INTERNAL OXIDATION OF ALLOY 690

by

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Abstract

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This dissertation studies the anomalous internal oxidation of Alloy 690 in a simulated primary water environment using time-resolved studies. Experiments were carried out in a steam/hydrogen mixture at atmospheric pressure and 480 °C in a tube reactor.

Samples were exposed for a total of 100 hours with several interruptions and were studied between consecutive exposures. Scanning Electron Eicroscopy (SEM) imaging was used to observe changes on the surface, and Energy Dispersive X-Ray (EDX) elemental analyses was performed on the grain boundaries and within grains. Crystallography of grain boundaries was also carried out using Electron Backscatter Diffraction (EBSD).

Results showed that the surface coverage of nodules increased with exposure time. The external oxide formed near grain boundaries had a fairly constant width over time, but the grain boundary region was dynamic, with signs of temporary internal oxidation, accompanied by stress relief due to diffusion of nickel to the grain boundary.
To my beloved family
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Chapter 1

Introduction

Alloy 690 is a nickel-based alloy that has recently started to replace the commonly-used Alloy 600 in nuclear power plants. Alloy 690 contains 30% Cr, which, according to the classical theory of oxidation (Young, 2008), is well above the transition from internal to external oxidation. Recently, Persaud et al. (2015) reported a surprising case of internal Cr oxidation in Alloy 690 exposed to hydrogenated steam at 480 °C, an environment considered to simulate and accelerate primary water exposure and potential stress corrosion cracking in a pressurized water reactor (PWR) or Canadian deuterium uranium (CANDU) system. Intragranular internal oxidation of Cr was accompanied by formation of nodules of metallic Ni on the alloy surface. A strip of material adjacent to each grain boundary formed a green external oxide and was free of large nodules; the large width of this zone (microns) contradicts theories of internal-external oxidation transitions.

The purpose of this study is to investigate the anomalous internal oxidation of Alloy 690 in a simulated primary water environment. We expose coupons of Alloy 690 to a steam/hydrogen mixture at atmospheric pressure and 480 °C while keeping the partial pressure of oxygen below the dissociation pressure of NiO. Coupons are exposed for a total of 100 h with interruptions at 1 h, 3 h, 10 h, and 30 h. Time-resolved formation of Ni
nodules is investigated and the changes in the grain boundary areas over time are studied using scanning electron microscopy (SEM) and Energy Dispersive X-Ray (EDX) analyses on the surface and cross section of the coupons. Crystallography of grain boundaries was also performed using the Electron backscatter diffraction (EBSD) technique to investigate whether grain orientation plays any role in internal/external oxidation of grains.

1.1 Literature Review

1.1.1 Nickel-based alloys

1.1.1.1 Application of Ni-Cr-Fe alloys in nuclear power plants

Nickel based alloys such as 690, 600, and 800 which have an austenitic structure are highly resistant to environmental degradation and have been widely used in the primary side of pressurized water reactors (PWR) or Canadian deuterium uranium (CANDU) systems. The locations where these alloys are used in a PWR system are shown in Figure 1.1 (Zinkle and Busby, 2009). The primary circuit temperature for PWR ranges from 286 °C to 342 °C and for CANDU systems from 280 °C to 320 °C. 20 to 50 cm³ of hydrogen at standard temperature and pressure (STP) is added for each kg of water to prevent the water decomposition in PWR systems (Scott, 1999).

Alloy 690 was developed in the early 1980’s and was applied in industry around 1989 for the first time. Since then, no SCC failures of Alloy 690 have been reported in the industry. Alloy 690 is currently used in nuclear power industry in a number of applications such as the control rod drive mechanism (CRDM) housing, and transport tubing in both the primary (irradiated) and secondary (non-irradiated) circuits (Miller, 2016).

Although no SCC failures of Alloy 690 have been reported so far, it is important to study the possibility of future failures and to identify potentially significant modes of
Figure 1.1: Schematic of key components utilizing structural materials in a PWR system (Zinkle and Bushy, 2009)
Figure 1.2: Fraction of replaced or shutdown steam generators vs calendar years for Alloy 600MA plants in the world. Data from Steam Generator Progress Report (Staehle and Gorman, 2003)

damage and their possibility of occurrence early on, so that preventative measures can be taken. Figure 1.2 shows the fraction of replaced or shutdown steam generators over years for Alloy 600MA plants in the world, which demonstrates an induction period followed by an almost constant failure rate (Staehle and Gorman, 2003). Conducting accelerated laboratory experiments on Alloy 690 under the same conditions as Alloy 600 would allow the calculation of an “improvement factor” (IF) that would help one predict SCC failures in Alloy 690.

1.1.1.2 Microstructure of Alloy 690

The Ni-Cr-Fe ternary phase diagrams for 400 °C, and 650 °C are shown in Figure 1.3. Alloy 690 is marked in red. Alloy 690 is stable and single-phase austenitic (γ), and does not show any secondary phase, similar to alloys 600 and 800 which are widely used in nuclear reactors. Another possible phase is the chromium carbide in the form of M_{23}C_{6}, in which metallic Cr content is greater than 90%. In comparison with Alloy 600, the solubility of carbon in 690 is much lower. Therefore, carbide precipitation happens at much higher temperatures (Was, 1990). Certain heat treatments will result in carbide
precipitation and chromium depletion at the grain boundaries (Was et al., 1981). The extent of chromium depletion increases with an increase in carbon contents or a decrease in temperature. The depth of the chromium depletion zone in Alloy 690 is shallower than that of Alloy 600 because of the different forms of their carbides: \( M_{23}C_6 \) in Alloy 690, and \( M_7C_3 \) for Alloy 600.

![Phase diagram for 650 °C Marucco (1995)](image1)
![Phase diagram for 400 °C Staehle and Gorman (2003)](image2)

Figure 1.3: The Ni-Fe-Cr ternary phase diagrams for 400 °C and 650 °C. Alloy 690 is identified in red and is single-phase austenitic.

1.1.1.3 Effect of element impurities

In Ni-Fe-Cr alloys, small amounts of impurities can accumulate (during refining and melting processes) which can result in slight advantages or disadvantages. Minor amounts of the following elements have the following effects:

- **Mn, Al, and Ti**: These elements often improve the mechanical properties of the alloy. Carbon precipitation in Al and Ti increases the hardness of the material. However, localized nucleation of these elements can have a negative effect (Khanna, 2002).
• Si: The advantage of Si is in reducing the rate of oxidation. However, if the amount of Si is larger than 3 wt%, it may result in embrittlement of the alloy (Khanna, 2002). If the corrosion potential is high, Si-rich passivating oxides can also occur.

1.1.1.4 Heat treatment

In nuclear plants, two types of heat treatment are common for Ni alloys to improve quality: a) annealing, and b) thermal treatment. The annealing process is performed in order to homogenize the composition of the alloy, to refine the grain structure, and to promote re-crystallization of the alloy. A high temperature solution anneal (SA) dissolves carbide and enhances the growth of grains. The amount of carbon in nickel-based alloys such as 690, 600, and 800 is low. Therefore, a solution annealing temperature in the range of 950 °C to 1100 °C is sufficient. To fully ensure that carbide is completely dissolved, a higher temperature can be used (Bauccio et al., 1993; Hoang et al., 1998). Figure 1.4 shows how a high SA temperature results in a complete dissolution of carbon. Saturation of carbon in the matrix can be obtained by a fast cooling step (quenching) right after the annealing process (International Atomic Energy Agency, 2011). Thermal treatment (TT), on the other hand, is done to precipitate chromium carbides intergranularly. Thermal treatment of nickel alloys is done at a temperature of 500 °C to 900 °C for a duration of more than 16 h (Was et al., 1981).

