THE EFFECTS OF THERMOMECHANICAL PROCESSING AND
ANNEALING ON THE MICROSTRUCTURAL EVOLUTION
AND STRESS CORROSION CRACKING OF ALLOY 690

by

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The effects of short-range order (SRO), long-range order (LRO), and plastic strain on the microstructure and stress corrosion cracking (SCC) susceptibility of Ni-Cr-Fe Alloy 690 have been investigated in detail. First, the presence of \( \frac{1}{3}\{422\} \) and \( \frac{1}{2}\{311\} \) diffuse intensities in \( B=[111] \) and \( B=[112] \) selected area diffraction patterns (SADPs), previously believed to indicate the presence of SRO, has been examined in Alloy 690, a Ni-Cr binary alloy, and a number of FCC materials in an effort to determine their source. It is shown that these intensities are not due to SRO, although their source remains somewhat unclear. However, an experiment was conducted that tracked the strong \{111\} reflections in a \( B=[112] \) SADP as the sample was tilted (19°) towards a \( B=[111] \) zone axis. Significantly, it was noted that the \{111\} intensities never fully disappear and that they fall in the \( \frac{1}{3}\{422\} \) positions within the \( B=[111] \) SADP. This indicates that these diffuse intensities are related to reflections that lie in the first order Laue zone (FOLZ) when the zone is aligned along \( B=[111] \), although theoretical calculations indicate scattering from these planes into the zero order Laue zone used to form the SADP should not occur. Thus, while calculations are inconsistent with the behavior expected, the diffuse intensities observed in a number of high index zones are consistent with projections of higher order Laue zone reflections into the zero layer, suggesting that the theory is in need of reassessment.

Second, the stability of the \( \gamma′-\text{Ni}_2\text{Cr} \) LRO phase present on the Ni-Cr phase diagram was examined in a Ni-55Cr binary alloy. The results indicate that the \( \gamma′-\text{Ni}_2\text{Cr} \) phase is indeed metastable, and that the two-phase \( \gamma-\text{Ni} + \alpha-\text{Cr} \) phase field extends all the way to room temperature. Likewise, the sluggish formation of the \( \gamma′-\text{Ni}_2\text{Cr} \) phase appears to occur only over a narrow composition and temperature range. It is speculated that this important phase in more complex alloys is also metastable and its metastability should be considered in applications involving long-term, high temperature exposures.

Third, the effects of thermomechanical processing and long-term aging on the microstructural evolution and SCC susceptibility of Alloy 690 were examined in detail. It is shown that cold working and subsequent aging have large impacts on the microstructures observed and on the mechanical properties, and it is these changes that are related to the differences in SCC behavior. Most importantly, it is shown that the very high work hardening in Alloy 690 leads to large increases in yield strength that appear to overshadow the more subtle variations in carbide distributions at grain boundaries and prior coherent twin boundaries, and that SCC initiation is difficult if not impossible under static loading conditions. Based on these observations, it is concluded that the long-term concerns by industry of SCC initiation in Alloy 690 in the thermally-treated condition can probably be ignored unless there are regions where the alloy has been significantly hardened mechanically and the material will undergo some type of dynamic loading.
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CHAPTER 1  INTRODUCTION

The first steam generators used in nuclear power applications during the 1960’s utilized 316SS for transport tubing, which was then changed to Alloy 600 in the early 1970’s. Shortly after this transition, it was observed that Alloy 600 exhibits a high susceptibility to stress corrosion cracking (SCC) in these environments, which spurred the development of Alloy 690. Since its development in the early 1980’s, and its first in-service application in mid-1989, no SCC failures of Alloy 690 have been reported by industry. Currently, Alloy 690 is used in a variety of applications in nuclear power plants and steam generators, such as the control rod drive mechanism (CRDM) housing, and transport tubing in both the primary (irradiated) and secondary (non-irradiated) circuits. Operating in an environment of pressurized steam/water with temperatures of ~325 °C, Alloy 690 is commercially used in the thermally treated (TT) or solution annealed (SA) condition.

Ni-Cr alloys such as Alloy 690 are prone to the formation of chemical-ordering reactions leading to the formation of embrittling precipitates, such as Ni₂Cr (Pt₂Mo-type) ordering. Short-range order (SRO) is a suspected precursor to their formation, as suggested by the diffuse scattering in TEM selected area diffraction patterns (SADPs). These ordering reactions can presumably occur under light water reactor (LWR) operating conditions and adversely affect the long-term structural stability and mechanical properties of this alloy.

Previous research into atomic ordering of Ni-Cr alloys has suggested that the formation of the long-range order (LRO) γ’-Ni₂Cr structure can result in the degradation of mechanical properties in Ni-Cr and Ni-Cr-Fe alloys such as Alloy 690. While the sluggish kinetics of this transformation in Alloy 690 requires years (or decades) of annealing at temperatures below ~590 °C, this time-temperature regime is of interest for nuclear power applications. Furthermore, while the solution annealed (SA) and thermally treated (TT) conditions of Alloy 690 currently used in industry exhibit significant SCC resistance, cold-rolled conditions (CR) of Alloy 690 have been shown susceptible to SCC in laboratory trials. The SCC susceptibility of the CR alloy is of interest if Alloy 690 is ever to be used in environments requiring higher strength and/or operating temperatures. Furthermore, while Alloy 690 has shown no susceptibility to SCC in the past ~30 years, a desire to extend these alloys to 60+ years of service requires a fundamental understanding of their behavior.

The main research objectives of this study are (1) to examine the presence of diffuse scattering in TEM SADPs and determine if it can be attributed to the presence of SRO, (2) to examine the phase stability of the γ’-Ni₂Cr phase in the Ni-Cr binary, (3) to evaluate the microstructural evolution of Alloy 690 as a function of thermomechanical processing and long-term aging, and (4) to correlate the
microstructural evolution of Alloy 690 to the SCC behavior under simulated primary water reactor (PWR) conditions (i.e. 360 °C pressurized steam/water).

The diffuse scattering in Alloy 690, a Ni-Cr binary alloy, and several other FCC alloys were examined in some detail, with the results presented in Chapter 4. The stability of $\gamma'$-Ni$_2$Cr was examined in a cast Ni-55Cr binary alloy annealed at 500 °C for 1,000 h, 900 °C for 4 h, and 900 °C for 4 h followed by 500 °C for 1,000 h, with the results presented in Chapter 5. The microstructural evolution of four thermomechanical processing (TMP) conditions of Alloy 690 were examined after long-term aging at 350, 475 and 550 °C for up to 10,000 hours, and the results are presented in Chapter 6. These TMP conditions include solution annealed (SA), 20% cold-rolled (CR), thermally treated (TT), and thermally treated followed by 20% cold-rolled (TTCR). The stress-corrosion cracking (SCC) resistance of Alloy 690 in these conditions was examined using slow strain rate tensile (SSRT) testing in simulated PWR water at 360 °C, with a strain rate of $1 \times 10^{-8}$ s$^{-1}$. The SCC susceptibility of Alloy 690 was determined by measuring overall crack length in SEM micrographs after testing to similar levels of uniform strain (~4%).
CHAPTER 2 BACKGROUND

The advent of the conventional “superalloy” was first recognized shortly after the end of World War II, and was used to describe a group of alloys used in turbochargers, superchargers, and turbine engines requiring exceptional properties at elevated temperatures. Today, these alloys have been expanded for use in rocket engines, highly corrosive chemical environments, and similar applications. Their ability to withstand applied stresses at temperatures exceeding 650 °C for extended times, combined with their good low-temperature ductility and excellent metallurgical stability make these alloys highly desirable in demanding applications.

Nickel-based superalloys in particular are the most widely used form of superalloy, with the ability for solid solution or precipitation strengthening. Solid solution alloys, such as several within the INCONEL and Hastelloy families, are typically used in applications requiring only moderate strength. The majority of Ni-base superalloys are precipitation hardened and contain, by wt. %, 10-20% chromium, up to 8% aluminum and titanium, 5-10% cobalt, and small additions of boron, zirconium, and carbon. Broadly categorized, the latter class of Ni-based superalloys can be characterized as having a gamma/gamma-prime (γ/γ’) microstructure along with strong carbide formers and other elements that segregate to grain boundaries. In addition, some Ni-base superalloys are strengthened by a variety of other precipitates.

