a good fit was obtained, as can be seen in Figure 5.23–25. The fitted impedance parameters are summarized in Table 5.8. For all three surface modified conditions, after 6 h immersion the n_1 or n_2 values are relatively similar and are independent on the immersion time, while the Q_1 or Q_2 values decrease with increasing immersion time, which indicates the continuous modification of the passive films either by increasing the thickness or by changing the composition. It is observed that the values of R_2 are much higher than R_1 , which means that the protection of the passive film is predominantly controlled by the barrier layer. The low values of R_1 can be attributed to the selective dissolution of Fe and Ni and to the low stability of Fe/Ni oxide and hydroxide, which results in an outer layer with a high degree of defects. The values of n_1 are lower than those of n_2 , which may be due to higher defectiveness and heterogeneity of the outer layer.

Table 5.8 Fitted EIS results for the MFU and MHPU specimens measured at OCP in a 3.5 wt.% NaCl solution at RT

Specimen	R_s ($\Omega \text{ cm}^2$)	R_1 ($\Omega \text{ cm}^2$)	Q_1 (F cm^{-2})	n_1	R_2 ($\Omega \text{ cm}^2$)	Q_2 (F cm^{-2})	n_2
MF-1h	1.35 ± 0.02	104 ± 23	$5.32 \times 10^{-4} \pm 5 \times 10^{-5}$	0.87 ± 0.04	$5.06 \times 10^4 \pm 2 \times 10^3$	$2.40 \times 10^{-4} \pm 2 \times 10^{-6}$	0.78 ± 0.006
MF-6h	1.27 ± 0.03	272 ± 31	$6.75 \times 10^{-4} \pm 5 \times 10^{-5}$	0.70 ± 0.01	$2.24 \times 10^5 \pm 2 \times 10^4$	$1.77 \times 10^{-4} \pm 2 \times 10^{-6}$	0.84 ± 0.007
MF-12h	1.24 ± 0.03	215 ± 30	$6.68 \times 10^{-4} \pm 5 \times 10^{-5}$	0.69 ± 0.01	$2.78 \times 10^5 \pm 2 \times 10^4$	$1.53 \times 10^{-4} \pm 2 \times 10^{-6}$	0.85 ± 0.005
MF-24h	1.22 ± 0.04	178 ± 33	$6.54 \times 10^{-4} \pm 5 \times 10^{-5}$	0.68 ± 0.01	$3.05 \times 10^5 \pm 2 \times 10^4$	$1.39 \times 10^{-4} \pm 1 \times 10^{-6}$	0.86 ± 0.005
MF-48h	1.26 ± 0.03	189 ± 23	$5.93 \times 10^{-4} \pm 3 \times 10^{-5}$	0.68 ± 0.01	$4.66 \times 10^5 \pm 4 \times 10^4$	$1.36 \times 10^{-4} \pm 1 \times 10^{-6}$	0.87 ± 0.004
MHP1-1h	1.15 ± 0.02	26.8 ± 10.9	$2.12 \times 10^{-3} \pm 4 \times 10^{-4}$	0.70 ± 0.02	$1.68 \times 10^5 \pm 5 \times 10^3$	$1.19 \times 10^{-4} \pm 6 \times 10^{-7}$	0.90 ± 0.003
MHP1-6h	1.13 ± 0.02	24.6 ± 1.9	$4.92 \times 10^{-4} \pm 4 \times 10^{-5}$	0.78 ± 0.04	$5.69 \times 10^5 \pm 3 \times 10^4$	$9.72 \times 10^{-5} \pm 4 \times 10^{-7}$	0.93 ± 0.002
MHP1-12h	1.13 ± 0.01	17.2 ± 0.6	$4.77 \times 10^{-4} \pm 2 \times 10^{-5}$	0.79 ± 0.04	$1.17 \times 10^6 \pm 5 \times 10^4$	$9.11 \times 10^{-5} \pm 2 \times 10^{-7}$	0.93 ± 0.001
MHP1-24h	1.11 ± 0.01	14.0 ± 0.7	$4.43 \times 10^{-4} \pm 4 \times 10^{-5}$	0.77 ± 0.04	$1.85 \times 10^6 \pm 3 \times 10^4$	$8.24 \times 10^{-5} \pm 2 \times 10^{-7}$	0.94 ± 0.001
MHP1-48h	1.09 ± 0.02	11.6 ± 0.7	$4.20 \times 10^{-4} \pm 5 \times 10^{-5}$	0.77 ± 0.04	$2.12 \times 10^6 \pm 3 \times 10^4$	$7.71 \times 10^{-5} \pm 2 \times 10^{-7}$	0.94 ± 0.001
MHP2-1h	1.47 ± 0.04	12.9 ± 2.5	$1.16 \times 10^{-3} \pm 2 \times 10^{-4}$	0.72 ± 0.03	$1.58 \times 10^5 \pm 5 \times 10^3$	$1.27 \times 10^{-4} \pm 7 \times 10^{-7}$	0.89 ± 0.002
MHP2-6h	1.48 ± 0.02	17.9 ± 1.6	$5.80 \times 10^{-4} \pm 6 \times 10^{-5}$	0.77 ± 0.01	$1.14 \times 10^6 \pm 1 \times 10^5$	$9.12 \times 10^{-5} \pm 3 \times 10^{-7}$	0.91 ± 0.001
MHP2-12h	1.48 ± 0.02	18.7 ± 1.2	$4.93 \times 10^{-4} \pm 4 \times 10^{-5}$	0.78 ± 0.01	$1.92 \times 10^6 \pm 2 \times 10^5$	$8.14 \times 10^{-5} \pm 2 \times 10^{-7}$	0.91 ± 0.001
MHP2-24h	1.49 ± 0.03	19.6 ± 2.0	$4.39 \times 10^{-4} \pm 5 \times 10^{-5}$	0.78 ± 0.01	$2.38 \times 10^6 \pm 4 \times 10^5$	$7.15 \times 10^{-5} \pm 3 \times 10^{-7}$	0.92 ± 0.002
MHP2-48h	1.49 ± 0.03	18.5 ± 2.3	$4.07 \times 10^{-4} \pm 6 \times 10^{-5}$	0.79 ± 0.02	$2.81 \times 10^6 \pm 6 \times 10^5$	$6.61 \times 10^{-5} \pm 3 \times 10^{-7}$	0.92 ± 0.002