1.1.2 Internal oxidation

Oxidation in alloys means formation of any compound such as oxide, carbide, or nitride of the metal. The internal oxidation phenomenon happens when selective oxidation of an alloy component happens but a scale does not develop because the oxide can not reach the surface quickly enough. In the internal oxidation process, an oxidant gas dissolves in an alloy, and diffuses inward. The oxidant gas then reacts with the solute metal (the more reactive element) and forms precipitates of metal oxide (Young, 2008).
Chapter 1. Introduction

Figure 1.4: Schematic of the carbide precipitation process (International Atomic Energy Agency, 2011)
Internal oxidation is the reason for a large percentage of high-temperature corrosion failures. The products of internal oxidation result in negative effects on the alloy subsurface, such as embrittlement and expansion, which might also cause the surface to flake off (Young, 2008). Internal oxidation occurs in binary or ternary alloys that include a noble solvent element, such as Ni or Ag, and a reactive solute element, such as Cr, Al or In (Young, 2008; Bradley et al., 1997; Yi et al., 1994; Brumm et al., 1994; Shida et al., 1982, 1981; Stott and Wood, 1988; Nesbitt, 1989; Niu et al., 2006).

Stott and Wood (1988) characterized four modes of internal/external oxidation as shown in Figure 1.5: a) internal oxidation, b) formation of a continuous healing layer of oxide at the internal oxide/alloy interface, c) external oxidation (in the absence of internal oxidation), and d) intergranular oxidation (Stott and Wood, 1988). With an increase in the concentration of the active solute element in the alloy, a transition from internal to external oxidation occurs (Stott and Wood, 1988). At sufficiently high temperature and extremely low partial pressure of oxygen, the “healing layer” of oxide can form regardless
of the concentration of solute, because the time-dependent inward flux of oxygen is less than the outward flux of the reactive element. Therefore, the oxide forms on the surface or on the area very close to the surface, which is called external oxidation (Newman and Scenini, 2008). Internal oxidation, on the other hand, occurs when the time-dependent inward flux of oxygen becomes greater than the outward flux of solute, especially when the solvent metal is noble (Newman and Scenini, 2008).

1.1.3 Internal oxidation kinetics

Internal oxidation happens when oxygen diffuses into the alloy and reacts with the more active element to form an oxide, while the noble element does not oxidize. As mentioned, internal oxidation to occur, the inward flux of oxygen must be greater than the outward flux of the solute element (Young, 2008). To initiate internal oxidation, the partial pressure of oxygen has to be less than the dissociation pressure of the solvent metal oxide. Conventional thermodynamic calculations can be used to calculate the threshold partial pressure of oxygen (Wagner, 1959).

Consider a binary AB alloy in which A is a noble element and B is the active element in the alloy. When the partial pressure of oxygen is below the threshold mentioned above, A does not oxidize (to form AO) while B forms a stable oxide. The reaction for forming the stable oxide of B (Young, 2008) is as follows:

$$B + \frac{\nu}{2} O_2 \rightleftharpoons BO_{\nu}$$

(1.1)

Component B can be either mobile or immobile. The internal precipitation of the stable oxide (BO\(_\nu\)) and the reactant concentration profiles are shown in Figure 1.6. When B is immobile, only oxygen diffuses, and when B is mobile, both B and oxygen diffuse. The
Gibbs free energy for reaction (1.1) can be calculated as follows:

\[
\Delta G_{\text{BO}^\nu} = -RT \ln \left( \frac{\alpha_{\text{BO}^\nu}}{(\alpha B)(\alpha O_2)^\nu/2} \right)
\]  

(1.2)

where \( R \) is the ideal gas constant, \( T \) is the temperature (K), and \( \alpha \) is the activity coefficient. We consider the value of \( \alpha \) to be 1 for gas and solids. Using Equation (1.2), we can calculate the minimum required partial pressure of oxygen needed to oxidize B as follows:

\[
P_{O_2} = \exp \left( \frac{\Delta G_{\text{BO}^\nu}}{RT} \right)^{2/\nu}
\]  

(1.3)

Detailed calculations for our experimental conditions are provided in Section 2.1.1. In the absence of external oxide scale, several studies have derived expressions describing the kinetics of internal oxidation (Young, 2008; Rapp, 1965; Wagner, 1959). Wagner (1952) calculated the depth of the internal oxidation zone as

\[
\xi = 2 \gamma (D_O t)^{1/2}
\]  

(1.4)
and the velocity of the reaction as

$$\frac{d\xi}{dt} = \gamma \left( \frac{D_O}{t} \right)^{1/2}$$  \hspace{1cm} (1.5)

where $\xi$ is the depth of the internal oxidation zone, $t$ is time, $D_O$ is the diffusivity of oxygen in the base metal, $\gamma$ is a dimensionless parameter calculated using the equations described in Rapp (1965). It is experimentally confirmed that the parameter $\gamma$ is a function of time at constant oxygen pressure in an isothermal oxidation reaction (Rapp, 1965). According to Fick’s second law, the diffusion of oxygen can be obtained as follows:

$$\frac{\partial N_O}{\partial t} = D_O \frac{\partial^2 N_O}{\partial x^2}$$  \hspace{1cm} (1.6)

and similarly, for the diffusion of B:

$$\frac{\partial N_B}{\partial t} = D_B \frac{\partial^2 N_B}{\partial x^2}$$  \hspace{1cm} (1.7)

where $N_O$ is the mole fraction of oxygen in the base metal and $N_B$ is the mole fraction of B. Considering the boundary conditions and applying Fick’s second law, $N_O$ and $N_B$ can be calculated by using the value of the mole fraction of oxygen at the external surface ($N_O^{(s)}$) and mole fraction of B in the bulk alloy ($N_B^{(o)}$). The details of these calculations are provided by Young (2008); Rapp (1965); Wagner (1959). On the internal oxidation front, the inward flux of oxygen and the outward flux of B have to be equal according to their stoichiometric coefficients at $x = \xi$. According to Fick’s first law:

$$\lim_{\epsilon \to 0} \left[ D_O \left( \frac{\partial N_O}{\partial x} \right)_{\xi-\epsilon} \right]_{\xi+\epsilon} = \nu D_B \left( \frac{\partial N_B}{\partial x} \right)_{\xi+\epsilon}$$  \hspace{1cm} (1.8)

If $\frac{D_B}{D_O} < \frac{N_O^{(s)}}{N_B^{(o)}}$, there is an excess amount of oxygen with respect to the diffusion of B, and, therefore, the internal oxidation layer will be thick. On the other hand, when $\frac{D_B}{D_O} >> \frac{N_O^{(s)}}{N_B^{(o)}}$
more number of atoms of B diffuse toward the internal oxidation zone; therefore, the internal oxidation zone will be rich in $BO_\nu$ and its density increases. Figure 1.7 shows the concentration profiles for internal oxidation.

![Concentration profiles for internal oxidation](image)

Figure 1.7: Concentration profiles for the exclusive internal oxidation of alloys (Rapp, 1965)

### 1.1.4 Transition from internal to external oxidation

Transition from internal to external oxidation depends on the inward flux of oxygen, the outward flux of the solute element, and the volume of internal oxide precipitation. When the concentration of the solute element surpasses a certain threshold, its outward flux increases which results in significant oxide growth and the formation of a continuous oxide layer which prevents further oxygen diffusion (Wagner, 1959; Young, 2008).

A large number of studies have focused on the transition from internal to external oxidation in different alloys. For example, Wagner (1968) studied Cu-Pt and Cu-Pd, Rapp (1961); Leblond et al. (2013) studied Ag-In, Atkinson (1982) studied Fe-Si, Lashgari et al. (2014) studied Mn steel, and Niu et al. (2006) and Nesbitt (1989) studied Ni-Al, Ni-Cr, and Ni-Cr-Al alloys.