2.1 Ni-Cr-Base Superalloys

Common Ni-Cr-based superalloys typically contain chromium contents in the range of ~10-30 wt. %, given that these sorts of concentrations are necessary for providing oxidation and corrosion resistance. The INCONEL series of alloys, such as Alloy 600 and Alloy 690, are used in applications such as heat exchanger tubing, chemical and food processing, thermocouple applications, ducting and combustion systems, and particularly in applications requiring sulfuric-corrosion resistance. Often, additions of iron (up to ~10 wt. %) are added for increased strength and workability. Both Alloy 600 and Alloy 690 are solid solution strengthened alloys, primarily due to additions of chromium, iron, and carbon. Compositions of these two alloys are provided in Table 2.1. In addition to solid solution strengthening, these alloys contain MC-type carbides that form during solidification, and the precipitation of $M_23C_6$-type carbides during subsequent annealing. Furthermore, Alloy 690 reportedly precipitates the $\gamma’$-Ni$_2$Cr phase after very long-term aging at temperatures below ~590 °C. However, in this system the $\gamma’$-Ni$_2$Cr phase has an orthorhombic (Immm) structure with sluggish precipitation kinetics. Further discussion of the $\gamma’$-Ni$_2$Cr precipitate is presented in Section 2.3.
Table 2.1: Compositions of Alloys 600 and 690, as specified by Special Metals Corporation.\textsuperscript{4}

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<th>Ni</th>
<th>Cr</th>
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<th>Cu</th>
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*Indicates maximum

2.1.1 Alloy 690

The first steam generators from the 1960’s utilized 316SS for transport tubing, which was then changed to Alloy 600 in the early 1970’s.\textsuperscript{9} Shortly after this transition, it was observed that Alloy 600 is susceptible to stress corrosion cracking (SCC) in these environments, which spurred the development of Alloy 690.\textsuperscript{10} Since its inception in the early 1980’s, and first in-service application in 1989, no SCC failure of Alloy 690 has been reported, and this behavior has been attributed to the increased chromium content of this alloy.\textsuperscript{9} Currently, Alloy 690 is used in a variety of applications in nuclear power plants and steam generators, such as the control rod drive mechanism (CRDM) housing, and transport tubing in both the primary and secondary circuits, as shown in Figure 2.1.\textsuperscript{11} Operating in an environment of pressurized steam/water with temperatures of \(\sim 325\, ^\circ\text{C}\), Alloy 690 is commercially used in the thermally treated (TT) or solution annealed (SA) condition.\textsuperscript{12}

Figure 2.1: Schematic illustration of a nuclear powered steam generator. Alloy 690 is used in the control rod drive mechanism (CRDM) housing, and steam generator (SG) tubing, both within the primary and secondary circuit, as indicated in yellow.\textsuperscript{11}
The development of this high chromium-containing alloy (~30 at.%) has been shown to eliminate primary water stress corrosion cracking (PWSCC) when used in the mill annealed (MA) and thermally treated (TT) conditions. However, recent work on cold rolled (CR) Alloy 690 has shown that this alloy is not impervious to SCC. Should Alloy 690 ever to be used in applications requiring higher strength and/or operating temperatures, an understanding of SCC in the work-hardened condition is crucial. While the mechanisms for SCC in predecessor alloys has been extensively studied and are fairly well understood, the mechanisms for SCC in Alloy 690 are not, and in the cold worked state Alloy 690 has been shown to exhibit crack growth rates (CGR) on the order of those seen in Alloy 600.

2.2 Short-Range Order (SRO)

Short-range order (SRO) is best explained as the probabilistic nature of atomic nearest neighbors within the lattice, and is the result of a negative enthalpy of mixing of the system ($\Delta H_{\text{mix}} < 0$). Domains of SRO exhibit a higher number of A-B bonds than expected for a fully disordered random solid solution. However, unlike long-range order, with well-defined atom arrangements, SRO is simply a non-random rearrangement of the matrix atoms. This is best described using the short-range order parameter, $s$:

$$s = \frac{P_{AB} - P_{AB}(\text{random})}{P_{AB}(\text{max}) - P_{AB}(\text{random})}$$

where $P_{AB(\text{max})}$ refers to the maximum number of A-B bonds possible, $P_{AB(\text{random})}$ is the number of A-B bonds in a random solution, and $P_{AB}$ is the actual number of A-B bonds. The number of A-B bonds is related to the enthalpy of mixing by:

$$\Delta H_{\text{mix}} = P_{AB} \varepsilon$$

where $\varepsilon$ is the difference in unlike (A-B) and like (A-A and B-B) bond energies:

$$\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB})$$

These energies are considered to be negative values, and dictate the functionality of the enthalpy of mixing. For the case where A-B bonding is stronger ($\varepsilon_{AB}$ more negative) than A-A and B-B bonding, $\varepsilon$ is negative, and therefore $\Delta H_{\text{mix}} < 0$. This results in a preference for ordering (SRO/LRO) within the system. For the case where A-A and B-B bonding is stronger ($\varepsilon_{AB}$ less negative), $\varepsilon$ is positive and therefore $\Delta H_{\text{mix}} > 0$, resulting in clustering of like atoms. The concept of SRO vs. LRO is shown schematically in Figure 2.2, where (a) is a fully disordered system, (b) exhibits SRO with an increased number of A-B bonds, and (c) is a fully ordered system exhibiting LRO.
Figure 2.2: Schematic representation of (a) a disordered A-B solution, (b) short-range order, with an increased number of A-B bonds, and (c) long-range order, exhibiting specific A and B sites within the lattice. Adapted from Porter and Easterling.\textsuperscript{13}

2.2.1 Microstructural Observations of Short-Range Order

A significant body of work has focused on the SRO behavior in the Ni-Cr both the binary system and more complex Ni-Cr-base superalloys. The evidence for SRO in Ni-Cr alloys has primarily come from TEM observations, resistivity measurements, and specific heat measurements. Marucco and Nath initially observed additional $1/3\{422\}$ diffuse scattering in $B=\{111\}$ selected area diffraction patterns (SADPs) taken from a Ni-25Cr binary alloy (Figure 2.3a), and further proposed the mottled contrast in bright-field TEM (BFTEM) images (Figure 2.3b) to be indicative of SRO.\textsuperscript{14} Subsequent authors reported similar observations from a Ni-33Cr alloy, in addition to mottled contrast in BFTEM images (Figure 2.3c).\textsuperscript{15} Examination of the Ni-Cr-Fe ternary yielded similar results, in addition to $1/2\{311\}$ diffuse scattering in $B=\{112\}$ SADPs (Figure 2.3d).\textsuperscript{16} These observations have been noted by a multitude of other investigators, both in the Ni-Cr and Ni-Cr-Fe systems as well as Alloy 600 and Alloy 690.\textsuperscript{6,7,17-22} However, the identification of SRO via TEM requires careful interpretation, and often these manifestations can be the result of effects other than SRO.

Electrical resistivity measurements are commonly used to examine subtle microstructural changes such as SRO. In the Ni-Cr system, changes in electrical resistivity have been related to what is known as the K-state effect, and are purportedly due to the formation of SRO domains.\textsuperscript{23,24} Further work measuring resistivity in a variety of Ni-Cr-Fe alloys by Marucco et al. also showed the K-state effect, as shown in Figure 2.4, and indicates the formation of SRO is delayed by additions of iron.\textsuperscript{16}
Figure 2.3: (a) B=[111] SADP from Ni-25Cr showing the presence of 1/3\{422\} diffuse intensities that were suggested to be indicative of SRO.\textsuperscript{14} (b) Corresponding bright field TEM (BFTEM) image in which the strain contrast was proposed to represent SRO domains.\textsuperscript{14} (c) BFTEM of a Ni-33Cr alloy showing mottle (SRO) contrast.\textsuperscript{15} (d) B=[112] SADP from a Ni-28Cr-5Fe showing 1/2\{311\} diffuse intensities also purportedly due to SRO.\textsuperscript{16}
Figure 2.4: Measurements of electrical resistivity in a variety of Ni-Cr-Fe alloys (solutionized and annealed at 700 °C – 16 h) after annealing at 450 °C, suggesting the formation of a short-range order (SRO) structure. The addition of iron appears to delay the transformation kinetics of SRO.\textsuperscript{16}

Another common method for identifying the formation of SRO is by specific heat measurements using differential scanning calorimetry (DSC). The initial work on specific heat measurements in Ni-Cr alloys was performed by Hinton and Taylor in 1952 on the Ni-25Cr alloy, and is presented in Figure 2.5.\textsuperscript{23} This experiment was performed on a Ni-25Cr alloy that was annealed at 1150 °C for 8 hours, followed by a direct water quench, which would be expected to result in a fully disordered state. Subsequent heating of this alloy results in an endothermic reaction at approximately 400-500 °C, followed by an exothermic reaction at higher temperatures. This behavior is purportedly due to the formation of ordered domains at 400-500 °C, followed by the dissolution of this structure at higher temperatures.
Figure 2.5: Specific heat measurements of a Ni-25Cr alloy after annealing at 1150 °C for 8 h, followed by water quench, showing an endothermic reaction consistent with an ordering transformation at ~500 °C. Heating rate was not reported.\textsuperscript{23}

2.3 Long-Range Order (LRO) of γ'-Ni\textsubscript{2}Cr

One of the first observations of the γ'-Ni\textsubscript{2}Cr structure was by Hirabayashi in the Ni-33Cr binary.\textsuperscript{17} In this work, an increase in hardness and yield strength and a decrease in electrical resistivity was observed, associated with the γ'-Ni\textsubscript{2}Cr structure. Since this initial observation, a substantial body of work has focused on this precipitate in Ni-Cr systems.\textsuperscript{14,17,25–34} The γ'-Ni\textsubscript{2}Cr structure is a body-centered orthorhombic (Immm space group) with nickel and chromium atoms at the 4g and 2a Wyckoff positions, respectively, and occurs as a fully coherent precipitate in the γ-Ni matrix (Figure 2.6).\textsuperscript{8,35} The γ and γ' structures are crystallographically related by a 45° rotation about the c-axis of the matrix, which can be defined in terms of:

\[
\langle 001 \rangle_\gamma \parallel \langle 001 \rangle_\gamma'
\]

\[
\{110\}_\gamma \parallel \{010\}_\gamma'
\]

with the lattice parameters of the orthorhombic phase being approximately related to the matrix as follows:\textsuperscript{36}

\[
a = \frac{3a_\gamma}{\sqrt{2}}; \quad b = \frac{a_\gamma}{\sqrt{2}}; \quad c = a_\gamma.
\]
Given that a detailed TEM diffraction analysis of $\gamma'$-Ni$_2$Cr was performed in this study, a short treatment of the expected TEM diffraction is presented here. Simulated SADPs for $\gamma + \gamma'$ down the [001], [112], and [110] zone axes are presented in Figure 2.7, with the aid of the JEMS crystallography software package. For the $B=[001]_\gamma$ simulation, two distinct variants of Ni$_2$Cr are shown, identified by the open and filled circles. For the $B=[112]_\gamma$ simulation, three distinct variants are present, and for the $B=[011]_\gamma$ simulation, one distinct variant is present.

