

## **Investigation on Localized Corrosion Resistance of Nickel-based alloy UNS N07718 under Sour conditions of PuGuang Field simulated Environment**

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### **ABSTRACT**

Appropriate material selection for high temperature and high hydrogen sulfide/carbon dioxide ( $H_2S/CO_2$ ) partial pressure environments within oil and gas wells is essential for a robust corrosion management strategy. Corrosion resistant alloys (CRA) are routinely considered as an alternative to carbon steel for oil and gas applications under such conditions. However, published research relating to CRA passive layer composition and their protective properties in combined  $H_2S/CO_2$ -containing environments is limited, particularly in the presence of chloride ions. This study focuses on understanding the pitting corrosion mechanisms of solution annealed and precipitation hardened UNS N07718. This paper provides an in-depth analysis of the microstructure of both specimens using XRD, SEM/EDX and TEM. Corrosion experiments are conducted in simulated environments analogous to the PuGuang field at 80°C and the testing brine containing chloride and sulfate ions. A combination of elevated temperature/sour gas conditions with electrochemical methods are employed to evaluate the corrosion performance and particularly its localized corrosion performance under the influence of  $H_2S$  and  $CO_2$  partial pressures. Results from potentiodynamic polarization experiments showed an anodic branch that exhibited a complete passivation for both UNS N07718 samples.

**Keywords:** Corrosion Resistant Alloys, Localized Corrosion, Sour Corrosion

## INTRODUCTION

Extremely corrosive environments of today's oil and gas exploration requires more expensive Corrosion Resistant Alloys (CRAs) to be used for equipment such as tubulars. Material selection for oil and gas wells, especially those containing high hydrogen sulfide ( $\text{H}_2\text{S}$ ) and carbon dioxide ( $\text{CO}_2$ ) partial pressure, is very crucial. Hydrogen sulfide and carbon dioxide are quite aggressive to the materials used in oil field environments. The material of choice for these oil wells has to be reliable and cost-effective. This makes the material selection process a very complex and difficult task involving both financial and safety risks analysis.

Although adding corrosion inhibitors along with carbon steel tubulars was employed as a method to control corrosion in some of the fields containing high concentration of sulfate and chloride ions, it was not found reliable especially at elevated temperatures. Another concern is related to the high cost of the effective inhibitors and the high amount required to be continuously dosed. Increasing wall thickness of the carbon steel manufactured tubes was another alternative which has its own disadvantages such as increased weight and reduced interior dimensions. Therefore, employing CRAs has been preferred as an alternative for manufacturing oil and gas well components. This will be useful considering the life-cycle economy and safety regulations of the industry.

Amongst the wide variety of CRAs, Nickel (Ni) alloys are known as high performance materials having Cr and Mo as primary alloying elements. Nickel alloy UNS N07718 is a nickel-chromium-iron base alloy that is widely used in oil and gas production due to its good mechanical and corrosion resistance properties. It is a versatile nickel alloy with excellent localized corrosion resistance properties, dealing with a wide variety of arduous environments.<sup>1-6</sup> UNS N07718 have been used in harsh sour oil fields but the investigation is limited in terms of published research in relation to their performance in environments where there is a coexistence of  $\text{H}_2\text{S}$ ,  $\text{CO}_2$  and chloride ions.<sup>7,8</sup>

Alloying elements in nickel alloys have a potent effect on corrosion resistance of the material. They affect the performance of the alloy by incorporating into the passive layer and changing its structure. Chromium addition is used for the purpose of forming a stable protective passive layer that is highly resistant to oxidizing media and high temperature oxidation.<sup>9</sup> Molybdenum is added to improve the pitting and crevice corrosion resistance of these alloys.<sup>10</sup> Iron is also used in some Ni alloys, such as UNS N07718 and UNS N08825, to reduce costs, not to improve corrosion resistance. Addition of iron is also considered to be beneficial in enhancing strengthening and imparting weldability and machinability.<sup>11</sup> Aluminum is used in minor amounts to promote deoxidation and to form a tightly adherent alumina scale at elevated temperatures, reducing the tendency of nickel-based alloys toward attack by oxidation, carburization, and chlorination.<sup>12</sup> The performance of the protective layer strongly depends on the composition and structure of the film formed at different temperatures and pH values.