Rapp (1961) was the first to investigate Wagner’s theory for internal to external oxidation in alloys (Wagner, 1959) for an Ag-In system and to calculate the critical
volume fraction of internal oxide precipitation required for a transition from internal to external oxidation. He conducted experiments at 550 °C and at oxygen partial pressure varying within a range of 1 atm to $10^{-4}$ mm Hg and modeled the solute element mole fraction as a function of the critical volume fraction, oxygen solubility, oxygen and solute element diffusivities, and the molar volumes of oxygen and the solute metal oxide (Rapp, 1961). The critical volume fraction calculated by Rapp (1961) has later been used to successfully approximate the critical fraction required for the transition from internal to external oxidation for other alloys as well (Atkinson, 1982; Wagner, 1968).

1.1.5 Relief of the internal stress caused by volume expansion

Volume expansion occurs as a result of internal oxide formation. This increase of volume in the metal lattice and along the grain boundaries causes large amounts of compressive internal stress between the surface and the oxidation front. To relieve this internal stress, the noble solvent metal is forced out to the surface of the alloy (Guan and Smeltzer, 1994; Bradley et al., 1997; Young, 2008; Guruswamy et al., 1986). This internal stress can also cause plastic deformation and dislocation generation, which in turn can accelerate the outward diffusion of the solvent element and result in internal oxidation. Several studies have shown that the volume of the metal accumulated on the surface of the alloy is equal to the internal oxide precipitation, which confirms that the solvent metal expulsion occurs as a result of the compressive stresses due to internal solute oxide formation (Guruswamy et al., 1986; Yi et al., 1994; Young, 2008). For example, Yi et al. (1994) showed that the volume of the expelled Ni in exposed Ni-Al and Ni-4Al-xSi alloys was comparable to the calculated volume of Al and Si internal oxides. Figure 1.8 shows this phenomenon where metallic Ag expulsion to the surface occurs in an Ag-In alloy exposed to air at high temperatures (Guruswamy et al., 1986).

Several studies have focused on this interesting mechanism through which the solvent expulsion occurs, and there exists a number of theories on this phenomenon, such as
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Figure 1.8: SEM micrographs of metallic Ag expulsion to the surface of a dilute Ag-In alloy after exposure for 2 hours in air at 1073 K (Guruswamy et al., 1986)

Nabarro-Herring diffusional creep (Yi et al., 1994; Bradley et al., 1997; Young, 2008), extrusion through mechanical action (Young, 2008), diffusion via oxide-metal interfaces (Brumm et al., 1994; Bradley et al., 1997), and dislocation pipe diffusion (Yi et al., 1994; Bradley et al., 1997; Young, 2008; Guruswamy et al., 1986).

1.1.6 Alloy 690

The presence of 10-30 wt.% chromium in Ni-Cr based superalloys results in corrosion resistance and concentrations necessary for providing oxidation. A concentration of less than 10 wt.% iron also results in increased strength and workability.

Alloy 690 is a superalloy that contains 30% chromium and 10% iron. It was first introduced in the 1980’s and has been used in many applications (Miller, 2016). Alloy 690 has been used in thermally treated or solution annealed conditions (Bruemmer et al., 2012), and it is one of the most resistant alloys with no stress corrosion cracking failure reported in the literature. Its resistance has been known to be due to the high chromium content of the alloy (Harrod et al., 2001).

The amount of Cr in Alloy 690 is well above the critical level required for transi-
tion from internal to external oxidation. However, in a recent study by Persaud et al. (2015), a surprising case of internal Cr oxidation in Alloy 690 was reported when it was exposed to hydrogenated steam at 480 °C, an environment considered to simulate and accelerate primary water exposure and potential stress corrosion cracking in a PWR or CANDU system. In this study, intragranular internal oxidation of Cr was accompanied by formation of nodules of metallic Ni on the alloy surface. A strip of material adjacent to each grain boundary formed a green external oxide and was free of large nodules; the large width of this zone (microns) offers challenges to theories of internal-external oxidation transitions. To the best of our knowledge, no further studies have investigated this interesting behaviour of Alloy 690.

1.2 Contributions

The contribution of this dissertation is to study of the anomalous internal oxidation of Alloy 690 in a simulated primary water environment. We expose coupons of Alloy 690 to a steam/hydrogen mixture at atmospheric pressure and 480 °C while keeping the partial pressure of oxygen below the dissociation pressure of NiO. The purpose of this study is to investigate the time-resolved formation of Ni nodules, to observe how the grain boundaries changes over time, and to examine whether crystallographic orientation of the grains affects their internal/external oxidation behaviour. We perform the following steps:

1. Expose the same samples several times in a time sequence for a total of 100 h with several interruptions.

2. Use scanning electron microscopy between subsequent exposures to investigate the surface and observe changes.

3. Perform Energy Dispersive X-Ray (EDX) elemental analyses on the grain boundaries and within grain boundaries.
4. Carry out cross-section investigations using SEM and EDX studies.

5. Study the crystallography of grain boundaries using the Electron backscatter diffraction (EBSD) technique.
Chapter 2

Materials and Experimental Procedures

Coupons of Alloy 690 were exposed to a steam/hydrogen mixture at atmospheric pressure and 480 °C in a tube reactor located at Western University. The partial pressure of oxygen was kept below the dissociation pressure of NiO. A schematic diagram of the tube reactor is shown in Figure 2.1. The reactor design was based on the original work of Scenini et al. (2005). One of the coupons was exposed 5 times for a total of 100 h with interruptions after 1 h, 3 h, 10 h and 30 h of cumulative exposure. Between the consecutive exposures, the coupon surface was imaged with SEM using FEI Quanta FEG 250 SEM and analyzed with EDX at 15 kV. The detector was silicon drift by EDAX. Indentations were used to locate the same area each time.

In the remainder of this section, we first provide calculations for the environmental conditions of the experiment and provide details for the thermodynamic calculations of the nickel oxide equilibrium, the Gibbs free energy at different temperatures, the ratio of water to hydrogen, and determining the set point. Next, we provide information regarding materials, sample preparation, and the experimental procedure.
2.1 Environmental Conditions of the Experiment

In this section, we calculate the environmental conditions of the experiment. To prevent oxidation of nickel while chromium is oxidizing, it is necessary to calculate the equivalent partial pressure of oxygen created by the steam-hydrogen mixture. The only parameters in this experiment are the hydrogen flow rate, the water flow rate and the temperature. The experiment is running under constant temperature. Therefore, determination of the flow rates of water (in gas phase) and hydrogen is very crucial. To this purpose, we use thermodynamic laws to calculate the partial pressure of the elements at equilibrium and find the critical amount of the oxygen required to oxidize nickel.

2.1.1 Thermodynamic calculations for nickel oxide equilibrium

The nickel oxidation equilibrium is as follows:

\[ \text{Ni}_\text{(s)} + \frac{1}{2} \text{O}_2\text{(g)} \rightleftharpoons \text{NiO}_\text{(s)} \quad K = \frac{1}{P_{O_2}^\frac{1}{2}} \]  

(2.1)
where $K$ is the equilibrium constant ($T$-dependent), and $P_{O_2}$ is the partial pressure of oxygen. The Gibbs free energy can be calculated as

$$
\Delta G^t = \Delta G^\circ + RT \ln(K) \quad (2.2)
$$

It is known that the total Gibbs free energy is zero ($\Delta G^t = 0$) at equilibrium. Therefore, at equilibrium, equation (2.2) can be written as

$$
\Delta G^\circ = -RT \ln(K) \quad (2.3)
$$

If we apply equation (2.3) for the reaction (2.1), we derive

$$
\Delta G^\circ_{NiO} = -RT \ln \left( \frac{1}{P_{O_2,eq}^\frac{1}{2}} \right) \Rightarrow P_{O_2,eq} = \exp \left( \frac{\Delta G^\circ_{NiO}}{RT} \right)^2 \quad (2.4)
$$