Figure 2.7: SADP simulations of $\gamma + \gamma'$ down the (a) $B=[001]_\gamma$, (b) $B=[112]_\gamma$, and (c) $B=[011]_\gamma$ zone axes, containing all observed variants of Ni$_2$Cr. The solid, shaded, and empty small circles correspond to the multiple variants of Ni$_2$Cr, and the large filled circles correspond to the $\gamma$-Ni matrix.
In the case of more complex superalloys, the precipitation of $\gamma'$-Ni$_2$Cr often occurs in proximity with the M$_{23}$C$_6$-type carbide. A consideration of the relative locations of these superlattice intensities is presented in Figure 2.8. It should be noted that in all cases, the identification of $\gamma'$-Ni$_2$Cr is difficult in the presence of M$_{23}$C$_6$, given the overlapping of diffracting intensities.

![Comparison of SADPs for (top) Ni$_2$Cr and (bottom) M$_{23}$C$_6$ precipitation in a γ-Ni matrix, taken down the B = <001>, <112>, and <011> zone axes of γ-Ni.]

Figure 2.8: Comparison of SADPs for (top) Ni$_2$Cr and (bottom) M$_{23}$C$_6$ precipitation in a γ-Ni matrix, taken down the B = <001>, <112>, and <011> zone axes of γ-Ni.

The work by Delabrouille in 2009 is one of the only investigations into the precipitation of $\gamma'$-Ni$_2$Cr in Alloy 690. He reported the presence of fine (~5-10 nm) $\gamma'$-Ni$_2$Cr precipitates occurring homogenously throughout the matrix of a 20% cold worked alloy after annealing for 70,000 hours at 420 °C. A centered dark field (CDF) image taken of the precipitate is shown in Figure 2.9, along with the accompanying B=[001] SADP.
2.3.1 Effects of γ’-Ni$_2$Cr Precipitation on the Properties of Ni-Cr Binary Alloys

Given the extremely delayed precipitation kinetics of γ’-Ni$_2$Cr in Alloy 690, which has been attributed primarily to the presence of iron, the majority of mechanical property data has been generated in the Ni-Cr binary. The precipitation of γ’-Ni$_2$Cr in the Ni-Cr system has been shown to result in significant degradation to the mechanical (and other) properties. This includes a contraction of the matrix lattice, increases in hardness, decreases in resistivity, increase in yield and ultimate tensile strengths, and reduction in elongation. Young et al. have reported a contraction of the matrix in the Ni-33Cr binary on the order of 0.2% due to γ’ precipitation, as well as an increase in Vickers microhardness of ~100 HV (Figure 2.10) after annealing at 470 °C. Similar observations have also been reported by several other authors in Ni-Cr and Ni-Cr-Fe.
Figure 2.10: The effects of γ'-Ni\textsubscript{2}Cr precipitation on (a) the matrix lattice parameter and (b) the Vickers microhardness, after annealing a Ni-33Cr alloy at 470 °C.\textsuperscript{7} Note the observed contraction of the matrix (a) on the order of 0.2%, with a concurrent increase in Vickers microhardness due to the precipitation of γ'-Ni\textsubscript{2}Cr.

In the work by Young et al., the precipitation of γ'-Ni\textsubscript{2}Cr was shown to result in significant lattice contraction of the matrix, which resulted in a tensile stress that reached ~200MPa on the sample that was held under constant displacement conditions.\textsuperscript{7} (Figure 2.11) This observation confirmed the results of several investigators, who reported that the precipitation of γ'-Ni\textsubscript{2}Cr resulted in lattice contraction of the matrix.\textsuperscript{7,26,40}

Figure 2.11: Fixed displacement, isothermal (418 °C) mechanical test of the Ni-33Cr alloy, showing the formation of internal stresses due to γ'-Ni\textsubscript{2}Cr precipitation and matrix lattice contraction.\textsuperscript{7}
In further work, Young and coworkers examined the effects of $\gamma'$-Ni$_2$Cr precipitation on the tensile behavior and fracture morphology of a binary Ni-33Cr alloy (Figure 2.12). The as-quenched condition of Ni-33Cr exhibited high ductility with a typical microvoid coalescence fracture morphology. However, annealing this alloy at 475 °C for 2,000 hours resulted in the precipitation of $\gamma'$-Ni$_2$Cr and an increase in yield and ultimate tensile strengths, along with a significant loss in ductility and an intergranular fracture morphology.

![Figure 2.12](image)

**Figure 2.12:** The effect of $\gamma'$-Ni$_2$Cr precipitation on the mechanical properties and fracture morphology of a Ni-33Cr binary alloy, after annealing at 475 °C for 2,000 hours. Note the significant increase in yield and ultimate tensile strengths, as well as the reduction in elongation.

### 2.3.2 Effects of $\gamma'$-Ni$_2$Cr Precipitation on the Hardness of Alloy 690

Limited data is available concerning the precipitation of $\gamma'$-Ni$_2$Cr in Alloy 690, due to its sluggish transformation kinetics. Experimentally, the precipitation of $\gamma'$-Ni$_2$Cr in Alloy 690 has been shown to require at least 30,000 hours of annealing at 360-420 °C. Significantly, this transformation can be delayed even further by increasing the iron contents and, in some cases, annealing Alloy 690 at 360 °C for 90,000 hours resulted in no precipitation of $\gamma'$-Ni$_2$Cr.
The study by Delabrouille examining the precipitation of γ’-Ni$_2$Cr and its effects on hardness variations in Alloy 690 is the only observation in this system to date. This study included Alloy 690 with 10.4 wt. % iron (condition A), 7.2 wt. % iron (condition B) and conditions in the cold-worked (20%) state, annealed at 360 and 420 °C for up to 90,000 hours. As seen in Figure 2.13, the addition of iron significantly reduced the precipitation kinetics of γ’-Ni$_2$Cr (as inferred by Vickers microhardness measurements), requiring on the order of 30,000 to 90,000 hours for a change in hardness to occur.

![Figure 2.13: The effects of aging Alloy 690 on the Vickers hardness at 360 °C. Conditions A and B contain 10.4 and 7.2 wt. % iron respectively, and CW-A/CW-B indicates a 20% cold-reduction applied to the material prior to aging.](image)

2.3.3 Stability of the γ’-Ni$_2$Cr Phase

A considerable body of work has focused on the precipitation behavior of the γ’-Ni$_2$Cr phase in Ni-Cr and Ni-Cr-Fe alloys. Interestingly, this behavior is rather peculiar and provides some indication that this structure is not the equilibrium phase in the Ni-Cr binary. First, a considerable incubation period is observed regarding the precipitation of γ’-Ni$_2$Cr, on the order of a few hundred hours in the binary and tens of thousands of hours in Alloy 690. The kinetics of LRO precipitation in the Ni-Cr binary and Ni-Cr-Fe ternary can be seen in Figure 2.14.
Figure 2.14: The kinetics of $\gamma'$-$\text{Ni}_2\text{Cr}$ precipitation in the Ni-Cr binary and Ni-Cr-Fe ternary, showing a considerable incubation period for precipitation. Taken from Young et al.\textsuperscript{7}

Additionally, nowhere in the literature has the precipitation of $\gamma'$-$\text{Ni}_2\text{Cr}$ been observed at grain boundaries of other interfaces. Rather, $\gamma'$ precipitates homogeneously within the grain interiors, and never coarsens to more than 5-10 nm in size, as seen in the work by Young et al. in Figure 2.15.\textsuperscript{6,7,17,40}

Figure 2.15: Centered dark field (CDF) images, showing the homogeneous nucleation of $\gamma'$-$\text{Ni}_2\text{Cr}$ in the Ni-30Cr-3Fe alloy, after annealing at 470 °C for (a) 3,000 hours and (b) 10,000 hours. Excerpt from Young et al.\textsuperscript{7}

This behavior seems contrary to the Ni-Cr binary phase diagram, which indicates that sufficient annealing of a Ni-33Cr (at. %) at temperatures below 590 °C should result in a single-phase structure of the $\gamma'$-$\text{Ni}_2\text{Cr}$ phase. However, in spite of long annealing times, this was never observed.
2.4 Diffuse Intensities in FCC Materials

The $1/3 \{422\}$ and $1/2 \{311\}$ diffuse scattering observed SADPs from Ni-Cr-based alloys has also been observed in other FCC materials. An examination of this work suggests the presence of this diffuse scattering is not necessarily indicative of SRO. Numerous authors have attributed the presence of additional reflections to be the result of relrod spiking due to the thin-foil effect in several thin-film systems.41–43 Davey et al. indexed these reflections on the premise of an HCP phase, while Pashley and coworkers describe the presence of twinning as the root cause.44 Several authors have suggested the presence of atomic steps on the sample surface, resulting in an incomplete stacking of the unit cell, as leading to these additional intensities.43,45–50

In 1974, Cherns proposed the presence of atomic steps in (111) oriented gold thin films (400 Å thick). In his work, centered dark field (CDF) imaging using a $1/3 \{422\}$ reflection suggested the presence of steps on the (111) surface.45 Specifically, he proposed that the presence of atomic steps on the surface resulted in incomplete stacking of the unit cell, resulting in additional intensities in TEM SADPs. In the work by Koch, the additional $1/3 \{422\}$ intensities in SADPs of SiC were also attributed to the presence of atomic steps on the sample surface, as shown in Figure 2.16.