As compared with the MF specimen, the MHP specimens show lower Q_2 values at all immersion times. Moreover, the decrease of Q_2 is accompanied by an increase of R_2 , suggesting that the barrier layer formed on the surface of the MHP specimens are thicker and more protective than the one did on the MF specimen. In contrast to the barrier layer, the outer porous layer formed on the surface of the MHP specimens is thicker but less protective than the MF specimen since Q_1 values at all immersion times are lower and R_1 values are lower. The R_2 values of the MHP specimens after 48 h immersion increase by almost 3.5 times and 5 times in comparison with the MF specimen, indicating higher resistance to charge transfer and species transport through the barrier layer. Polarization resistance R_p is represented by the sum of the resistance of the inner and outer passive layer ($R_1 + R_2$). Since in the present case the value of R_2 is much larger than R_1 , the R_2 value can be considered corresponding to R_p .

The EIS measurements were carried out at OCP after 24 h immersion in a 3.5 wt. % NaCl solution to investigate the electronic and ionic properties of the oxide films formed on the surface-treated specimens after aging treatment.

Figure 5.27 shows the EIS results of all aged specimens using both Nyquist and Bode plot formats. The two time constants are well defined for the MFA and MHPA samples in the Bode diagram at high frequency and medium-low frequency, respectively.

Figure 5.27 EIS spectra measured after 24 h immersion in a 3.5 wt.% NaCl solution for the MFA and MHPA specimens after aging treatment.

The equivalent circuit of Figure 5.28 was fitted to the experimental data. In this model, R_s corresponds to the resistance of the electrolyte. The high frequency time constant, $R_{f/e}Q_{f/e}$, is attributed to processes at the film/solution interface, and the medium-low frequency time constant, R_fQ_f , is attributed to the oxide film and a diffusion process. Warburg element W_o was added to the circuit to improve the goodness of fit and could represent transport of ions within the passive film, in the frame of the point defects model. In general, the surface is expected to be non-homogeneous because of its roughness, impurities, dislocations, etc.; therefore, the capacitance is replaced with a constant phase element (CPE) instead of an ideal capacitor.

Figure 5.28 Equivalent electrical circuit used for fitting the EIS data.

The fitted impedance parameters obtained for all the aged surface-treated specimens are summarized in Table 5.9. It can be seen that for all three samples $R_{f/e}$ values are much smaller than R_f values, indicating the very slow corrosion processes that occurs in the passive alloys. MHP2A

specimen show higher R_f values as compared with the MFA specimen, corresponding higher corrosion resistance. Also, the decreased Q_f and Y_w values demonstrate the difficult diffusion capability of the ionic species within the passive film. This means that the film formed on the MHP2A specimen are more compact and homogeneous than the one on the MFA sample.