Wang et al.<sup>13</sup> investigated the influence of NaCl concentration, 0-0.2 mol/L, on corrosion resistance of Ni alloys at  $300 \pm 2$  °C. They found that the passive layer is less stable at higher concentrations of NaCl and the corrosion current density is higher. They also suggested that Al and Mg alloying elements contribute in protection of the surface by forming hydroxides which convert to oxides at high temperatures. Yubi Zhang et al.<sup>14</sup> investigated the corrosion performance of UNS N07718 at different partial pressures of  $\text{CO}_2$  ( $P_{\text{CO}_2}$ ) in NaCl aqueous solution at 150 °C and 205 °C. The potentiodynamic polarization results have shown that anodic branch exhibits complete passivation at all  $P_{\text{CO}_2}$  from 1.8 MPa to 9.8 MPa while the anodic branch shows a much weaker passivity for 11.6 MPa and 205 °C. This observation was also confirmed by the electrochemical impedance spectroscopy (EIS) measurements. Yin et al.<sup>7</sup> found that  $\text{H}_2\text{S}$  promotes localized corrosion in nickel alloys by acting as a cathodic depolarizer in  $\text{CO}_2/\text{H}_2\text{S}$ -containing environments. Furthermore, Klapper et al.<sup>10</sup> proved that high-Mo-content nickel alloys, above 3%, resist localized corrosion up to 150 °C while others were prone to pitting around 120 °C. Chen et al.<sup>15</sup> findings showed that temperature also plays a major role in pitting corrosion resistance of oil-grade UNS N07718 alloy. Potentiodynamic polarization experiments conducted by Chen et al.<sup>15</sup> suggested that pitting corrosion resistance of UNS N07718 in 3.5% NaCl solution decreased with increasing temperature

from room temperature to 50°C and 80°C. They also found that oil-grade UNS N07718 alloy exhibits active corrosion behavior when tested in a 21% NaCl containing solution at 80°C.

The purpose of this study is to investigate the corrosion performance of UNS N07718 alloy in simulated corrosion environment of PuGuang field. This sour corrosive field contains H<sub>2</sub>S/CO<sub>2</sub> and chloride ions. UNS N07718 is used in this study in the form of Solution Annealed (SA) and Precipitation Hardened (PH). Electrochemical techniques at elevated temperature in combination with surface analysis are performed to measure localized corrosion performance of this material in a CO<sub>2</sub>/H<sub>2</sub>S-containing environment.

## EXPERIMENTAL PROCEDURE

### Materials

UNS N07718 material used in this study was received in the form of SA and also subsequently PH after SA. The SA material was heated at 1025 °C for 2 hours followed by water quenching and the single-aged material was then heated at 788 °C for 6 hours followed by cooling in air.

### Experimental Methods

Different techniques were employed to characterize the as-received materials. This includes microstructure analysis, x-ray diffraction (XRD), scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS) and transmission electron microscopy (TEM). For microstructure observation, an etchant solution with composition of (36% HCl + 68% HNO<sub>3</sub> + H<sub>2</sub>O) was used for times ranging from 15 to 30 s.