![Figure 2.16: (a) BFTEM in a SiC thin film showing the presence of atomic steps, and the accompanying B=[111] SADP showing the presence of 1/3 \{422\} additional intensities.50](image)

The more contemporary work from Reyes-Gasga51 et al. expanded on the initial work of Cherns.52 In the examination of flat triangular gold nanoparticles, these additional intensities were primarily attributed to relrod spiking from the first-order Laue zone into the zero layer, resulting in additional intensities in SADPs. The authors proposed (using the SimulaTEM software package and dynamical multislice theory) that this occurs due to what is known as the thin-foil effect, but further admitted that the presence of atomic steps on the surface may play a role.
Figure 2.17: (a) Weak-beam dark-field image of a triangular Au nanoparticle, and (b) a B=[111] SADP taken from the particle showing additional 1/3{422} scattering.\textsuperscript{51}

While numerous authors have examined the presence of additional diffracting intensities, and provided a number of hypotheses as to their cause, there does not appear to be a generally accepted origin. The examination of this effect in thin-films makes the isolation of the thin-foil effect and the presence of atomic steps difficult, given the additional scattering due to these features can often occur at the same locations in SADPs. Furthermore, several investigators have observed similar intensities in conventional thickness TEM foils, indicating this is not simply a thin-foil effect.\textsuperscript{6,18,53}

2.4.1 Higher-Order Laue Zone (HOLZ) Diffraction

The reciprocal lattice and Ewald sphere constructions provide a useful means for visualizing TEM diffraction under a particular set of conditions. As shown in Figure 2.18, the lattice points in the reciprocal lattice are related to planes in the real space lattice that have non-zero structure factors (diffraction intensities). The intersection of the Ewald sphere with the reciprocal lattice is used to determine which planes are oriented for diffraction (i.e. are at or close to their Bragg orientation). Finally, because TEM samples are thin, the reciprocal lattice points are depicted as rods of intensity (relrods) that extend in a direction orthogonal to the thin direction (i.e. parallel to the foil normal); this is the reason that diffraction occurs at angles near to but not exactly at the Bragg angle in the TEM and is represented by the Ewald sphere intersection with the relrods.\textsuperscript{42}
Figure 2.18: Schematic of the Ewald sphere interaction with the reciprocal lattice for a parallel beam condition, resulting in the presence of first-order Laue zone (FOLZ) reflections at large reciprocal distances from the transmitted beam. This construction is used to explain the diffracting intensities observed in selected area diffraction patterns (SADPs). The Ewald sphere construction effectively illustrates the location of higher-order Laue zone (HOLZ) reflections that are observed at large angles in TEM diffraction patterns taken at low camera lengths (Figure 2.19). These reflections essentially form HOLZ rings as shown for a conventional SADP in Figure 2.19, and occur at locations where the Ewald sphere intersects the HOLZ.

Figure 2.19: Low camera length SADP along $B=\langle 111 \rangle$ of Alloy 690 showing the reflections in the first-order Laue zone (FOLZ) The ring was drawn in an effort to highlight the similar location of the FOLZ reflections.
2.4.2 Relrod Spiking and the Thin Foil Effect

While the Ewald sphere construction is commonly used to explain the presence of HOLZ rings in SAD and CBED patterns, it can also be used to visualize what might be used to explain the presence of HOLZ diffraction spots in locations near to the transmitted beam, occurring due to the thin-foil effect. For example, if the lengths of the relrods depicted in Figure 2.18 are large, and the spacing of the HOLZ layers are sufficiently small, it is conceivable that the relrods in the HOLZ layers might extend into the zero layer and produce additional diffracting intensities near the transmitted beam, a phenomenon referred to as “spiking”. This manifestation can occur under certain conditions, namely, very thin foils (long relrods) and small HOLZ spacings (large lattice parameter materials and/or higher index zones), the diffraction effects due to HOLZ interactions with the Ewald sphere are not limited to the HOLZ ring in convergent and parallel beam diffraction patterns. The Weiss zone law for diffraction is still valid for determining the presence of reflections in the different Laue zones, namely:

\[
\begin{align*}
    hU + kV + lW &= 0 \quad \text{for ZOLZ} \\
    hU + kV + lW &= \pm 1 \quad \text{for FOLZ} \\
    hU + kV + lW &= \pm 2 \quad \text{for SOLZ}
\end{align*}
\]

where h, k, and l represent the diffracting plane indices, and U, V, and W the beam direction. For non-primitive structures such as BCC and FCC, there are some zone axes in which there are no FOLZ intensities present due to the zone axis examined and the structure factor calculation. An example of this is for the B=[112] zone axis in FCC, where a g=100 reflection would be required for the FOLZ, but is not allowed based on the structure factor. As a result, only reflections from the SOLZ are observed due to relrod effects in a B=[112] SADP of a FCC structure.

A schematic representation of a reciprocal lattice, superimposed with relrods representing the broadening due to the thin nature of the TEM specimen, is shown in Figure 2.20a. In this construction, each relrod is associated with a point in the reciprocal lattice, and is a function of the morphology of the foil or feature causing spiking. In the case of thin foils, the relrods are extended (spiking) along the foil normal. The relation between the real space foil geometry and the reciprocal space relrod spiking is shown in Figure 2.20b, showing in this case that the relrod extension occurs normal to the TEM foil.
In addition to feature size and morphology effects, diffracting intensities are a function of the deviation of the planes from their Bragg angle (or the distance of the Ewald sphere from the actual reciprocal lattice point corresponding to an infinite crystal). This distance is known as the deviation parameter, \( s_g \), and is depicted in Figure 2.21. The diffracting intensity as a function of deviation parameter (i.e. rocking curve) shows the change in intensity expected as a function of this deviation from the Bragg angle.\(^{42}\)

In contrast to the presence of conventional HOLZ diffraction, which occur at large reciprocal distances from the transmitted beam, diffracting intensities due to the thin foil effect occur very close to the transmitted beam.\(^{54}\) Additionally, rather than occurring solely due to the interaction with the HOLZ layers above the ZOLZ, contributions from the layers below the ZOLZ also occur. This is shown schematically in Figure 2.22.
2.5 The Microstructure of Alloy 690

The microstructure of Alloy 690 in SA or TT condition typically exhibits large grain sizes on the order of 50 – 150 μm. In the solution-annealed condition, the structure also contains FCC annealing twins, and occasional TiN inclusions. The thermally-treated condition (700 °C – 17h) also contains M$_{23}$C$_6$-type carbides at both high-angle grain boundaries and incoherent annealing twin boundaries.$^3$ These carbides occur as both regular grain boundary precipitates, and as a cellular product.$^{12}$

2.5.1 M$_{23}$C$_6$-Type Carbides

The precipitation of Cr-rich M$_{23}$C$_6$-type carbides in Alloy 690 has been studied extensively, both with regards to its effects on mechanical properties and stress corrosion cracking. Lee and coworkers examined the precipitation of M$_{23}$C$_6$ in Alloy 690 as a function of both annealing time at 720 °C and boundary character,$^{55}$ and observed no precipitation at coherent annealing twin boundaries (CSL Σ3), sluggish precipitation at random low angle boundaries and other CSL boundaries, and both the continuous and discontinuous precipitation of carbides at random high angle boundaries. Similar observations have been noted in Ni-Cr-W alloys,$^{56,57}$ Ni-Cr-Fe-C alloys,$^{58}$ and austenitic stainless steels.$^{59,60}$
In addition to the characterization of $\text{M}_2\text{C}_6$ precipitation, Lee et al. examined the change in mechanical properties via tensile testing as a function of these carbides. In their examination, a reduction in both ultimate tensile strength and elongation (Figure 2.23) occurred with annealing time at 720 °C; both drops were attributed to the presence of the brittle carbides and a reduction of chromium in the matrix.

![Figure 2.23](a) The effects of Cr-rich $\text{M}_2\text{C}_6$ precipitation in solution annealed Alloy 690 during annealing at 720 °C, showing (a) a reduction in ultimate tensile strength and (b) a reduction in elongation.