Table 5.9 Fitted EIS results for the MFA and MHPA specimens measured at OCP in a 3.5 wt.% NaCl solution at RT

Specimen	R_s ($\Omega \text{ cm}^2$)	$R_{f/e}$ ($\Omega \text{ cm}^2$)	$Q_{f/e}$ (F cm^{-2})	$n_{f/e}$	R_f ($\Omega \text{ cm}^2$)	Q_f (F cm^{-2})	n_f	Y_w ($\Omega^{-1} \text{ s}^{-0.5}$)
MFA	3.17	54.2	7.46×10^{-3}	0.57	4.79×10^5	1.07×10^{-4}	0.93	1.38×10^{-5}
MHP1A	2.66	656.4	1.07×10^{-3}	0.88	2.68×10^5	0.95×10^{-4}	0.88	2.57×10^{-5}
MHP2A	2.98	604.2	2.15×10^{-3}	0.79	6.23×10^5	0.83×10^{-4}	0.90	1.06×10^{-5}

5.3.3.2 Potentiodynamic Polarization

Figure 5.29 illustrates the potentiodynamic polarization curves recorded for the MF and MHP specimens in a 3.5 wt.% NaCl solution at room temperature. Electrochemical parameters, such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic Tafel slope (β_c), anodic Tafel slope (β_a), passive current density (i_{pass} , at 0 V_{Ag/AgCl}) and critical pitting potential (E_{pit}) were obtained from potentiodynamic polarization curves. E_{pit} was defined as the potential at which the current density increases significantly and rather rapidly above the passive current density. E_{corr} , i_{corr} , β_c and β_a were determined with the Tafel extrapolation method. On the one hand, the cathodic current density of the corrosion system should be ascribed to the reduction of oxygen dissolved in a 3.5 wt.% NaCl solution open to the air. It is seen that the cathodic branches of the polarization curves display a typical Tafel behavior instead of a limiting diffusion current which is in about the magnitude of $10^{-4} \text{ A cm}^{-2}$ [83-86]. Therefore, the cathodic process is controlled by activation polarization rather than concentration polarization. Moreover, the well-defined cathodic Tafel regions exist over one decade of current density, which satisfies another requirement for an accurate extrapolation [83, 85]. On the other hand, the anodic branches of the polarization curves do not display a well-defined experimental Tafel region because the anodic

curves show an active to passive transition. This definitely makes it impossible to get an accurate calculation of the anodic Tafel slopes by Tafel extrapolation. It has been reported that in the Tafel extrapolation method, use of both the anodic and cathodic Tafel region is preferred over the use of only one Tafel region. However, the corrosion rate can also be determined by Tafel extrapolation of either the cathodic or anodic polarization curve alone. If only one polarization curve is used, it is generally the cathodic branch which usually produces a longer and better defined Tafel region, while anodic polarization may sometimes produce concentration effects, such as passivation and pitting, as well as surface roughening which can lead to deviations from Tafel behavior [83, 86]. Thus, in our case, the cathodic branches can be extrapolated back to the corrosion potential E_{corr} to give the corrosion current density i_{corr} . Then the anodic current density (i_a) is calculated from

$$i_a (\text{net experimental}) = i_a - |i_c| \quad \text{Equation 5.3}$$

where $|i_c|$ is the cathodic current density. Accordingly, the calculated anodic current density is the sum of the experimentally observed anodic current density and the extrapolated cathodic current density. The corresponding electrochemical parameters obtained from the potentiodynamic polarization curves are listed in Table 5.10.

Figure 5.29 Potentiodynamic polarization curves measured in a 3.5 wt.% NaCl solution at RT for (a) the MFU and MHPU specimens, (b) the MFA and MHPA specimens.

Table 5.10 Calculated potentiodynamic polarization results for the MF and MHP specimens in a 3.5 wt.% NaCl solution RT.

Specimen	$E_{\text{corr}}(\text{mV}_{\text{SCE}})$	$i_{\text{corr}}(\mu\text{A}/\text{cm}^2)$	β_c (mV/dec)	β_a (mV/dec)	$i_{\text{pass}}(\mu\text{A}/\text{cm}^2)$	$E_{\text{pit}}(\text{mV}_{\text{SCE}})$	$E_{\text{pit}} - E_{\text{corr}}(\text{mV})$
MF	-275 ± 5	0.22 ± 0.05	110 ± 8	364 ± 12	1.01 ± 0.02	370 ± 15	646 ± 15
MHP1	-269 ± 3	0.16 ± 0.03	141 ± 6	429 ± 10	0.56 ± 0.01	461 ± 12	731 ± 12
MHP2	-259 ± 4	0.13 ± 0.03	158 ± 5	560 ± 11	0.44 ± 0.01	504 ± 13	763 ± 13