The elevated temperature environment was simulated using an autoclave test system with a three-electrode setup described elsewhere.<sup>16</sup> A wet-ground sample, an Ag/AgCl high temperature high pressure reference electrode (in KCl solution) and a platinum electrode were used as working, reference and counter electrode, respectively. Test coupons with a surface area of 0.5 cm<sup>2</sup> were wet-ground up to 800 grit silicon carbide grinding paper one day before the corrosion tests. The brine solution was prepared according to the PuGuang formation water and its composition is listed in Table 1. The test solution was purged with nitrogen for at least 12 hours prior to starting the experiment. Just before commencement of the electrochemical test, the test samples were initially placed in the nitrogen-saturated electrolyte, a thermometer was installed near the specimen and the autoclave was heated using a hot-plate to reach 80 °C. It takes about 20 minutes for the solution to reach 80 °C, after which H<sub>2</sub>S-containing gas mixture (10 mol.% H<sub>2</sub>S-90 mol.% CO<sub>2</sub>) was bubbled into the solution for 1 hour until the open circuit potential (OCP) reached steady state with potential changing within the range of ±2 mV per 10 seconds. Then, the autoclave was pressurized until 0.1 MPa pressure and the experiment started. For the potentiodynamic polarization measurement, the scan started after 7 hours, 24 hours, 5 days and 7 days from the start of the test. The scan started from -50 mV vs. OCP with a scan rate of 0.5 mV/s and moving towards the anodic direction until the 3,000 µA/cm<sup>2</sup> of current density was reached. Each experiment was conducted at least two times to ensure the repeatability of the results. In case of observing 10%, or more, difference between the main electrochemical parameters, a third test was carried out to eliminate one experimental result with the highest deviation.

**Table 1**  
**Electrolyte composition**

| Ion                   | Na <sup>+</sup> | K <sup>+</sup> | Ca <sup>2+</sup> | Mg <sup>2+</sup> | Li <sup>+</sup> | NH <sub>4</sub> <sup>+</sup> | Cl <sup>-</sup> | SO <sub>4</sub> <sup>2-</sup> |
|-----------------------|-----------------|----------------|------------------|------------------|-----------------|------------------------------|-----------------|-------------------------------|
| <b>Content (mg/L)</b> | 22500           | 1150           | 2280             | 49.7             | 10.6            | 107                          | 41000           | 834                           |

## RESULTS

### Microstructural Characterization

The microstructure of SA as well as PH UNS N07718 samples after etching are shown in Figure 1 and Figure 2, respectively. The annealing twins and grains were observed in these micrographs. The comparison of the microstructures in these two figures with the reference images presented in API<sup>(1)</sup> 6ACRA standard proves that these microstructure are acceptable for oil-grade alloys.<sup>17</sup> There are also dispersed particles observed on both samples. The XRD patterns of both samples in Figure 3 show identical microstructures with only the  $\gamma$ -matrix being detected.  $\gamma$ -phase is an austenitic solid solution phase that retains its FCC structure up to the melting point. According to the previous studies,<sup>18, 19</sup> other phases such as  $\delta$  should be present within the microstructure. Most probably those phases were below the minimum detection limit of the instrument and therefore did not reveal in the XRD patterns.