In addition to the reduction in UTS and elongation, several interesting microstructural observations were noted. First, in regions along the gauge section near the fracture surface, several intergranular cracks were observed after tensile testing the condition of Alloy 690 annealed at 720 °C for 7 h, as seen in Figure 2.24a. Bruemmer et al. have shown similar cracking in Alloy 600 occurring at the carbide/matrix interface, suggesting a low cohesive strength. Examination of the fracture surface for solution annealed specimens show a typical microvoid coalescence (Figure 2.24b), and the transition to an intergranular fracture after testing material annealed at 720 °C for 15 h (Figure 2.24).
Figure 2.24: Tensile behavior of Alloy 690 after annealing at 720 °C for 7 h. (a) The presence of several cracks on the gauge surface. (b) The solution annealed condition, exhibiting a highly ductile fracture morphology. (c) The observation of intergranular fracture after annealing at 720 °C for 15 h.\textsuperscript{55}

The precipitation of Cr-rich M\textsubscript{23}C\textsubscript{6}-type carbides in Alloy 690, and the effects on local chemistry, have been examined by Was and Angelieu\textsuperscript{62} and Kai et al.\textsuperscript{63} In both studies, the local chromium concentration near the grain boundary as a function of annealing time at 700 °C was examined and modeled, and the data from Kai et al. is shown in Figure 2.25. The initial precipitation of M\textsubscript{23}C\textsubscript{6} during annealing for 1 to 10 hours resulted in a significant depletion of chromium (~10 wt. %) adjacent to the boundary. With further annealing for 24 to 100 h, this depletion is reduced due to the back-diffusion of chromium and the slowed growth of the carbide. Furthermore, previous work in the Ni-Cr binary by Mishima et al. has shown that a 10 wt. % difference in chromium results in a 120 MPa change in the yield stress in solid solution nickel, solely due to solid solution strengthening effects, and presumably can affect the SCC behavior of Alloy 690.\textsuperscript{64}
Figure 2.25: The evolution of the chromium concentration profile in Alloy 690 containing 28.6 wt. % Cr, adjacent to a grain boundary due to Cr-rich M\textsubscript{23}C\textsubscript{6} precipitation while annealing at 700 °C for (a) 1 h, (b) 5 h, (c) 10 h, (d) 24 h, (e) 48 h and (f) 100 h.\textsuperscript{63}
2.5.2 Theory of Cellular Precipitation

The mechanism of cellular precipitation is in many ways similar to a solid-state eutectoid reaction, resulting in the transformation of one phase into two separate phases. However, in the case of cellular precipitation, this transformation occurs by:

$$\alpha' \rightarrow \alpha + \beta$$

where $\alpha'$ and $\alpha$ are the same phase with different solute contents. The cellular precipitation of $M_{23}C_6$ in Alloy 690 results in a matrix depleted of chromium. In order to transport a significant amount of solute to the precipitate, this growth occurs in conjunction with grain boundary migration as shown in Figure 2.26.

The precipitating phase ($\beta$) first nucleates at a favorable site, in this case, a high-angle boundary. As the precipitate begins to grow into the grain with which it has no orientation relationship ($\alpha'$), solute transport along the incoherent and stationary grain boundary alone is insufficient, and the original boundary begins to migrate with the growing interface to continually provide solute to the precipitate. As the grain boundary migrates with the growing $\beta$ phase, it transports solute to the tip of the precipitate, and produces the adjacent matrix phase that is no longer supersaturated in solute with the equilibrium composition $C_\alpha$.

Figure 2.26: Schematic showing the development of a cellular precipitation event, as adapted from Porter and Easterling.\textsuperscript{13}
2.5.3 The Effects of Cold-Rolling Deformation

The application of a 20% cold reduction has been shown to have significant effects on the mechanical and stress corrosion cracking properties of Alloy 690. A 1992 study by the Electric Power Research Institute (EPRI) showed that Alloy 690 in the cold-drawn conditions exhibits a yield stress on the order of 1,000 MPa, while the solution annealed condition has a yield stress of around 300 MPa. This work hardening also results in a significant decrease in ductility during subsequent tensile deformation, as seen in Figure 2.27.

![Stress-strain behavior of Alloy 690 in the cold-drawn condition, and the effects of recrystallization at 980, 1038, and 1066 °C for 30 min.](image)

In addition to the effects on mechanical properties, the application of a 20% cold reduction can result in significant microstructural changes. Sangid et al. examined the deformation behavior of coherent annealing twin boundaries (CSL Σ3) in 310 stainless steel, using combined atomistic modeling and in-situ TEM. In their examination, it was observed that, during initial deformation, annealing twin boundaries are highly resistant to slip transmission, resulting in dislocation pile-ups as shown in Figure 2.28a. However, as deformation proceeds, dislocations are eventually absorbed into the boundary, and eventually result in transmission of dislocations across the coherent boundary (Figure 2.28b).
Zhilyaev et al. also examined similar deformation effects in copper after the equal channel angular pressing (ECAP).\textsuperscript{67} In their study, significant deformation of CSL Σ3 annealing twin boundaries was observed, to the point of forming ledges on the twin boundary and steps at the twin/matrix interface. Orientation imaging microscopy (OIM) analysis of one such twin is presented in Figure 2.29, with an IPF map and misorientation profile indicating significant distortions to the twin. Clearly, the deformation of low stacking fault energy (SFE) materials such as 310SS, copper, and Alloy 690 can result in the disruption of coherent annealing twin boundaries, presumably transforming them into effective high angle boundaries.

Figure 2.28: BFTEM of 310 stainless steel that was strained in-situ in order to examine the deformation behavior of coherent annealing twin boundaries (CSL Σ3). (a) Slip is initially impeded by the twin, resulting in dislocation pile-ups. (b) As the applied stress increases and deformation proceeds, slip eventually transmits past the twin boundary. \textsuperscript{66}

Figure 2.29: Inverse pole figure (IPF) map of commercially pure copper after the ECAP process, showing the significant distortion of a previously coherent annealing twin. The misorientation profile across the twin indicates significant deformation of the boundary character. Note that the black lines indicate high angle boundaries.\textsuperscript{67}
Several mechanisms have been proposed for the deformation of grain boundaries and, in particular, special boundaries. One of the most fundamental mechanisms for plastic deformation can be considered in terms of a single-crystal plastic deformation model.\textsuperscript{68} As deformation proceeds, the slip direction rotates towards the tensile axis as depicted in Figure 2.30a. This results in dislocation pile-ups at various obstacles within the microstructure, such as high angle and special boundaries. In addition to the slip transmission mechanisms proposed by Sangid et al., it is clear that slip band interactions with the boundary play a role in boundary deformation. This slip band interaction with the boundary results in a step of an integral number of Burger’s vectors, as depicted in Figure 2.30b. In this case, slip band interaction with the coherent boundary of an annealing twin results in a step at the boundary.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure230.png}
\caption{Mechanisms of grain boundary deformation. (a) The single-crystal grain rotation mechanism, where the grain rotates towards the tensile axis during deformation (adapted from Dieter).\textsuperscript{68} (b) The interaction of a slip band with an annealing twin boundary, resulting in the formation of a step at the boundary.}
\end{figure}

The deformation of a \textit{<111>} twist boundary, as is the case for an FCC annealing twin, results in an increase in boundary energy. Sangid et al.\textsuperscript{69} have simulated the increase in boundary energy as a function of rotation from this ideal boundary character, using the LAMMPS open-source software.\textsuperscript{70} As shown in Figure 2.31, while the coherent Σ3 boundary type exhibits inherently low energy, slight angular deviations from this boundary results in a drastic increase in boundary energy. Based on the deformation mechanisms and increase in boundary energy detailed above, it is not surprising to see a high degree of carbide precipitation at these boundaries upon subsequent aging.
Figure 2.31: Grain boundary energy as a function of rotation angle from a \(<111>\) twist boundary. Adapted from Sangid et al.\(^6\)

Bruemmer et al. also studied the microstructural damage occurring in Alloy 690 during the cold-rolling process.\(^7\) An SEM examination of this damage accumulation after a 26\% cold reduction of thermally treated Alloy 690 is shown in Figure 2.32. Note the presence of grain boundary voids and cracked carbides due to the rolling process. During subsequent SCC testing, Bruemmer suggested that these defects may act to blunt the crack tip and reduce crack propagation, decreasing SCC susceptibility.

Figure 2.32: SEM micrograph showing the grain boundary damage after a 26\% cold reduction on the thermally treated (TT) condition of Alloy 690. The formation of grain boundary voids and cracked carbides is ubiquitous in the microstructure.\(^7\)

2.6 Stress Corrosion Cracking of Alloy 690

In the discussion of stress corrosion cracking (SCC) of Alloy 690, it is important to understand the mechanisms controlling SCC in related alloys used in industrial service. For the predecessor Alloy 600, the generally accepted mechanism of SCC is related to grain boundary sensitization, due to the precipitation of Cr-rich carbides or the formation of Cr-rich oxides during exposure.\(^7\),\(^3\) The study by Sennour et al. showed the formation of Cr-rich oxides at the sample surface and crack walls, depleting the matrix of chromium.\(^4\) Due to the lower amount of chromium present in the alloy (~16 wt.% compared to
~30 wt. % in Alloy 690), the successful formation of a passive oxide of chromia is not possible, and therefore the continual oxidation (and chromium depletion) results crack initiation at the grain boundary. Crack initiation occurs when the formation of Cr-rich oxides pulls chromium solute from the nickel matrix, resulting in void formation within the matrix, as shown schematically in Figure 2.33.

Furthermore, the precipitation of Cr-rich carbides, either due to annealing or in service aging, can further increase the degree of chromium depletion near the grain boundary. It should be noted that the formation of Ni(Cr,Fe)$_2$O$_4$ spinel is the result of contributions from the autoclave, and not due to a true oxidation mechanism of the alloy. The work by Thierry et al. has shown that the use of a titanium-based autoclave, as opposed to a Ni- or Fe-based system, eliminates the formation of surface spinels during SCC testing.