The results show a significant influence of MHP on the pitting corrosion behavior of nickel-base alloy 718. For these surface modified specimens the corrosion potential shifted towards a less negative value while the corrosion current densities of the MHPU specimens are decreased compared to the MFU specimen. The most positive value of corrosion potential is achieved with the MHPU specimen using the 4 m/min feed rate. Also, there is an evidence of a diminution of i_{corr} by 27 % for MHP1U and 41 % for MHP2U, respectively. After MHP, a more pronounced passive plateau is observed with evidence of a significant increase in the critical pitting potential compared to the MF specimen. The MHP1U and MHP2U specimens exhibit a large anodic shift of the critical pitting potential, i.e., +91 mV and +134 mV, respectively, compared to the MFU specimen. Thus, MHP has a beneficial effect on pit initiation. The properties of the passive films

seem improved as well from MHP, resulting in a diminution of i_{pass} from $1.01 \mu\text{Acm}^{-2}$ (MFU) to $0.56\mu\text{Acm}^{-2}$ (MHP1U) and to $0.44\mu\text{Acm}^{-2}$ (MHP2U), respectively. The values of $E_{\text{pit}}-E_{\text{corr}}$ for MHP1U and MHP2U specimens are 85 mV and 117 mV higher than the MF specimen, respectively, which indicates that MHP provides a larger region of passivity. These results indicate better passive film growth due to the MHP treatment, which shows good agreement with the EIS results.

After aging treatment, the corrosion potentials of the MFA and MHPA specimens shifted in the less negative direction, compared with those of the MFU and MHPU specimens. This may be attributed to the formation of thicker oxide films and γ'/γ'' precipitates. For the MFU specimen, the corrosion current density and passive current density decreased by one half after the two-step aging treatment. It should be pointed out that, after aging treatment the compressive residual stress value of the MFA specimen decreased to one half that of the MFU specimen, which may decrease the corrosion resistance of the alloy. However, the results showed an opposite phenomenon. It could be that a thicker Cr-enriched oxide film with better “protectivity” was formed on the surface during the aging treatment, which is in accordance with the EIS results.

For the MHPU specimens, it was interesting to find that both the corrosion current density and the passive current density slightly increased after the two-step aging treatment. Also, the critical pitting potential of the MHPA specimens dramatically decreased by $106 \text{ mV}_{\text{Ag/AgCl}}$ and $130 \text{ mV}_{\text{Ag/AgCl}}$ in comparison with the MHPU specimens (feed rates of 2 m/min and 4 m/min, respectively). This means that the potential for pit initiation decreased. These results indicate that the pitting corrosion resistance of the MHPU specimens decreased due to the aging treatment because of the large decrease in compressive residual stress. On the basis of EIS results, the protectivity of the passive film of the MHPU specimens was decreased after aging treatment since the polarization resistance was decreased. Thus, it is hypothesized that the compressive residual stress played a critical role in corrosion resistance of the MHP material. Moreover, it was found

that the critical pitting potential of the MFA specimen was 76 mV_{SCE} less than that of the MF specimen.

Nevertheless, the critical pitting potentials of the MHP1A and MHP2A specimens shifted in a more positive direction with increases of 61 mV_{Ag/AgCl} and 80 mV_{Ag/AgCl}, respectively, in comparison with the MFA specimens. This might be due to the decreased surface roughness after MHP. Also, results showed that among all aged specimens, the MHP2A specimen showed the lowest i_{pass} and i_{corr} , and most positive E_{corr} values. All this evidence indicates a lower susceptibility to pitting corrosion after MHP when using a feed rate of 4 m/min followed with the two-step aging treatment.

5.3.3.3 Corrosion Pits Morphology

Figure 5.30 shows the SEM images of corrosion pits for the all surface-treated specimens after potentiodynamic polarization tests. For the unaged specimens, the MF specimen displays circular-shaped isolated corrosion pits on the surface in the size range of 1-3 μm (Figure 5.30 (a)). The MHPU specimens showed corrosion pits with similar morphology but were smaller in size (i.e., about 500 nm; see Figure 5.30 (b)). It was observed that large numbers of circular-shaped isolated deeper pits were formed on the MFA specimen surface (see Figure 5.30 (c) and (d)). Conversely, less numerous shallow corrosion pits of smaller sizes were found on the surface of MHPA specimens (Figure 5.30 (e) and (f)). The diameters of the corrosion pits on the MHPA specimens remained small, in the range of 1-5 μm , whereas those of the MFA sample were in the range of 5-15 μm . Also, the total numbers of corrosion pits on the MHP specimens decreased when compared to the MF ones.

The observed reduction in number and size of corrosion pits may be attributed to the combined effects of compressive residual stresses and microstructure change. The magnified views of the corrosion pits on the surface of aged surface-treated specimens reveal details of the morphologies of the corrosion pits. The breakdown of the oxide film and the exposure of the

γ'/γ'' precipitates were observed in the deeper corrosion pit as shown in Figure 5.30 (c). High magnification SEM images (Figure 5.30 (d)) show that the γ'/γ'' precipitates are range in size from 100-300 nm. The dissolution of the oxide films was revealed in the shallow corrosion pits as shown in Figure 5.30 (f).