Using equation (2.4), the partial pressure of oxygen at equilibrium for nickel oxidation (2.1) at temperature $T$ can be calculated. For any partial pressure below $P_{O_2,eq}$, based on Le Chatelier’s principle, reaction (2.1) will go towards the left and prevent the oxidation of nickel. We need to calculate the amount of water needed to produce the required amount of oxygen present in reaction (2.5).

$$
H_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons H_2O(g) \quad (2.5)
$$

To perform this calculation, we can rewrite equation (2.3) as

$$
\Delta G^\circ_{H_2O} = -RT \ln \left( \frac{P_{H_2O}}{P_{H_2} P_{O_2,eq}^\frac{1}{2}} \right) \quad (2.6)
$$
and thus the partial pressure of oxygen can be derived as follows:

\[ P_{O_2} = \left( \frac{P_{H_2O}}{P_{H_2}} \right)^2 \exp \left( \frac{\Delta G_{H_2O}^0}{RT} \right) \]

(2.7)

The critical ratio of water to hydrogen required to form nickel oxide can be obtained using equations (2.7) and (2.4) and setting \( P_{O_2} = P_{O_2,\text{eq}} \). We then obtain

\[ R_{H_2O/H_2} = \frac{P_{O_2,\text{eq}}^2}{\exp\left( \frac{\Delta G_{NiO}^0}{RT} \right)} \]

(2.8)

Equation (2.8) shows that the ratio of water to hydrogen is related to the square root of the partial pressure of oxygen. Therefore, to keep the partial pressure of oxygen below the equilibrium for forming nickel oxide, the ratio of \( R_{H_2O/H_2} \) has to be decreased. For the experiment, \( R_{H_2O/H_2} \) has to be below the critical value of this ratio. In what follows, we calculate this ratio for the specific experimental conditions.

### 2.1.2 Gibbs free energy at different temperatures

Gibbs free energy, \( \Delta G^0 \), is a function of the equilibrium constant \( K \) (Equation (2.3)). The effect of the temperature on \( K \) is as follows:

\[ \frac{d \ln(K)}{dT} = \frac{\Delta H^0}{RT^2} \]

(2.9)

where \( \Delta H^0 \) can be obtained by substituting \( \Delta C_P \) as follows:

\[ \Delta H^0 = J + \int \Delta C_P dT \quad J: \text{integration constant} \]

(2.10)

\[ C_P = R(A + BT + CT^2 + DT^{-2}) \]

(2.11)
After following all mathematical steps and substituting the corresponding values, we get:

\[
\Delta G^\circ = \Delta H^\circ + 2.303AT \ln(T) + BT^2 + CT^3 + DT^{-1} + IT. 
\] (2.12)

The values of the variables in equation (2.12) for NiO and H\(_2\)O are given in Table 2.1.

<table>
<thead>
<tr>
<th></th>
<th>(\Delta H^\circ)</th>
<th>2.303A</th>
<th>(B \times 10^3)</th>
<th>C</th>
<th>D</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O(_g)</td>
<td>-56930</td>
<td>6.75</td>
<td>-0.64</td>
<td>0</td>
<td>-0.08</td>
<td>-8.74</td>
</tr>
<tr>
<td>NiO</td>
<td>-57640</td>
<td>-4.61</td>
<td>2.16</td>
<td>0</td>
<td>-0.10</td>
<td>34.41</td>
</tr>
</tbody>
</table>

The partial pressure of oxygen at the equilibrium point for the nickel oxide reaction can be calculated using equation (2.1) and (2.4) and the values provided in Table 2.1 at the experimental temperature \(T = 480^\circ\)C as follows:

\[
\Delta G^\circ_{\text{NiO}} = -169455.2 \text{ J/mol} \quad \text{at } T = 480^\circ\text{C}
\]

and similarly for H\(_2\)O:

\[
\Delta G^\circ_{\text{H}_2\text{O},\text{g}} = -206107.2 \text{ J/mol} \quad \text{at } T = 480^\circ\text{C}
\]

We then get

\[
P_{O_2,\text{eq}} = \exp \left( \frac{\Delta G^\circ_{\text{NiO}}}{RT} \right)^2 = 3.12 \times 10^{-24} \text{ bar} \tag{2.13}
\]

\[
R = 8.314 \text{ J/mol.K}, \quad T = 480 + 273 \text{ K}
\]

The same procedure can be used to calculate the partial pressure of oxygen required to
oxidize chromium and iron at $T = 480^\circ C$. According to Persaud (2015):

\[
2 \text{Cr}(s) + \frac{3}{2} \text{O}_2(g) \rightleftharpoons \text{Cr}_2\text{O}_3(s) \quad P_{O_2,eq} = 5.21 \times 10^{-37} \text{ bar}
\]

\[
3 \text{Fe}(s) + 2 \text{O}_2(g) \rightleftharpoons \text{Fe}_3\text{O}_4(s) \quad P_{O_2,eq} = 2.83 \times 10^{-28} \text{ bar}
\]

Comparing the $P_{O_2,eq}$ for oxidation of these two elements (Fe, Cr) with that for oxidation of Ni, it appears that the former two are much lower (4 and 13 orders of magnitudes lower, respectively). This means that they can easily be oxidized internally or externally.

The ratio of water to hydrogen at the equilibrium of nickel oxide can be calculated by using equation (2.8) and using $P_{O_2,eq}$ for NiO.

\[
R_{\text{H}_2\text{O}/\text{H}_2} = \frac{P_{O_2,eq}^{\frac{1}{2}}}{\exp \left( \frac{\Delta G_{\text{H}_2\text{O}}^\circ}{RT} \right)} = \frac{\sqrt{3.12 \times 10^{-24}}}{\exp \left( \frac{206107.2}{(8.314)(753.15)} \right)} = 348.4 \quad (2.14)
\]

The NiO formation will be prevented if the ratio of the water to hydrogen is below this threshold ($R_{\text{H}_2\text{O}/\text{H}_2} < 348.4$). Persaud (2015) used $R_{\text{H}_2\text{O}/\text{H}_2} = 60$ to simulate the primary water condition. The partial pressure of oxygen at $T = 480$ °C for this ratio can be calculated using equation (2.7) as follows:

\[
P_{O_2} = \left[ \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \exp \left( \frac{\Delta G_{\text{H}_2\text{O}}^\circ}{RT} \right) \right]^2 = \left[ 60 \exp \left( \frac{-206107.2}{(8.314)(480 + 273.15)} \right) \right]^2 = 9.25 \times 10^{-26} \text{ bar} \quad (2.15)
\]

Although this value is much smaller than $P_{O_2,eq}$ for nickel (33.7 times smaller), it is still above the equilibrium point for oxidation of both Fe and Cr (i.e., 100 times smaller than that of Fe). As a result, only Cr$_2$O$_3$ and Fe$_3$O$_4$ will be formed in this setup and there will be no NiO formation.
2.1.3 Determining the set point

To set up the flow rate of water and hydrogen, we use the water to hydrogen ratio determined in the previous section \(R_{\text{H}_2\text{O}/\text{H}_2} = 60\). By setting the flow rate of water to or 1.5 ml/min at 25 °C and using a water to hydrogen ratio of 60, the flow rate of hydrogen can be calculated. We assume that both \(\text{H}_2\) and \(\text{H}_2\text{O} \text{(g)}\) are ideal gases and thus the principles of ideal gas law can be applied.

\[
\frac{PV}{T} = \text{constant} \tag{2.16}
\]

The volume and density of gas will change with a change in temperature \(T\). Using equation (2.16), volume \((V)\) and density \((\rho)\) can be calculated for different temperatures at the same pressure:

\[
\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad \rho_2 = \frac{\rho_1 T_1}{T_2}
\]

where \(\rho = \frac{m}{V}\)