![Figure 2.33: A schematic detailing the formation of chromia (Cr$_2$O$_3$) and a Ni-rich spinel along the crack wall in Alloy 600, as well as the formation of chromia at the crack tip, resulting in chromium depletion within the matrix.](image)

The most extensive work to date on crack initiation and propagation in Alloy 690 has been performed by Bruemmer and coworkers at Pacific Northwest National Laboratories (PNNL). With extensive testing under constant-K (load control) loading on samples of various TMP conditions, they have shown that Alloy 690 is primarily susceptible to SCC degradation in the cold-worked condition. This is consistent with a large number of other investigations. The constant-K testing in their work was performed on sub-size compact tension (0.5CT) specimens with side grooves loaded in an autoclave to simulate primary water reactor (PWR) conditions. This testing typically involves several steps in order to initiate SCC. Sample pre-cracking was performed by fatigue, followed by corrosion fatigue, and finally SCC testing is performed. This method is an attempt to overcome the significant hurdles in causing initiation, and allows examination of SCC on a more reasonable time scale.

The application of constant-K is performed by measuring in-situ crack length using the direct current potential drop (dcpd) method, and subsequently adjusting the applied load to maintain constant-K conditions in accordance with ASTM Standard E1681. The dcpd method for crack growth measurements compares voltage across the crack plane, in this case the side-grooves in the 0.5CT specimen, and compares it to the voltage away from the crack plane, enabling accurate measurements of crack growth rate.
2.6.1 SCC Initiation in Alloy 690

The work by Bruemmer et al. on Alloy 690 indicates a mixed-mode oxidation process during SCC, controlled by the diffusivities of chromium and oxygen. This consists of a penetrative oxidation of chromia and MO-type oxides in transgranular locations, and the formation of a passive chromia film at intergranular locations. In Figure 2.34, a SEM/TEM examination of surface oxidation after SCC testing is shown. In (a), the centered dark field image shows a continuous film of chromia at locations where the grain boundary intersects the surface. This is the result of enhanced chromium diffusion along the boundary, enabling successful passivation at these locations. This enhanced diffusion at the boundary results in diffusion induced grain boundary migration (DIGM), in order to continually feed solute to the surface, which can be seen in (b). Conversely, at transgranular locations, a type of penetrative oxide exists, with discrete particles of chromia forming in the grain interior. Additional work by Moss has shown that, at transgranular locations, the formation of a continuous passive film of chromia will eventually form given adequate time.

![Figure 2.34: Cold-rolled (20%) Alloy 690 exposed to 360 °C simulated PWR primary water for 1,000 hours. (a) TEM BF/DF pair showing the formation of a passive film of chromia where the grain boundary intersects the surface, and a penetrative oxide at transgranular locations. (b) SEM micrograph showing mixed-mode oxidation and diffusion induced grain boundary migration (DIGM), resulting from the transport of chromium at the GB.](image)

Atom probe tomography (APT) analysis was used to confirm the DIGM effect, associated with the grain boundary diffusion of chromium (Figure 2.35a), and the presence of a passive film of chromia at the grain boundary/surface intersection (Figure 2.35b). It is interesting to note that, while Bruemmer et al. show DIGM in conditions absent of grain boundary carbides, Bertali et al. show this phenomenon occurs in Alloy 600 in the presence of grain boundary carbides as well.
Figure 2.35: Atom probe tomography (APT) reconstruction of Alloy 690 + 20%CR material exposed to 360 °C simulated PWR primary water for 1,000 hours. (a) Atom maps within 50 nm of the surface, indicating DIGM associated with the diffusion of chromium to the surface. (b) The nature of the passive Cr$_2$O$_3$ film at the grain boundary / surface intersection, showing the presence of a continuous, passive oxide.$^{12}$

Extensive STEM-EDS examination of Alloy 690 was performed by Bruemmer et al. in 2012.$^{12,71}$ STEM-EDS maps of Alloy 690 in the TT plus 30% CR condition after SCC testing are shown in Figure 2.36. In addition to the formation of Cr$_2$O$_3$ on grain boundary carbides (Figure 2.36b), there appears to be Cr$_2$O$_3$ ahead of the crack tip, shown in the top right corner of Figure 2.36a. Similar work by Moss using scanning Auger microscopy confirms this, indicating the presence of oxides ahead of the crack tip as shown in Figure 2.37.$^{77}$

Figure 2.36: STEM-EDS analysis of Alloy 690, thermally treated and 30% cold rolled, after SCC testing. Note (a) the presence of a chromia oxide film ahead of the crack tip, (b) in addition to the carbide/matrix interface.$^{12}$ Blue corresponds to the nickel matrix, green the Cr-rich M$_{23}$C$_6$ carbide, and orange/pink the presence of Cr$_2$O$_3$. 

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The work of Bruemmer et al. provides key insights into the mechanisms of SCC initiation and propagation in Alloy 690. Figure 2.38 details the proposed oxidation mechanisms in this alloy, based on extensive microscopy analysis. Initial oxidation occurs by the formation of Cr$_2$O$_3$ on the surface, resulting in chromium depletion within the matrix. At regions where the grain boundary intersects the surface, chromium transport is rapid enough to form a passive film of chromia, and results in a DIGM effect. At transgranular locations, a penetrative oxide of chromia and Cr-rich MO-type oxides is present. Further exposure results in the eventual passivation at these locations as well, as shown by Moss. Given the high chromium content of Alloy 690, it is proposed that a dynamic testing environment is required to initiate SCC. This consists of an iterative process where the surface forms a passive film of chromia, which is then damaged due to straining of the matrix, resulting in further oxidation and chromium depletion of the matrix. Bruemmer et al. have explicitly stated the difficulty in initiating SCC in Alloy 690 under static (constant-K) testing conditions, as the passive film of Cr$_2$O$_3$ continually protects the underlying chromium-depleted matrix from corrosion. The rupture of this passive film is required to get true SCC initiation. The repetitive formation and rupture of the passive oxide results in the continual depletion of chromium from the matrix, and can eventually lead to crack initiation at grain boundary/surface intersections.
Figure 2.38: Proposed mechanism of mixed-mode oxidation behavior in Alloy 690. Locations where the grain boundary intersects the surface forms a passive layer of chromia. Transgranular locations first observe a penetrative oxide of Cr₂O₃ and MO-type oxides, and finally passivates with a film of chromia.⁹⁷

2.6.2 SCC Propagation in Alloy 690

Bruemmer et al. also conducted a year-long constant-K test on Alloy 690 in the solution annealed (SA) and thermally treated (TT) conditions, which culminated in very similar crack growth rates (CGR), on the order of 5x10⁻¹⁰ mm/s.¹² Furthermore, they went on to show that crack growth rates increase with the degree of cold work, regardless of the prior TMP condition, on the order of 5x10⁻⁷ mm/s. Figure 2.39 shows a summary of CGR measurements in Alloy 690, as a function of K and material condition.

Figure 2.39: Summary of crack growth rate (CGR) measurements on Alloy 690 control rod drive mechanism (CRDM) material at Pacific Northwest National Laboratories, illustrating cold-rolling effects on crack growth rate.⁸⁰ The MRP-55 indicates the threshold for acceptable CGR’s based on the behavior of Alloy 600.
It is of interest to note that the CGR for the thermally treated and 31% cold-rolled (RE243 TT+31% CR SL) alloy is significantly higher than that measured for the solution annealed and 31% cold-rolled alloy (RE243 SA+31% CR SL), indicated by the blue arrow in Figure 2.39. While Bruemmer shows the presence of cracked grain boundary carbides and voids present at the grain boundary in the RE243 TT+31% CR SL alloy, he also suggests this does not directly enhance SCC crack growth. Rather, the evidence suggests that the higher degree of local strain at the grain boundary is the driving factor in SCC crack propagation. This is further substantiated when comparing the CGRs of RE243 TT+31% CR SL before and after a recovery anneal.

Examination of crack morphology by Bruemmer et al. indicates that crack propagation follows one side of the grain boundary along the carbide/matrix interface, as shown for the RE243 TT+31% CR SL alloy in Figure 2.40. However, in the absence of grain boundary carbides (i.e. RE243 SA+31% CR SL), crack propagation also follows the grain boundary in a similar fashion.

Figure 2.40: SEM-BSE micrographs showing SCC cracking in the thermally treated and 31% cold-rolled (RE243 TT+31% CR SL) condition of Alloy 690.
CHAPTER 3  EXPERIMENTAL METHODS

Procedures for alloy processing, microstructural characterization and analysis, and stress corrosion cracking (SCC) testing will be discussed in this chapter.

3.1 Thermomechanical Processing (TMP) and Aging of Alloy 690

The various alloys examined in this study were produced by Dr. Young Suk Kim at the Korean Atomic Energy Research Institute (KAERI). The entirety of Alloy 690 for this study was produced from a single heat to ensure chemical homogeneity. The composition of Alloy 690 was verified via chemical analysis conducted at POSCO, South Korea, and is presented in Table 3.1.