Figure 5.30 Corrosion pits morphologies of all surface-treated samples: (a) MFU, (b) MHPU, (c) MFA, (d) high magnification of MFA, (e) MHPA, and (f) high magnification of MHPA.

5.4 Discussion

5.4.1 Grain Refinement Mechanism

The grain refinement mechanisms of plastically deformed materials are strongly dependent on the crystal structure of the material and the deformation conditions. In general, slipping is the predominant mode of deformation for materials those have medium to high stacking fault energy (SFE), while twinning is very popular in lower SFE materials, especially at high strain rates or very large strains [65, 87, 88]. It is known that the SFE of nickel-base alloy 718 is of an intermediate value, and it has been shown in some publications that twinning dominated the deformation process in alloy 718 under different mechanical treatments [65, 89]. Sundararaman et al. [65] have investigated the deformation microstructure beneath the machined surface of alloy 718 and they have noticed that two distinct subsurface layers were formed, one in which grains were heavily fragmented and the other below this layer where grains still maintained their identity through heavy deformation had occurred within them. They proposed that the predominant mode of deformation in the heavily fragmented zones on the machined surface of alloy 718 appeared to be multiple twins with very fine size, and it changed to elongated twins to slip because the plastic

strain sharply decreased with increase in depth from the machine surface. Tao et al. [87] have also studied the grain refinement process during plastic deformation induced by surface mechanical attrition treatment on Inconel 600, which processes a low–medium SFE. They have observed that the plastic deformation mode was dislocation slip in the region of low strain and strain rate. However, the stain-induced nanocrystallization occurred in the high strain and strain rate region through formation of mechanical micro-twins and subsequent interaction of the micro-twins with dislocations in the surface layer. As shown in our microstructure results, nano-grains are formed at the surface and both parallel and multi-directional nano-twins are generated in the very near surface region during the MHP treatment. The formation of twins is due to the high values of dislocation density which make further slip become very difficult. With increasing strain and strain rate in the near surface layer, the thickness of mechanical twins decreases dramatically to several microns as much as a few nanometers. Moreover, owing to the increase of strain and strain rate at higher feed rate, the density of nano-twins increases. It is suggested from previous TEM observations that two mechanisms might lead to the evolution from micro-twins or nano-twins to nano-grains: (1) twin–twin intersections and (2) twin–dislocation interactions. In the first case, when two sets of nano-twins are activated during deformation, twin–twin intersections could produce rhombic blocks with some misorientation. In like manner, other shaped blocks will be generated with different sets of twin–twin intersections. Consequently, the original micron-sized grains will be subdivided into nanometer scale domains via twin–twin intersections. As plastic deformation proceeds, these refined blocks will subsequently change to randomly orientated nanocrystallines through grain boundary sliding or grain rotation. In the second case, the formation of thinner nano-twins is inhibited due to the effective confinement of the nano-twin boundaries. As a result, more dislocations are generated and trapped between twin boundaries with increasing strain and strain rate. These dislocations could either pile up against the nano-twins to form an incipient grain boundary, or form high density walls which are not parallel to the nano-twins, gradually subdividing the nano-twins lamellae into equiaxed nano-structured blocks, eventually

into randomly orientated nano-grains. Similar observations of nano-grains and nano-twins have been found by Villegas and his co-investigators [90-93] in their study on the nanocrystallization process produced by surface severe plastic deformation in a nickel-base Hastelloy[®]C–2000 superalloy with a very low SFE. Their results have showed that deformation twinning occurs at the earliest stages of deformation and the deepest layers of the materials where plastic deformation takes place.

On the basis of the above discussion, it may not be unreasonable to suggest that twinning could be the leading deformation mechanism for the formation of nanocrystallization layer on the impacted surface of alloys with low or intermediate SFE, via severe plastic deformation treatments such as machine hammer peening, shot peening, ultrasonic peening, surface mechanical attrition treatment and so on.

5.4.2 Passivation and Pitting Corrosion Mechanisms

The polarization resistance R_p values of all surface-treated specimens are displayed in Figure 5.31.

Figure 5.31 Polarization resistance obtained from fitted EIS results for all surface-treated samples.