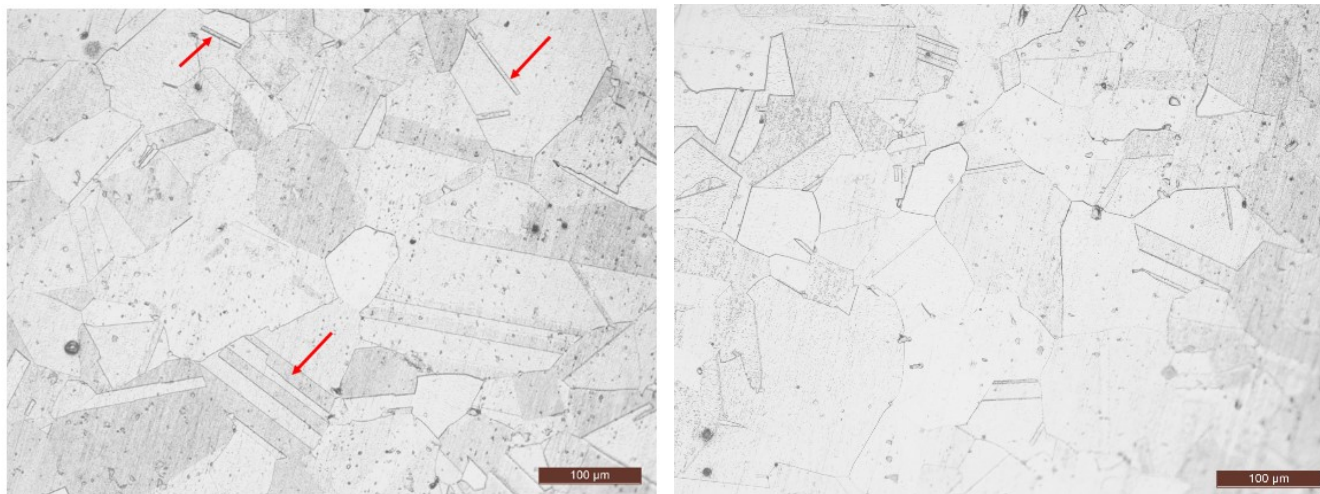


**Figure 1: Microstructure of as-received SA UNS N07718 (arrows show annealing twins)**

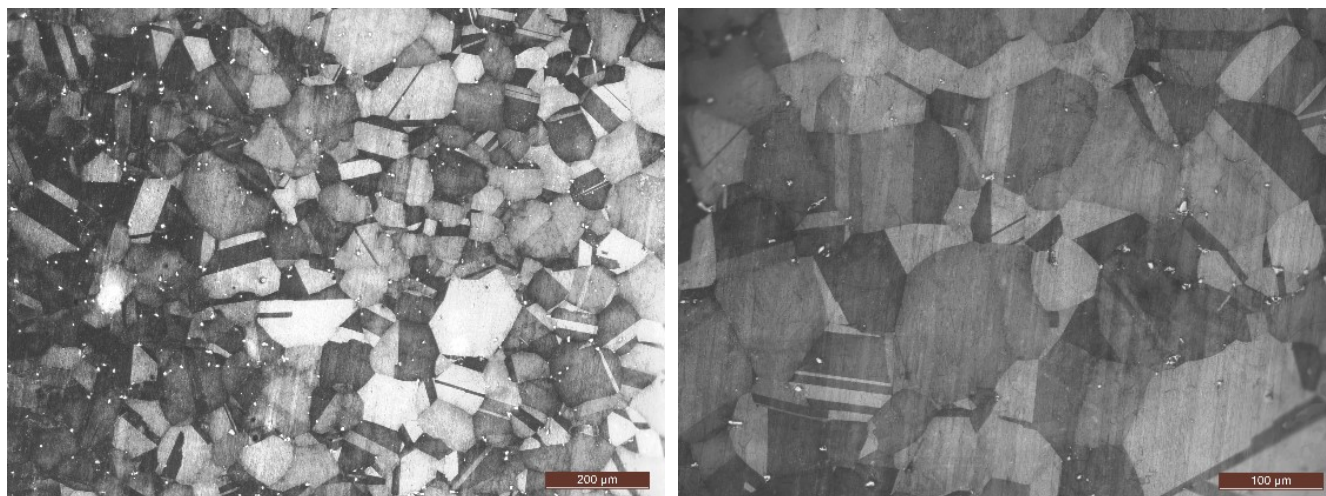


**Figure 2: Microstructure of as-received PH UNS N07718**

<sup>1</sup> American Petroleum Institute (API), 200 Massachusetts Avenue NW, Suite 1100, Washington, DC 20001-5571, USA.