Table 3.1: Composition of Alloy 690 used in this study, as determined by chemical analysis at POSCO, South Korea.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt. %</td>
<td>58.23</td>
<td>32.70</td>
<td>8.64</td>
<td>0.020</td>
<td>0.080</td>
<td>0.250</td>
<td>0.080</td>
</tr>
<tr>
<td>at. %</td>
<td>55.50</td>
<td>35.18</td>
<td>8.66</td>
<td>0.070</td>
<td>0.160</td>
<td>0.256</td>
<td>0.166</td>
</tr>
</tbody>
</table>

Four thermo-mechanical processing (TMP) conditions were examined, to emulate the various conditions observed in industry (SA and TT) as well as examine conditions shown to be more susceptible to SCC (CR and TTCR). All of these TMP conditions were given an original solution anneal at 1100 °C for 1 h. Following this solution anneal, a single pass cold reduction of 20%, a thermal treatment of 700 °C for 17 h, or a combination of the two (TT followed by CR), were provided. The details regarding the TMP process, and the specimen geometry can be seen in Table 3.2 and Figure 3.1, respectively. The microstructural evolution of all conditions in this study was examined with specimens in the T-S orientation, or parallel to the rolling direction, as indicated in Figure 3.1.

Table 3.2: The thermo-mechanical processing (TMP) of Alloy 690, as produced by KAERI.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
<th>Specifics</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA</td>
<td>Solution Annealed</td>
<td>1100 °C – 1 h</td>
</tr>
<tr>
<td>CR</td>
<td>Cold Rolled</td>
<td>20% Reduction</td>
</tr>
<tr>
<td>TT</td>
<td>Thermally Treated</td>
<td>700 °C – 17 h</td>
</tr>
<tr>
<td>TTCR</td>
<td>Thermally Treated then Cold Rolled</td>
<td>TT then 20% CR</td>
</tr>
</tbody>
</table>
Representative as-received geometry of Alloy 690 used in this study, in this case the as-cold-rolled condition (CR-00-00).

Following thermo-mechanical processing, each of these conditions of Alloy 690 was aged at four temperatures for two times. The full experimental matrix of these conditions can be seen in Appendix B. Annealing conditions of 350, 420, 475 and 550 °C for 3,000 and 10,000 hours were provided. A lower temperature limit of 350 °C was chosen to closely mimic the conditions in service, while an upper limit of 550 °C was chosen to accelerate the precipitation kinetics for the duration of this study. The condition annealed at 420 °C, while provided from KAERI, was not examined in this study. The nomenclature for these alloys, detailed in Figure 3.2, is as follows: AA-BB-CC, where AA is the original TMP condition, BB is the annealing temperature in °C, and CC is the annealing time in hours.

The nomenclature used for the various conditions of Alloy 690 in this study. Formatted as AA-BB-CC, where AA is the original TMP condition, BB is the annealing temperature in °C, and CC is the annealing time in hours. This example is a thermally treated then cold rolled condition of Alloy 690, annealed at 475 °C for 10,000 hours.
3.2 Arc-Melting and Annealing of Ni-55Cr

Several Ni-Cr binary specimens were prepared in order to examine the precipitation behavior in this system, as it relates to Alloy 690. Given the sluggish precipitation kinetics in Alloy 690, specifically with regards to $\gamma'$-Ni$_2$Cr and $\alpha$-Cr precipitation, this study was performed on a Ni-55Cr (wt. %) alloy. This model alloy was produced by non-consumable arc melting under a purified argon atmosphere after previously melting a titanium getter, to remove any remaining oxygen in the chamber. Each button was flipped and re-melted 6 times in order to ensure homogeneity. The button was then sectioned in order to complete various heat treatments to examine the precipitation behavior of Ni$_2$Cr and $\alpha$-Cr. The sum weight of each button was measured before and after arc melting, in order to verify that no elemental loss occurred during production.

The binary Ni-Cr phase diagram, with the casting composition used in this study, is shown in Figure 3.3. A Ni-55Cr alloy composition was chosen, with subsequent heat treatments at 900 °C for 4 h, 500 °C for 1,000 h, or 900 °C followed by 500 °C. The 900 °C – 4 h anneal was chosen to precipitate $\alpha$-Cr within the Ni-rich interdendritic regions, providing substantial Ni/Cr interfacial area for $\gamma'$-Ni$_2$Cr precipitation during the subsequent anneal at 500 °C, assuming that this phase is stable. Additionally, the 500 °C – 1,000 h annealing condition was performed to ensure $\gamma'$ was provided sufficient time for precipitation, given the sluggish kinetics reported by other authors. Finally, the combination of a 900 °C – 4 h anneal followed by a 500 °C – 1,000 h anneal was performed, in order to precipitate $\alpha$-Cr within the $\gamma$-Ni interdendritic regions, and examine the phase stabilities of $\alpha$-Cr, $\gamma$-Ni, and $\gamma'$-Ni$_2$Cr.

![The Ni-Cr binary phase diagram as adapted from Nash, showing the Ni-55Cr composition, and the two annealing temperatures (500 and 900 °C).](Figure 3.3)
3.3 Metallographic Preparation

The metallographic preparation of the alloys in this study varied with characterization technique, as detailed below. Specimens were originally sectioned using either a LECO MSX250 saw using an alumina blade, or an Allied TechCut 4 low speed diamond saw, to approximately 3 mm in thickness, or ~500 μm for the case of TEM preparation. For the case of cold-rolled conditions of Alloy 690, samples were cut perpendicular to the rolling direction and mounted in the T-S orientation, as shown in Figure 3.4.

![Figure 3.4](image)

Figure 3.4: (a) Sample sectioning and (b) mounting orientation for all conditions.

Metallographic preparation consisted of grinding the sample using sequentially decreasing grit size. Polishing steps consisted of 6, 3, 1, and 0.05 μm diamond suspensions on various polishing pads, as outlined in Table 3.3. Each step in polishing consisted of approximately 3-5 min at 200-400 RPM on an 8” wheel. After the final polishing step, each sample was rinsed under hot water, rinsed using laboratory grade isopropyl alcohol, washed with micro-organic soap, rinsed with ultra high purity (UHP) ethanol, and finally dried with a heated air dryer.

<table>
<thead>
<tr>
<th>Step</th>
<th>Grit/Polish</th>
<th>Paper/Pad</th>
<th>Media</th>
<th>LECO Part No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>320</td>
<td>PSA</td>
<td>SiC</td>
<td>810-265-300</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>PSA</td>
<td>SiC</td>
<td>810-267-300</td>
</tr>
<tr>
<td>3</td>
<td>600</td>
<td>PSA</td>
<td>SiC</td>
<td>810-269-300</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
<td>PSA Premium</td>
<td>SiC</td>
<td>810-035-100</td>
</tr>
<tr>
<td>5</td>
<td>1200</td>
<td>PSA Premium</td>
<td>SiC</td>
<td>810-036-100</td>
</tr>
<tr>
<td>6</td>
<td>1200</td>
<td>PSA Premium Fine</td>
<td>SiC</td>
<td>810-036-500</td>
</tr>
<tr>
<td>7</td>
<td>6 μm</td>
<td>Ultra Silk</td>
<td>Diamond</td>
<td>812-437</td>
</tr>
<tr>
<td>8</td>
<td>3 μm</td>
<td>Ultra Silk</td>
<td>Diamond</td>
<td>812-437</td>
</tr>
<tr>
<td>9</td>
<td>1 μm</td>
<td>Imperial</td>
<td>Diamond</td>
<td>810-545-010</td>
</tr>
<tr>
<td>10</td>
<td>0.05 μm</td>
<td>Imperial</td>
<td>Diamond</td>
<td>810-545-010</td>
</tr>
</tbody>
</table>
3.3.1 Hardness, Optical, and Scanning Electron Microscopy (SEM)

Samples prepared for Vickers microhardness, optical microscopy, and standard SEM characterization were first cut to approximately 3 mm thickness using either a LECO MSX250 high speed saw using an alumina blade or an Allied TechCut 4 low speed diamond saw. Samples were mounted in bakelite mounts and then polished to a 1 μm finish in accordance with ASTM Standard E3.94 Following polishing, samples were thoroughly cleaned using ultra high purity (UHP) ethanol and then plasma cleaned in an Evactron CombiClean at 10 W for 20 min.

3.3.2 High-Resolution SEM (HRSEM) and Electron Back-Scatter Diffraction (EBSD)

In order to meet the unique imaging and geometric requirements for HRSEM and EBSD, samples were mounted on 12.7 mm aluminum pin stubs for examination. This mounting technique not only allowed for shorter working distances during imaging and EBSD analysis, but also for these samples to be bulk electropolished to remove any surface deformation remaining from mechanical polishing. The benefits of bulk electropolishing are two-fold. First, by removing the surface deformation from mechanical polishing, EBSD confidence indices are significantly increased. Second, applying a light etch to the sample, very small (10-50 nm) grain boundary carbides are noticeable. In mechanically polished samples under typical SEM operating conditions, these fine grain boundary precipitates are difficult to resolve. The various electropolishing conditions and results are detailed in Table 3.4.