For \(\text{H}_2\text{O} \text{(g)}\) we have:

\[
\rho_{\text{H}_2\text{O}(g), 100^\circ C} = 0.6 \times 10^{-3} \text{ g/ml at 1 atm}
\]

\[
\rho_{\text{H}_2\text{O}(g), 480^\circ C} = 0.297 \times 10^{-3} \text{ g/ml at 1 atm}
\]

The weight balance of water as liquid at 25 °C or gas at 480 °C is the same. Therefore:

\[
Q_{\text{H}_2\text{O}, 25^\circ C} \rho_{\text{H}_2\text{O}, 25^\circ C} = Q_{\text{H}_2\text{O}(g), 480^\circ C} \rho_{\text{H}_2\text{O}(g), 480^\circ C}
\]

\[
Q_{\text{H}_2\text{O}(g), 480^\circ C} = \frac{Q_{\text{H}_2\text{O}, 25^\circ C} \rho_{\text{H}_2\text{O}, 25^\circ C}}{\rho_{\text{H}_2\text{O}(g), 480^\circ C}}
\]
Recall we set the ratio of water to hydrogen at 60 for the temperature of the experiment \(T = 480 \, ^\circ C\). Thus:

\[
\frac{R_{H_2O/H_2}}{Q_{H_2,480^\circ C}} = \frac{Q_{H_2O,g,480^\circ C}}{Q_{H_2,g,480^\circ C}}
\]

\[
Q_{H_2,480} = \frac{Q_{H_2,25}}{T_{480}} T_{25}
\]

After replacing value of flow rates of \(H_2O\), and \(H_2\) for 480 \(^\circ C\) to 25 \(^\circ C\) :

\[
Q_{H_2,25} = \frac{Q_{H_2O,g,25^\circ C}}{R_{H_2O/H_2}} \frac{\rho_{H_2O,25^\circ C}}{\rho_{H_2O,480^\circ C}} \frac{T_{25^\circ C}}{T_{480^\circ C}}
\]

\[
Q_{H_2,25} = 33.31 \, \text{ml/min}
\]

The experimental conditions are:

\[
Q_{H_2O,25^\circ C} = 1.5 \, \text{ml/min}
\]

\[
Q_{H_2,25^\circ C} = 33.31 \, \text{ml/min}
\]

\[
T = 480 \, ^\circ C
\]

\[
P = 1 \, \text{atm}
\]

This set up keeps \(R_{H_2O/H_2} = 60\), which is below the nickel oxidation equilibrium, and therefore nickel will not be oxidized to make NiO, while \(Cr_2O_3\) and \(Fe_3O_4\) will be formed.

### 2.2 Sample Preparation

Coupons for oxidation experiments, 10 \(\times\) 10 mm, were cut from 2 mm thick rolled sheet of alloy A690 supplied by Rolled Alloys. The composition of the Alloy 690 used is shown in Table 2.2.

Coupons were solution annealed for 1 h at 1200\(^\circ\)C in an Ar/2.5\% \(H_2\) gas mixture.
Table 2.2: Alloy 690 Composition (wt%)

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>Al</th>
<th>Ti</th>
<th>Si</th>
<th>Mn</th>
<th>Cu</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>59.52</td>
<td>10.13</td>
<td>29.60</td>
<td>0.029</td>
<td>0.21</td>
<td>0.34</td>
<td>0.02</td>
<td>0.15</td>
<td>&lt; 0.01</td>
<td>0.003</td>
<td>0.001</td>
</tr>
</tbody>
</table>

followed by water quenching to ensure saturation of carbon in the matrix. The profile of Cr shows the depth of the depletion zones on both sides which is not exceeding 40 µm. More than 80 µm of the surface was removed using abrasive paper to ensure there was no Cr depletion in the final sample. The polishing process began using grade 400 grit paper, followed by grade 600, 800, and 1200 grit papers. Next, samples were polished with 1 µm diamond paste. Subsequently, coupons were polished with 0.05 µm alumina suspension. To remove the remainder of the polishing material and to clean the surface, the samples were cleaned ultrasonically with an inert detergent solution for 1 minute, rinsed with de-ionized (DI) water, and again ultrasonically cleaned with DI water for 2 minutes. Finally, the samples were ultrasonically cleaned with ethanol and dried by blowing air.
Figure 2.2: Cross-sectional EDX for Alloy 690 annealed for 1 h at 1200 °C in Ar/2.5% H2. Figures (a) and (c) show sample points on the left hand side of the sample and Figures (b) and (d) show those on the right hand side.
2.3 Experimental Procedure

Coupons were exposed to a steam/hydrogen mixture at atmospheric pressure and 480 °C in a tube reactor, with the partial pressure of oxygen kept below the dissociation pressure of NiO. One of the coupons was exposed 5 times for a total of 100 h with interruptions after 1 h, 3 h, 10 h and 30 h of cumulative exposure. A step-by-step set of instructions for setting up and running the exposures was prepared and followed. The details of these instructions are provided in Appendix A. Here we provide a brief summary of the experimental procedure for each exposure.

First, the reactor’s inside (quartz tube) was cleaned twice, once with methanol and once with acetone. The sample(s) were then positioned in the tube in the center of the heating zone, with the surface of interest faced up. The condenser and the collector were assembled and the system was set up according to the instructions. The system was then purged for 30 minutes with high-purity argon gas. The system was heated after purging. The heating was programmed to reach the desired temperature (480 °C) in several intermediate steps to avoid overheating. The flame was then turned on to burn the released hydrogen. The system was purged with high hydrogen flow for 10 minutes. The de-ionized water and hydrogen were injected to the system by the set ratio. The exposure was performed for the specific duration required. The water pump was stopped and hydrogen flow was continued for 10 minutes. The system was purged with high purity argon while the system cooled down to the ambient temperature.
Chapter 3

Surface Studies and Analyses

3.1 SEM Surface Imaging and EDX

Optical images of the samples after exposure to 480 °C after 1 h are shown in Figure 3.1. The appearance of the surface is shiny with different densities of features within the grains. The surfaces of the grains are covered by nodules and many twin boundaries are observed, while the grain boundaries are featureless and wide (about 1 µm).

![Figure 3.1](image)

Figure 3.1: Optical images of the surface of an Alloy 690 coupon after exposure. (a) low magnification, (b) high magnification.

To reveal the nature of the features on the surface of the sample that appeared after...
the exposure, an area analysis using EDX is performed on the flat sample. The selected areas are marked with red in Figure 3.2.

The EDX spectra of these areas are shown in Figure 3.3. For each area, the EDX results as percentage of the elements are given in Table 3.1. The marked area over the nodule (area 1) shows that the nodules are made of metallic nickel, while in the other areas (areas 2 and 3) all elements (Ni, Cr, Fe) are present. The percentage of the elements on the non-nodule areas are similar.

Table 3.1: EDX results (in w%) of the elements in the selected areas.