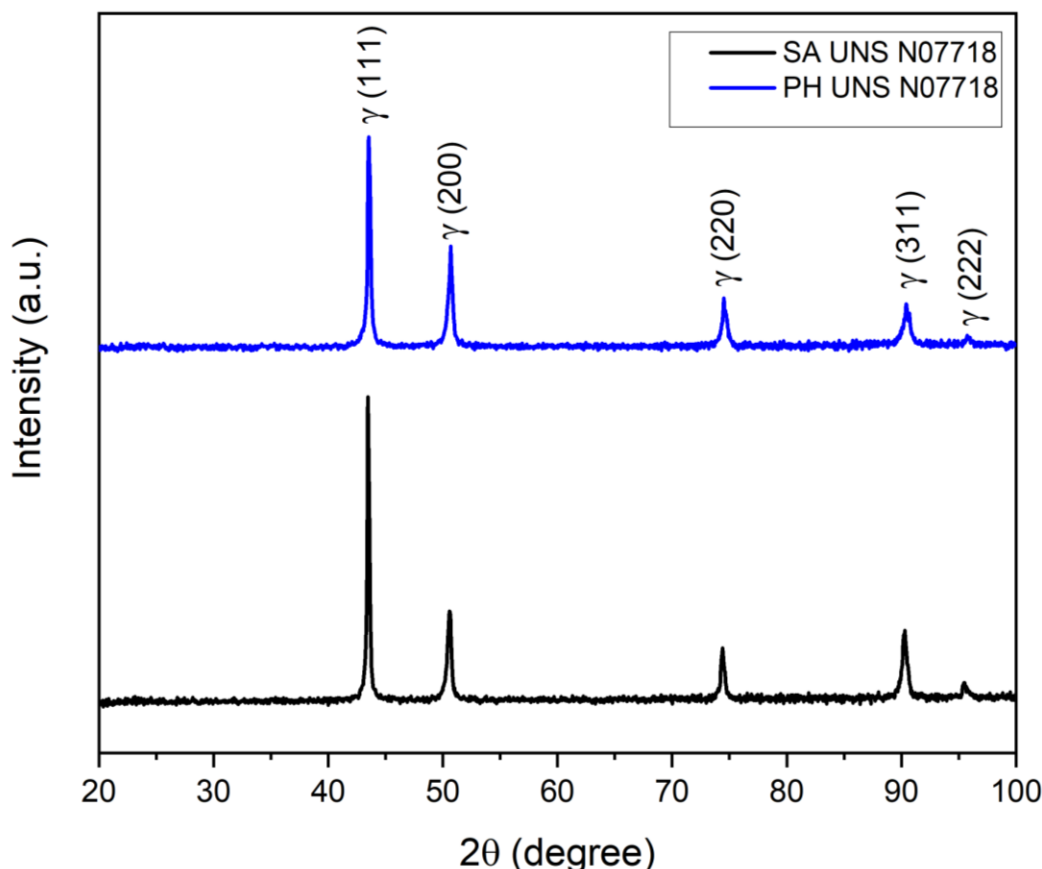


**Figure 3: XRD pattern of as-received SA and PH UNS N07718 samples**

The SEM/EDS results of both UNS N07718 samples, (shown in Figure 4), show that the light grey particles are rich in niobium (Nb) and the dark grey particles are rich in titanium (Ti). The SEM micrographs show that the Nb-rich particles significantly outnumber the Ti-rich particles in both samples. Niobium and titanium alloying elements are added to Ni-based alloys to prevent sensitization due to carbide precipitation along grain boundaries. These elements could also promote high temperature strength through solid-solution and precipitation-hardening mechanisms. Elemental composition of the particles, (shown in Figure 5 and Figure 6), shows that the light grey particles are NbC and the dark grey particles are TiN. The presence of these particles at grain boundaries are favorable for grain size control.

The surface analysis results presented so far did not show any difference between the SA and the PH specimens. However, the TEM dark field images in Figure 7 show the formation of  $\gamma'$  and  $\gamma''$  phases in the PH sample while no such phases were observed for the SA sample.  $\gamma'$  and  $\gamma''$  are the main precipitation strengthening phases in UNS N07718 alloy.  $\gamma'$  is an intermetallic  $\text{Ni}_3(\text{Ti},\text{Al})$  strengthening precipitate formed in Ni- alloys.  $\gamma''$  is another intermetallic ( $\text{Ni}_3\text{Nb}$ ) which forms in alloys containing around 5 wt.% Nb.<sup>20, 21</sup> It is a metastable compound which converts to delta phase at temperatures above 850 °C. The relative amount of the two phases ( $\gamma'$  and  $\gamma''$ ) depends on the ratio of Nb to (Ti+Al) content.<sup>22</sup> These results show that the ageing treatment was successful, and the relevant phases were formed during heat treatment.