The results show that R_p is increased after MHP, proving this surface treatment has a beneficial effect on the corrosion resistance of nickel-base alloy 718 in a 3.5 wt.% NaCl solution. Based on

the microstructure analysis, nano-grains and nano-twins were formed as well as a smoothing of the surface due to MHP. The increase in corrosion resistance of the MHP specimens is mainly due to the formation of nano-grains and nano-twins induced by the MHP treatment. Li and her co-workers [94-100] have studied on the effects of nanocrystallization on the corrosion behavior of 304 stainless steel, 309 stainless steel, Fe–10Cr and Ni-based superalloy. They have confirmed that the localized corrosion resistance in the solution with chloride ions was greatly increased by nanocrystallization due to the formation of a compact and stable passive film on the nanocrystallized coatings. It has been reported by Meng et al. [99] that nanocrystallization can change the chemical composition of the passive films because the high density grain boundaries could promote the diffusion of Cr to the surface, thus rapidly forming a homogenous passive film rich in Cr that would offer a better corrosion resistance. Ye et al. [96] have found that the Cr element distributed uniformly in the passive film on nanocrystallized coating, thus the interfacial reactions were decelerated and the corrosion resistance of the 309 stainless steel has been greatly improved. Liu et al. [101] have investigated the compositions of passive films formed on the nanocrystallized coating and the cast alloy by using XPS. The results have showed that the continuous and uniform passive film that enriched with Cr and Ti was rapidly formed on the nanocrystallized coating, resulting in higher corrosion resistance in a 3.5 wt. % NaCl solution. It was also showed that Cl^- ions took part in the formation of the passive film and incorporated in the film on the cast alloy while they were not detected in the passive film of the nanocrystallized coating, which indicated that nanocrystallization could decrease the adsorption ability of Cl^- on the surface of the material, thus retarding Cl^- to incorporate in the film. In addition, Sun and Meng et al. [102-104] have reported the beneficial influence of nano-scale twins on passive film properties as well as pitting corrosion resistance of nickel coating in solution with Cl^- . Their results demonstrated that the passive film formed on nano-scale twins coating was more compact and homogeneous than those on industrial electrodeposited nickel. On the basis of the above discussion, it is logical to suggest that the reason for the increase in the corrosion resistance of

the MHP specimens is due to the nano-grains and nano-twins which facilitate the formation of the homogeneous inner layer with higher concentration of Cr oxides and less defects.

From potentiodynamic polarization results as shown in Figure 5.32, it is also seen the beneficial effect of MHP.

Figure 5.32 Potentiodynamic polarization results of all specimens.

The increased corrosion potential and pitting potential, as well as decreased corrosion current density for the MHPU specimens might be associated with the formation of the nano-grains and nano-twins in the near surface region as well as a much smoother surface. Wang et al. [19] have investigated the effect of surface nanocrystallization induced by shot peening on corrosion resistance of 1Cr18Ni9Ti stainless steel. They found that shot peening significantly improved the

polarization behavior of the steel by decreasing both anodic current density and cathodic current density due to surface nanocrystallization. It was further suggested by Lee et al. [14] that the surface roughness is one of the main factors affecting the corrosion behavior and ‘the smoother the surface the better’ is a general rule of thumb to improve localized corrosion resistance because increase in surface roughness is likely to increase active surface area and the corrosion rate. According to Lee et al. [14], the corrosion current density of AISI 304 stainless steel decreased by a factor of 3 and the corrosion potential shifted to the anodic direction by 25 mV after ultrasonic peening because of the smoother surface.

On the one hand, the nano-grains could promote the diffusion of Cr to the surface, thereby facilitating rapid formation of the protective passive film with higher concentration of Cr. On the other hand, nanocrystallization could decrease the adsorption ability of Cl^- on the surface of the material, thus retarding Cl^- to incorporate in the film. It was suggested by Intrui et al. [105] that nanocrystallization could increase the density of lattice defects because of the reduced grain size, resulting in the reduced adsorption of Cl^- at single lattice defect and then decreasing the sensitivity to pitting corrosion. Sun and Meng [103, 104] have reported that the adsorption capability of Cl^- on the passive film on nano-scale twins coating was significantly attenuated, thus decreasing the susceptibility to pitting corrosion, which was responsible for the higher pitting potential. They suggested that formation of a twin could introduce a low energy segment into the random high angle grain boundary and could sometimes result in low coincidence site lattice structure, both of which might decrease the adsorption amount of Cl^- at the boundaries, where the pits always preferably initiate and develop.

Another most likely hypothesis is that the compressive residual stress makes penetration through the passive film of Cl^- more difficult. This is supported by Krawiec et al. [24] and Trdan et al. [16], who have reported a big increase of charge transfer and oxide film resistance of AA2050–T8 and AA6082–T651 aluminium alloys as a consequence of the compressive residual stress developed through laser shock peening process. It has been reported by Peyre et al. [21]

that a significant improvement in pitting potential (+0.1 V) was observed in 0.05 M NaCl solution after a pure mechanical laser peening treatment. Based on their findings, Peyre et al. [21] have suggested that the increase in critical pitting potential is most likely due to the combined effects of compressive residual stress and work hardening. The anodic shift of the pitting potential was also detected for AA6082-T651 aluminium alloy after laser shock peening, which was attributed to high compressive residual stresses due to the shockwave effect of the laser shock peening process [16]. Liu et al. [106] have confirmed the beneficial effects of compression on localized corrosion, indicated by the significantly increased breakdown and repassivation potentials, and a decrease in passive current density for samples under compression or with compressive residual stress. This is also consistent with the results reported by Peyre et al. [12] that the pitting corrosion resistance improved due to laser peening through an anodic shift of the pitting potential and a reduction of passive current density.