<table>
<thead>
<tr>
<th>w%</th>
<th>O</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area 1</td>
<td>3.0</td>
<td>3.4</td>
<td>3.2</td>
<td>90.4</td>
</tr>
<tr>
<td>Area 2</td>
<td>4.4</td>
<td>28.9</td>
<td>8.7</td>
<td>58.0</td>
</tr>
<tr>
<td>Area 3</td>
<td>2.2</td>
<td>29.4</td>
<td>9.2</td>
<td>59.2</td>
</tr>
</tbody>
</table>
Figure 3.3: EDX spectra of the areas marked on Figure 3.2
Another EDX mapping analysis is performed on a marked area of the surface of the same coupon as shown in Figure 3.4(a). The distributions of chromium, nickel, and oxygen with respect to the reference image are shown in Figure 3.4. The different colors show the concentration of each element on the surface. The brighter the color, the higher the density of the corresponding element. Figure 3.4(b) shows that oxygen density is low on the nodule areas and high in the areas between nodules which indicates that the non-nodule areas were highly oxidized. Figure 3.4(c) shows that although Ni is distributed everywhere, the areas with high density of Ni are nodules. Figure 3.4(d) shows a rich area of Cr between the nodules and considering the high amount of oxygen in these areas, it must be that chromium is oxidized. Similarly for Fe, Figure 3.4(e) shows that Fe is distributed throughout the surface between the nodules. Figure 3.4(f) shows the overlay of all elements, which further confirms the previous observations.
Figure 3.4: Mapping EDX for the surface of an Alloy 690 coupon exposed to 1 atm hydrogenated steam at 480 °C for 10 h. (a) marked area, (b) O, (c) Ni, (d) Cr, (e) Fe, (f) O, Cr, Ni, and Fe overlay.
3.2 Grain Boundaries and Twin Boundaries after Exposure

The surface of a coupon exposed to hydrogenated steam for 10 h is shown in Figure 3.5(a). Interiors of grains intersecting the surface are covered with nodules of metallic Ni (also observed by Persaud et al. (2015)). The presence of nickel in the form of nodules on the surface indicates that internal oxidation has occurred and that Cr (a solute element) was oxidized intergranularly and intragranularly. The stress created by internal formation of chromium oxide is released by pushing the metallic nickel to the surface. The coverage is uniform within each grain, but the size and arrangement of nodules vary between differently-oriented grains (Figure 3.5(b)). A nodule-free zone, roughly 1-2 µm wide, formed along high-angle grain boundaries as shown in Figure 3.5(a). Twin boundaries do not show a significant nodule-free zone, as indicated in Figure 3.5(c). The nodules on the surface do not appear to follow a specific pattern.
(a) Two grains separated by a high angle grain boundary
(b) Coverage and size of nodules vary for different grains
(c) Twins separated by a Σ3 twin boundary

Figure 3.5: SEM micrographs of grain boundaries and twin boundaries after 10 h exposure
3.3 Crystallography of Grains

The purpose of crystallography was to study the orientation of the grains and to determine if there is any relationship between the grain orientation and its oxidation behaviour. To produce a surface suitable for EBSD, a coupon was first polished, its surface was ion-milled, and then it was sent for EBSD analysis. The area was marked and SEM images were taken from the sample to allow for tracking the same area after exposure. Figure 3.6(a) shows the marked area after 1 h exposure at 480 °C, and Figure 3.6(b) shows a higher magnification of the area under study. Different grains have different density of nodules across the marked area. A closer look at the grains in the marked area is shown in Figures 3.6(c) and 3.6(d). Darker shades indicate nodule-free grains.

The variety of grain orientations are demonstrated using different colors in the EBSD orientation map in Figure 3.7(a). Figure 3.7(b) shows the random high-angle grain boundaries and twins and their orientation. All the twin boundaries are Σ3.
Figure 3.6: SEM image of the marked EBSD area. Darker shades indicate nodule-free grains.
(a) EBSD orientation map

(b) Black lines: Random high angle boundaries. Green lines: Spatial $\Sigma 3$ grain boundaries.

Figure 3.7: EBSD results
Nodule-free grains were selected and included in a subset. Figure 3.8 shows the orientation maps of all grains in the marked area as well as the selected subset that only includes nodule-free grains. To analyze the orientation of the grains, we divided them into two groups: a) the selected grains (nodule-free), and b) all other grains. We then generated inverse pole figures (IPF) for these two groups of grains as shown in Figure 3.9. Figure 3.9(a) shows the IPF for the group of nodule-free grains, and Figure 3.9(b) shows the IPF for all other grains. It can be seen that the nodule-free grain surfaces are mostly close to a $\{001\}$ orientation while other grains have all other random orientations. In a $\{001\}$ orientation, chromium diffuses at a much higher rate than nickel, which may explain the formation of a protective chromium oxide layer that prevents internal oxidation. A more detailed investigation on the effect of grain orientation on the diffusion of oxygen versus chromium is a topic for future studies.
Figure 3.8: EBSD orientation map and the selected nodule-free grains
Figure 3.9: Inverse pole figures for the selected nodule-free grains and the other grains
3.4 Cross-sectional Analysis of Alloy 690

A 120 h exposed coupon of Alloy A690 was selected for the purpose of a cross-sectional study. The sample was mounted in epoxy and polished to a final finishing of 0.05 µm alumina on the cross section of the sample. After cleaning the sample, it was carbon coated. SEM imaging and EDX analysis were then carried out on this sample.

3.4.1 Internal oxidation zone

Cross sections through a grain interior and a grain boundary are shown in Figure 3.10(a) and Figure 3.10(b), respectively. Three regions can be distinguished on the cross section: the external Ni nodules, the internal oxidation zone (IOZ), and the unoxidized alloy. These are indicated in Figure 3.11 as A, B and C, respectively. The interface between the Ni nodules and IOZ corresponds to the original surface of the coupon. The IOZ is continuous through the grain interior (See Figure 3.10(a)) and discontinuous in the vicinity of GBs (See Figure 3.10(b)).

![Cross section of Alloy 690 after 120 h exposure](image)

Figure 3.10: Cross section of Alloy 690 after 120 h exposure
3.4.2 Composition of the internal oxidation zone

EDX results for zones B and C (in Figure 3.11) are summarized in Table 3.2. According to the EDX results, roughly half of the Ni was pushed out from the IOZ to the surface. This may be in line with the molar volume difference between Cr oxide and the alloy.

<table>
<thead>
<tr>
<th>det</th>
<th>mag</th>
<th>WD</th>
<th>HV</th>
<th>pressure</th>
<th>temp</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100 000 x</td>
<td>10.7 mm</td>
<td>15.00 kV</td>
<td>1.27e-4 Pa</td>
<td>---</td>
</tr>
</tbody>
</table>

Table 3.2: Elemental analysis of regions B and C (metallic components only) on the cross section of the oxidized coupon as marked in Figure 3.11 (atomic percent).

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>37.9</td>
<td>48.2</td>
<td>13.9</td>
</tr>
<tr>
<td>C</td>
<td>58.5</td>
<td>31.8</td>
<td>9.7</td>
</tr>
</tbody>
</table>

Figure 3.11: Grain interior: A, B and C designate Ni nodule, internal oxidation zone and bulk alloy, respectively.
By measuring the thickness of the internal oxidation zone (Figure 3.12) and using composition of the IOZ from Table 3.2, the amount of nickel that was pushed out as nodules was calculated to be equivalent to an approximately 0.2 µm nickel layer that would cover the surface of the grain\(^1\). Figure 3.13 shows an EDX line elemental scan performed over a nodule. The Cr profile is almost the same for the bulk alloy and the IOZ, while no Cr is present in the nodule. The signal of Ni decreases through the IOZ, but it shows Ni-enrichment over the nodule. The Fe profile is similar with a slight decrease in the IOZ and an increase toward the nodule, which suggests that the diffusion of Fe toward the surface is very low. Therefore, no Fe scale could be formed on surface.

Figure 3.12: The IOZ thickness after 120 h exposure

\(^1\)Percentage of nickel that diffused from IOZ to the surface is \((\frac{(58.5)(48.2)}{31.8} - 37.9)/(\frac{(58.5)(48.2)}{31.8}) = 57.2\%\). Given that the depth of IOZ is roughly 0.790 µm (Figure 3.12), the thickness of the equivalent nickel layer on the entire surface would be approximately \((0.79)(0.572)(58.5\%) = 0.26\mu m\)
Chapter 3. Surface Studies and Analyses

Figure 3.13: Elemental profile of the cross section

(a) Cross-sectional EDX line scan over a nodule

(b) Grain interior
3.5 Comparison with Alloy 800

Both Alloy 690 (Ni-30Cr-10Fe) and Alloy 800 (Fe-35Ni-21Cr) contain a high percentage of Cr and/or Fe, and according to high temperature oxidation theory (Young, 2008), they are not expected to undergo internal oxidation. Alloy 800 has recently replaced Alloy 600 and is currently used for steam generator tubing in Canada deuterium uranium (CANDU) nuclear reactors. Alloy 690 is used in pressurized water reactors instead of the previous Alloy 600 because of its high resistance against stress corrosion cracking (SCC).