Another possible reason for the significant improvement of pitting potential is that MHP leads to a decrease of the potential gap between the surrounding matrix and inclusions such as carbides and nitrides, resulting in a reduction of local galvanic coupling and pit initiation sensitivity. Rouleau et al. [23] have reported that laser shock peening either preserves or reduces precipitate-matrix Volta potential gradients, which could explain the corrosion improvement in aluminum alloys. As observed from microstructure analysis, (Nb, Ti)C and (Ti, Nb)N are randomly distributed in the alloy. These inclusions could act as local cathodes with regard to the γ matrix, and the nearby region of these inclusions in the alloy would be easier to be attacked and corroded along with the film breakdown. Thus, it is suggested that the compressive residual stress introduced by MHP could decrease the potential drop between (Nb, Ti)C or (Ti, Nb)N and the γ matrix, which might be responsible for the high pitting potential.

MFA specimen shows higher R_p value in comparison with the MF specimen, indicating a higher corrosion resistance. This may be due to the formation of a Cr-enriched oxide film with the thickness of 200–300 nm on the surface of the alloy after aging treatment. For the MHP specimens,

a big drop of R_p values are observed after aging treatment, which means the corrosion resistance of the alloy is decreased. This may be due to the big relaxation of compressive residual stress during the two-step aging treatment. As compared with the MFA specimen, the R_p value of the MHP1A specimen increases and one of the MHP2A specimen decreases, which might be ascribed to the different compressive residual stress left after aging treatment. Potentiodynamic polarization results show that the corrosion current density and the passive current density slightly increased after the two-step aging treatment for the MHP specimens. Also, the critical pitting potential of the MHPA specimens dramatically decreased in comparison with the MHPU specimens. Based on microstructure analyses, both the MFA and MHPA specimens possessed nano-sized γ'/γ'' precipitates in the very near surface region. Thus the shift of pitting potential in a much more negative direction for all surface-treated specimens after aging treatment might be caused by γ'/γ'' precipitation, which can be harmful due to the galvanic effect between γ and the γ'/γ'' phases. Also, results showed that among all aged specimens, the MHP2A specimen showed the lowest corrosion current density, and most positive corrosion potential and pitting corrosion. The reason for this might result from the high compressive residual stress and smooth surface for this modified condition.

5.5 Summary

The effects of surface modifications induced by machine hammer peening and the two-step aging treatment on pitting corrosion behavior of oil-grade alloy 718 in 3.5 wt.% NaCl solution at RT were investigated, and some important conclusions can be summarized as follows:

- (1) Severe work hardening and high compressive residual stress are generated with surface smoothing and microstructure evolution in terms of formation of nano-sized grains and multi-directional nano-twins in the near surface region after machine hammer peening.

- (2) Two grain refinement mechanisms including twin–twin intersections and twin–dislocation interactions lead to the evolution from micro-twins or nano-twins to nano-grains due to machine hammer peening in oil-grade alloy 718 is proposed based on the microstructure observations.
- (3) Electrochemical tests results show that machine hammer peening has a beneficial influence on the pitting corrosion resistance of oil-grade alloy 718 in 3.5 wt.% NaCl solution at RT, indicated by a significant increase of the critical pitting potential (+134 mV) accompanied with lower corrosion current density and higher polarization resistance.
- (4) The improvement of pitting corrosion behavior of oil-grade alloy 718 in 3.5 wt.% NaCl solution at RT is mainly attributed to the surface smoothing, the generation of a larger compressive residual stress in the near surface region, and the formation of nano-grains and nano-twins produced by the MHP surface treatment.
- (5) After a two-step aging treatment, a Cr-enriched oxide layer is formed along with a nano-precipitates layer that consists of high precipitate fractions of γ'/γ'' on the top surface of the surface-treated specimens. Surface hardness increases after aging and the compressive residual stress is almost relaxed.
- (6) The two-step aging treatment results in higher susceptibility to pitting corrosion of oil-grade alloy 718 in 3.5 wt.% NaCl solution at RT, as manifested by a significant decrease in polarization resistance and critical pitting potential. However, the hammer-peened specimen processed at a feed rate of 4 m/min followed by aging treatment showed the best pitting corrosion resistance among the aged surface-treated samples.
- (7) The improvement in pitting corrosion behavior of oil-grade alloy 718 in 3.5 wt.% NaCl solution at RT is mainly attributed to surface smoothing and the larger compressive residual stress left after the aging treatment.

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Chapter 6: Conclusions

Following conclusions are drawn from research presented in the previous chapters:

- (1) Based on the microstructure analysis, the average grain sizes of oil-grade alloy 718 increased from 46 μm (solution-annealed) to 52 μm (one-step aged) and 60 μm (two-step aged). Isolated platelet δ phases were precipitated at some of the grain boundaries in both one-step aged and two-step aged specimens. The one-step aged specimen showed a uniform distribution of fine spherical (γ' , in 20–30 nm diameters) and elongated (γ'' , 5–15 nm in the c dimension and 30–150 nm in diameters) precipitates in the grains. On the contrary, the two-step aged sample showed much finer precipitates (γ' , in 2–10 nm diameters; γ'' , 2–12 nm in the c dimension and 5–35 nm in diameters).
- (2) Solution temperature is an influencing factor on the pitting corrosion resistance of oil-grade alloy 718 in 3.5wt.% NaCl solution. The corrosion current density was increased by one time, the polarization resistance was decreased by one time and the pitting potential sharply dropped about 715 mV as the temperature increased to 50°C and 80°C. Nevertheless, oil-grade alloy 718 showed an active corrosion behavior in 21 wt.% NaCl solution at 80°C. Aging treatment had no obvious influence on pitting corrosion resistance of oil-grade alloy 718 in all tested NaCl solutions.
- (3) The passive films formed on oil-grade alloy 718 in 3.5 wt% NaCl solution at three different temperatures at open-circuit potential exhibited n-type double-layer structure. The outer layer was composed of Cr and Ni hydroxides and small amounts of NbO, Nb₂O₅ and MoO₃ oxides, while the inner layer consisted of Cr₂O₃, NiO, Nb₂O₅ and NbO oxides. The passive film became more porous and the polarization resistance was decreased as the temperature increased to 50°C and 80°C due to the increased amount of hydroxides in the passive film. The thickness of the

outer layer was increased but the thickness of the inner layer was decreased with increasing temperature.

(4) There was no obvious effect of 3.5 wt.% NaCl solution on the CFCG rates of three types of oil-grade alloy 718 samples with different aging treatments, regardless of solution temperature. Nevertheless, the CFCG rates of oil-grade alloy 718 in 21 wt.% NaCl solution were increased in comparison with the ones tested in laboratory air and in 3.5 wt.% NaCl solution. Furthermore, aging treatments led to lower CFCG rates of oil-grade alloy 718 in all tested environments. However, no visible difference of CFCG rates in NaCl solution was observed between one-step aged and two-step aged specimens. Fractographic examination of the fractured surfaces indicated that the fatigue cracks propagate in the transgranular mode in oil-grade alloy 718 in all tested conditions, in spite of solution temperature and NaCl concentration. The CFCG mechanism of oil-grade alloy 718 in 3.5 wt.% NaCl solution at different temperatures was predominated by mechanical variables due to the very small dissolution rate and fast repassivation kinetics at the crack tip, while both anodic dissolution and mechanical loading were controlling mechanisms for the CFCG of oil-grade alloy 718 in 21 wt.% NaCl solution at 80°C because the higher concentration of Cl^- retarded the rate of repassivation and preserved the higher dissolution rate at the crack tip, resulting in obvious increase in CFCG rate.

(5) Severe work hardening and high compressive residual stress were generated with surface smoothing and microstructure evolution in terms of formation of nano-sized grains and multi-directional nano-twins in the near surface region after MHP. Two grain refinement mechanisms including twin–twin intersections and twin–dislocation interactions led to the evolution from micro-twins or nano-twins to nano-grains due to MHP in oil-grade alloy 718 was proposed based on the microstructure observations. MHP had a beneficial influence on the pitting corrosion resistance of oil-grade alloy 718 in 3.5 wt.% NaCl solution at RT, indicated by a significant increase of the critical pitting potential (+134 mV) accompanied with lower corrosion current density and higher polarization resistance. The improvement of pitting corrosion

behavior was mainly attributed to the surface smoothing, the generation of a larger compressive residual stress in the near surface region, and the formation of nano-grains and nano-twins produced by the MHP surface treatment.

(6) After a two-step aging treatment, a Cr-enriched oxide layer was formed along with a nano-precipitates layer that consists of high precipitate fractions of γ'/γ'' on the top surface of the surface-treated specimens. Surface hardness increased after aging and the compressive residual stress was almost relaxed. The two-step aging treatment resulted in higher susceptibility to pitting corrosion of oil-grade alloy 718 in 3.5wt.% NaCl solution at RT, as manifested by a significant decrease in polarization resistance and critical pitting potential. However, the MHP specimen processed at a feed rate of 4 m/min followed by aging treatment showed the best pitting corrosion resistance among the aged surface-treated samples. The improvement in pitting corrosion behavior was mainly ascribed to surface smoothing and the larger compressive residual stress left after the aging treatment.