Figure 3.14 compares SEM images of the surface of Alloy 690 and Alloy 800 samples after exposure to 480 °C hydrogenated steam with conditions maintained below the Ni/NiO equilibrium. In Figure 3.14(b), the grain boundary area is visible and it is approximately 1 µm wide with an external protective Cr oxide. The same is true for Alloy 690 (almost the same width). Both alloys showed a protective region on the grain boundaries. The thickness of these protective Cr oxide layer on the grain boundary is about 50 nm in Alloy 800 (Persaud et al., 2016). The surface of Alloy 800 is covered with uneven features. It is reported that Fe covered the surface as a primarily element and metallic Ni expulsion occurred to relieve the stress caused by volume expansion as a result of internal oxidation (Persaud et al., 2016). In Alloy 690, on the other hand, metallic Ni is spread all over the surface within the grains instead of the Fe-scale observed in

Figure 3.14: SEM images of the surface of (a) Alloy 690 and (b) Alloy 800 after exposure
Persaud et al. (2016) showed that oxygen did not penetrate Alloy 800 intergranularly, and the percentage of Cr was dropped significantly along the grain boundaries. Although both alloys were internally oxidized, the depth of the internal oxidation is different in the two alloys. The maximum internal oxidation depth reported for Alloy 800 was about 2.5 \( \mu \)m, while it was less than 1 \( \mu \)m in Alloy 690. The higher percentage of Cr in Alloy 690 may be limiting the penetration of the oxygen.

### 3.6 Time Sequence Exposures

Time resolved SEM micrographs of a selected triple point after 1 h, 3 h, 10 h, 30 h, and 100 h of exposure on a sample area are shown in Figure 3.15 (Other sample areas are provided in Appendix B). The surface coverage of nodules increases with exposure time, mostly through growth of the existing nodules rather than nucleation of new ones. In some cases, adjacent nodules experience enough growth to impinge on one another and consolidate into one nodule. Nodules close to the GB area grow less than the nodules in grain interiors and, in some places, stop growing altogether. The growth measurement of these nodule is done in Section 3.6.1. The cross-sectional image revealed that internal oxidation depth is almost the same within grain boundaries; therefore, the metallic Ni that forms nodules comes from this entire area and not just the area right under the nodules. There is a dark contrast on the surface of the grain boundaries which gets darker and wider over time. This can be due to an increase in the external Cr oxide film density.

The relatively nodule-free zone along GBs undergoes changes as the exposure time increases. Figure 3.16 compares the images of the sample exposed to steam and \( \text{H}_2 \) at 480 °C for 10 h with those exposed for 10 h with two interruptions: after 1 h and 3 h. The two images appear to be similar, and there are no significant differences visible.
Figure 3.15: SEM micrographs of a triple point after 1 h, 3 h, 10 h, 30 h, and 100 h of exposure
Figure 3.16: Comparison of two different 10 h exposures; left (a, c, e): three exposures $1+2+7=10$ h; right (b, d, f): one exposure of 10 h
3.6.1 Growth rate of the nodules

Nodules appeared on the surface after just one hour of exposure. The size and shape of the nodules changed over time and most of the nodules grew as the exposure was extended. The growth of the nodules within the grain boundaries and even some clusters are notable with comparing the images of the same area during the time. Nodules close to the grain boundary do not show a fast growth in size. It seems that diffusion of Ni toward the surface is lower. To have a better understanding of the nodules behavior along the grains over time, the sizes of the nodules along the grain boundary (marked on Figure 3.17) are measured over time, and the results are shown as graphs in Figure 3.18. Measurement was performed by contouring around the nodules. Calculations are based on two dimensional pictures and the height of the nodules is not considered in the calculation.

![Figure 3.17: Nodules marked for measuring size over the time. Selected area from Figure 3.15.](image)

Figure 3.18 shows the growth of nodules along the grain boundary over time, for both sides of a grain boundary (the two sides belong to two different grains). It shows that the
speed of growth is higher at the beginning and the growth rate reduces over time until
the size of nodules remains constant after 10 h of exposures. As the growth of nodules
indicate the progress of internal oxidation, this slow growth of nodules could be because
of internal oxidation in this area is getting slow (forming protective Cr oxide layer) or a
different mechanism is contributing to stress relief in this area.

Figure 3.18: Growth of nodules along the grain boundary
3.6.2 Line scanning EDX across grain boundaries

Line scan EDX across the grain boundaries after 10 h and 100 h exposure are shown in Figures 3.19 and 3.20, respectively. The signal for Fe through the grain is almost constant which shows there are no changes in its concentration. The signal of oxygen drops over the grain boundary. The oxygen profile reflects the difference in thickness of the oxide at the nodule-free zone and adjacent grain interior.

As oxidation process continued, oxygen penetrated in deeper layers. The difference in the signal of oxygen is related to the thickness of the oxide layer. The changes in the signal becomes more extensive from 10 h to 100 h exposure time. This suggests that while internal oxidation is progressing within grains, the grain boundary area is resisting against oxygen penetration. In other words, this area is protected against oxidation due to the formation of external oxidation layer.

The other interesting aspect of the nodule-free grain boundaries is depletion of Cr and enrichment in Ni which become more extensive over time. The depletion of Cr at grain boundaries increases over time which suggests that the healing Cr-rich oxide layer is forming because the diffusion around the grain boundary is higher. Formation of the external oxide could be a reason to prevent of nodules from growing in the vicinity of grain boundary. The enrichment of Ni suggest that the Ni expulsion as a result of the volume expansion of Cr may not only be in the upward direction. This means that Ni could also be pushed to the sides trying to release the internal stress. When Ni finds a way toward the surface, it forms a nodule on the surface. Therefore, the enrichment of Ni in the vicinity of grain boundaries can be a mechanism for stress relief. The relationship between Cr and Ni atoms in the grain boundary area is shown in Figure 3.21. This may explain the slow growth of nodules around the grain boundaries as opposed to within the grain boundaries.

Figure 3.21 shows the elemental profile over the nodule-free zone of the grain boundary. Atomic percent of the elements are provided for each point of the line scan in
Figure 3.19: Elemental profiles across a grain boundary. The samples were exposed for 10 h.
Figure 3.20: Elemental profiles across a grain boundary. The samples were exposed for 100 h.
Figure 3.21(b). Although the percentage of Al, and Ti are very small in the alloy, a small increase in their profile is detected. This can be a random noise, but it is a potential topic to be considered in further studies.

(a) Line EDX profile of the grain boundary

(b) Atomic percent of the elements by EDX analysis

Figure 3.21: Elemental profiles across grain boundaries. The sample was exposed for 100 h.
3.6.3 Image of the grains over time

The initially smooth GB zone (Figure 3.22(a)) develops topographic contrast with increased exposure time (Figure 3.22(b)). Such observations may explain the large width of the “externally oxidized” zone - there is always some internal oxidation initially, but it ceases close to the GB. As demonstrated by line scanning EDX in the previous section, the elemental profiles of the grains change as exposure time increases. The enrichment of Ni on the grain boundaries and the migration of grain boundaries can develop a topographic contrast on GB zone over time.

(a) After 1 h exposure  
(b) After 100 h exposure

Figure 3.22: SEM micrographs of the grain boundary zone over time
Chapter 4

Conclusions

Internal oxidation of Alloy 690, which is a Ni-based alloy with a high Cr content, was studied by exposing samples to 480 °C hydrogenated steam. Samples were exposed for a cumulative 100 hours with several interruptions, and SEM imaging and EDX analyses were performed between consecutive exposures to study the surface of the samples. Crystallography of grains was also performed through an EBSD analysis.

The results confirmed that Alloy 690 oxidizes internally under simulated PWR conditions despite its Cr content of 30%. To release compressive stresses associated with internal formation of Cr$_2$O$_3$, Ni diffuses towards the surface where it forms nodules and towards the grain boundaries. SEM images showed that there was a variety of nodule coverage on grains, and some grains were entirely nodule free, which means they were externally oxidized. Crystallography showed that most of the nodule-free grains had an orientation close to \{001\}, whereas other grains in which internal oxidation occurred had other random orientations. Surface nodules formed within the first hour of exposure. With an increase in the exposure time, the nodules grew in size within grains, but not near grain boundaries, while their areal density remained practically constant. The growth in Ni nodules within the grains continued for up to 100 hours, which confirms the progression of internal oxidation in the underlying areas. Near the grain boundaries,
the growth rate significantly reduced after 10 h of exposure, and the size of nodules re-
mained constant which can be due to the formation of a protective Cr oxide layer which
prevents internal oxidation. Alternatively, it could indicate that a different mechanism
is contributing to stress relief in this area.

Although there have been no failure reports of Alloy 690 in industry, it is not immune
to future failures. The growth of nodules within grains shows intragranular oxidation,
which means that Alloy 690 can be susceptible to intragranular stress corrosion cracking
(INGSCC). The results demonstrated in this study will contribute to predicting the
conditions that would cause possible failures.

In this thesis, we focused on experiments at 480 °C and atmospheric pressure. Future
work includes experiments at a lower temperature (i.e., \( T < 480 \, ^\circ\text{C} \)) and/or a higher pres-
sure (i.e., \( P > 1 \, \text{bar} \)). To reduce the effects of minor elements, custom laboratory alloys
can be made and used in the experiments. Another future direction includes performing
a more accurate microscopic analysis using advanced Transmission Electron Microscopy
(TEM) and Atom Probe Tomography (APT) for further investigations. Finally, a better
understanding of the effect of \{001\} grain orientation on lattice diffusion and why it
results in nodule-free grains is another topic for future studies.
Bibliography


Nesbitt, J. A. (1989). Predicting minimum aluminum concentrations for protective scale


Appendix A

Experiment Setup Instructions

Cleaning the heating tube  Take the long rod, and cover its head with large kimtech wipes. Then, spray methanol on it and clean the inside of the tube. Repeat cleaning with acetone.

Load the sample/samples  To load the samples:

- Use a tray and put the samples on it.
- Put this tray at the end of the tube.
- Slowly push the samples into the tube using the long rod.
- Leave the samples in the middle of the heater.

The surface of interest should be faced up.

Assemble the system  To assemble the condenser and the collector, follow the steps below to make a system as shown in Figure A.1.

- Close the cap at the end of the tube (Figure A.2, A). Do not close it too tight because the glass is very fragile, just apply finger tip pressure.
- Connect the 4-way connection (Figure A.2, B) to the tube using a clip (Figure A.2, C).
Appendix A. Experiment Setup Instructions

Figure A.1: System after assembly

- Use two supports to hold the 4-way connection (Figure A.2, D). The weight of all connections should stay on these supports.

- Connect the condenser (Figure A.2, E) to the top of the 4-way connection. Input of the cooling water should be from above.

- Connect the collector:
  - Connect to the top of the condenser (Figure A.1).
  - Connect to the bottom of the 4-way connection using a clip. You may need to release the supports one-by-one to put the clip in its place. Keep the weight using your hand and replace the support.
  - Connect the output of the collector to the lab torch. This connection has a one-way valve to avoid any backward flow from the flame (Figure A.3).
Appendix A. Experiment Setup Instructions

Figure A.2: Connection to the tube

Figure A.3: A: One-way valve, B: Lab torch
Appendix A. Experiment Setup Instructions

**Purge the system**  To purge the system with argon, first open the main valves from cylinder, and then open the small valve (Figure A.5, part B). Continue purging for 30 min.

**Heating the system**

- Close the door of the heating chamber.
- Turn on the 3 elements that support the two ends of the tube.
- Turn on the heater of preheat injection block (Figure A.4, part B).
- Press “Run” on the heating controller. It should be programmed for a set point in advance.
- Wait until the temperature is stable at the set point.

![Figure A.4: A: Preheat injection block, B: Block heater, C: Tube heater](image)
**Flame**  Turn on the torch to burn the released hydrogen. The flame should be on during the flow of hydrogen to prevent any hazard. Keep the flame at its lowest to save gas (methane) consumption. In order to easily see the low flame, it is best to turn the lights off when adjusting the flame.

**Hydrogen purging**  After the temperature is set, continue purging with hydrogen for 10 min.

- Open the hydrogen valve (cylinder).
- Open the valve after flow-meter.
- Close the argon’s valve slowly and increase the hydrogen flow (Figure A.5, B).
- Increase the flow of hydrogen to the max of flow-meter (Figure A.5, A).
- Purge the system with high hydrogen flow for 10 min.

Figure A.5: A: Hydrogen flow-meter B: Argon valve C: Water pump
Appendix A. Experiment Setup Instructions

Start the exposure

- Turn the water pump on to “forward” (Figure A.5, C).
- Start the timer.
- Adjust the flow of hydrogen (decrease to set point).

Stop the exposure

- Turn off the water pump (It should be set in advance).
- Stop the timer.
- Turn off all heaters.
- Keep hydrogen’s valve open for 5 min then close the hydrogen valve slowly.
- Open the argon valve slowly.
- Close the main valve of hydrogen.
- Turn the lab torch off.
- Let the system cool down.
- When temperature has dropped to 300 °C, open the heater’s chamber door to speed up cooling.
- When the temperature is low, open the clip between the tube and the 4-way connection.
- Open the tube’s cap.
- Bring the samples to the end of the tube.
- Take your sample/samples.
- Close the argon valve.

To speed up cooling the system, a small fan can be used to cool down the tube when the temperature is around 100 °C.
Programming the heater  To set the heating control, program the heating to reach to the aimed temperature by several steps to avoid any high temperature. For example, to reach to 480 °C, the first step is 350 °C then 400 °C, 450°C and finally 480°C. In my case, when I set it for 350°C, the temperature went to 433°C so instead of waiting for it to cool down, we can do as follows: reset the program and set it for 460°C and the temperature will go up to 484 °C. At this point, set it for 480°C. Wait until system cools down and becomes stable at 480°C (The total heating time is almost 15 min).

For each step just press reset button and follow the programming steps.

Set the water pump  The flow rate of the water should be set early. Start the pump and measure the volume of the water after 10 min. Increase or decrease the rate and measure again until you reach the set point. Then attach the output of the pump to the system.
Appendix B

Samples of time-series of SEM micrographs
Appendix B. Samples of time-series of SEM micrographs

Figure B.1: SEM micrographs of alloy 690 after 1 h, 3 h, 10 h, 30 h, and 100 h of exposure (Sample A)
Figure B.2: SEM micrographs of alloy 690 after 1 h, 3 h, 10 h, 30 h, and 100 h of exposure (Sample B)
Figure B.3: SEM micrographs of alloy 690 after 1 h, 3 h, 10 h, 30 h, and 100 h of exposure (Sample C)
Figure B.4: SEM micrographs of alloy 690 after 1 h, 3 h, 10 h, 30 h, and 100 h of exposure (Sample D)
Figure B.5: SEM micrographs of alloy 690 after 1 h, 3 h, 10 h, 30 h, and 100 h of exposure (Sample E)