Table 3.4: Bulk electropolishing solutions and conditions used in this study.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Voltage</th>
<th>Current</th>
<th>Temperature</th>
<th>Time</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>45% Acetic Acid</td>
<td>10-15 V</td>
<td>10-15 mA</td>
<td>-30 °C</td>
<td>15s</td>
<td>Very good. In some cases, a grain boundary film develops</td>
</tr>
<tr>
<td>45% Methanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Perchloric Acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% Phosphoric Acid</td>
<td>10 V</td>
<td>1 A</td>
<td>25 °C</td>
<td>8 s</td>
<td>Even etch, does not specifically attack grain boundaries.</td>
</tr>
<tr>
<td>80% DI Water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10% Perchloric Acid</td>
<td>30 V</td>
<td>15 A</td>
<td>-30 °C</td>
<td>10 s</td>
<td>Very aggressive etch</td>
</tr>
<tr>
<td>90% Methanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kalling’s No. 2</td>
<td>---</td>
<td>---</td>
<td>25 °C</td>
<td>2 min</td>
<td>Good macro etch, but unsuitable for HRSEM grain boundary analysis</td>
</tr>
</tbody>
</table>

---

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3.3.3 Transmission Electron Microscopy (TEM)

Sample preparation for transmission electron microscopy (TEM) was performed using traditional methods. Each sample was sectioned orthogonal to the rolling direction, as detailed in Figure 3.4, using an Allied TechCut 4, to approximately 500 μm in thickness. Following sectioning, the sample was then mounted to a 25.4 mm aluminum stub using QuickStik 135, a low melting point polymer adhesive. The sample was then thinned to approximately 100 μm using 600-grit SiC abrasive paper with the aid of a 1” bubble level, to ensure planarity. Once thinned, the samples were removed from the aluminum stubs and given a final grinding using 800-grit SiC immediately prior to electropolishing in order to remove surface oxides. Once sufficiently thinned, samples were punched using a SPI TEM punch to create 3 mm blanks.

Following metallographic preparation, TEM foils were thinned to electron transparency using a Fischione Model 110 Automatic Twin-Jet Electropolisher. While multiple electrolytes and parameters were used, a solution of 45% acetic acid, 45% methanol, and 10% perchloric acid at -30 °C, 10 V, ~15 mA was found to be the most effective. Additionally, given the unequal flow rates through each jet, the sample was rotated 180° every 60 s for an even polish. Once thinned, all foils were cleaned using a 5-step rinse: (1) Submerge the foil+holder in ethanol, (2) repeat step 1 in secondary bath, (3) remove foil and submerge in ethanol, (4) submerge foil in isopropanol, (5) rinse/soak in high-purity ethanol, and (6) air dry.

3.4 Vickers Microhardness Measurements

All Vickers microhardness measurements were taken on a LECO Series 200 machine. A 260 HV Antonik standard, serial number 882592, was tested with 5 indents at the beginning and end of each testing session to ensure calibration. Samples were mounted in a bakelite mounting medium, and polished to a 1 μm finish as detailed in Section 3.3. For microhardness testing, a load of 500 gmf for 10 s was used for a minimum of 10 indents. Vickers testing methodology, and reported values were all in accordance with ASTM Standard E92.

3.5 Dual-Beam Focused Ion Beam (FIB)

The majority of SEM imaging, EBSD analysis, and EDS were performed in an FEI Helios Nanolab 600i. This instrument is equipped with an EDAX SSD EDS detector, an EDAX Hikari Super EBSD detector capable of 1,400 indexed points per second, a STEM imaging detector, a 30 kV electron source and a 30 kV gallium ion source. The procedures used for TEM sample preparation, EBSD data collection, and HRSEM imaging in the Helios Nanolab 600i is detailed in the following sections.
3.5.1 High-Resolution Scanning Electron Microscopy (HRSEM)

For high-resolution SEM, the FEI Helios Nanolab 600i was used due to its immersion mode capabilities. Imaging was performed at 5 kV and 22 nA on etched specimens. With the immersion mode technique, the specimen is at a ~2 mm working distance, and then immersed in an electric field, shown schematically in Figure 3.5. This method allows for very clear and accurate imaging at magnifications well over 100,000X, but relies on the sample being clean and conducting.

![Figure 3.5: Schematic of the immersion mode imaging technique in the FEI Helios Nanolab 600i. An electric field is applied around the column and sample, enabling significantly higher resolutions for SEM imaging.](image)

3.5.2 Liftout Procedure for Transmission Electron Microscopy (TEM) Specimens

Samples used for TEM liftouts were mounted on a 12.7 mm pin stub after electrolytic etching, as detailed in Section 3.3.2. The detailed stage tilts, accelerating voltages and currents, and pattern types for a standard TEM liftout are detailed in Table 3.5. The initial step in the liftout process begins with the deposition of a protective platinum layer, approximately 2 μm thick, using the ion-beam (Figure 3.6). In the event that immediate surface features are of interest, this layer can be initially deposited using the electron beam, followed by the bulk deposition via ion beam.
Table 3.5: Sequential thinning and cleaning process of FIB-produced TEM liftouts on the FEI Helios Nanolab 600i.

<table>
<thead>
<tr>
<th>Step</th>
<th>Beam</th>
<th>Purpose</th>
<th>Tilt</th>
<th>Voltage (kV)</th>
<th>Current (nA)</th>
<th>Pattern Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>E</td>
<td>Pt-Dep</td>
<td>0°</td>
<td>5</td>
<td>11</td>
<td>PT Dep Surface</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>Pt-Dep</td>
<td>52°</td>
<td>30</td>
<td>0.43</td>
<td>PT Dep</td>
</tr>
<tr>
<td>3</td>
<td>I</td>
<td>Trench</td>
<td>52°</td>
<td>30</td>
<td>47-65</td>
<td>Regular Cross Section - Multiscan</td>
</tr>
<tr>
<td>4</td>
<td>I</td>
<td>Pre-Thinning</td>
<td>52°</td>
<td>30</td>
<td>9.3</td>
<td>Rectangle</td>
</tr>
<tr>
<td>5</td>
<td>I</td>
<td>U-Cut</td>
<td>7°</td>
<td>30</td>
<td>9.3</td>
<td>Parallel</td>
</tr>
<tr>
<td>6</td>
<td>I</td>
<td>Omniprobe Weld</td>
<td>0°</td>
<td>30</td>
<td>0.43</td>
<td>PT Dep - Rectangular</td>
</tr>
<tr>
<td>7</td>
<td>I</td>
<td>Final Cut</td>
<td>0°</td>
<td>30</td>
<td>9.3</td>
<td>Si</td>
</tr>
<tr>
<td>8</td>
<td>I</td>
<td>Cu Grid Weld</td>
<td>0°</td>
<td>30</td>
<td>0.43</td>
<td>PT Dep - Rectangular</td>
</tr>
<tr>
<td>9</td>
<td>I</td>
<td>Omniprobe Cut</td>
<td>0°</td>
<td>30</td>
<td>9.3</td>
<td>Rectangle</td>
</tr>
<tr>
<td>10</td>
<td>I</td>
<td>Square Lamella</td>
<td>52°</td>
<td>30</td>
<td>9.3</td>
<td>Cleaning Cross Section</td>
</tr>
<tr>
<td>11</td>
<td>I</td>
<td>Thinning</td>
<td>50-54°</td>
<td>30</td>
<td>2.5</td>
<td>Cleaning Cross Section</td>
</tr>
<tr>
<td>12</td>
<td>I</td>
<td>Thinning</td>
<td>50-54°</td>
<td>30</td>
<td>0.79</td>
<td>Cleaning Cross Section</td>
</tr>
<tr>
<td>13</td>
<td>I</td>
<td>Thinning</td>
<td>50-54°</td>
<td>30</td>
<td>0.43</td>
<td>Cleaning Cross Section</td>
</tr>
<tr>
<td>14</td>
<td>I</td>
<td>Final Cleaning</td>
<td>45°</td>
<td>2</td>
<td>0.72 pA</td>
<td>Rectangle</td>
</tr>
</tbody>
</table>

Figure 3.6: Ion beam micrographs of the deposition of protective platinum on the sample surface, taken using the ion beam at (a) 0° and (b) 52° stage tilt.

Once a protective layer of platinum is present, the initial trench can be made using the ion beam at high currents, followed by a pre-thinning to remove excess re-deposition. At this point, a U-cut is made around the periphery of the lamella, with the exception of the top corner. The U-cut is performed in order to minimize the duration of milling once the Omniprobe has been welded to the sample. These intermediate steps can be seen in Figure 3.7.
Figure 3.7: Focused ion beam (FIB) preparation of a TEM liftout. (a) The first trench cut during the milling process. (b) The U-Cut, immediately before removing the lamella from the bulk specimen.

Once the bulk material surrounding the lamella has been removed and the U-Cut has been performed, the liftout is ready for retrieval. At this point, the Omniprobe micro-manipulator is welded to the lamella via platinum deposition as seen in Figure 3.8a, removed from the bulk specimen, and welded to a copper half-grid (Figure 3.8b).

Figure 3.8: (a) Welding of the Omniprobe manipulator to the lamella, followed by the final cut, freeing it from the bulk specimen. (b) Welding of the lamella to the copper grid for final thinning.
The final thinning steps (detailed above in Table 3.5) can be performed once the lamella has been welded to the copper half-grid, and cut free from the Omniprobe. It is suggested that if the protective platinum layer is rapidly depleting during the thinning process to adjust the angle of incidence with respect to the ion beam (+/-), which should reduce this effect. Additionally, following the final thinning step to ~100 nm in thickness, a low voltage (2 kV) cleaning step is used to remove any remaining surface damage and gallium implantation.

Figure 3.9: The TEM lamella after the final thinning step, still requiring a 2 kV cleanup.

3.5.3 Electron Back-Sscatter Diffraction (EBSD) Geometry

The specimen and stage geometry for EBSD data collection in the FEI Helios Nanolab 600i can be seen in Figure 3.10. In this configuration, a combination of a stage extender, 70° pre-tilt pin-stub holder, and a pin-stub extender places the 12.7 mm stub in the ideal position for EBSD data collection. This 70° pre-tilt can be adjusted slightly to increase the quality of pattern collection by monitoring the “hot-spot” on the camera as a function of stage tilt.
In this instance, while the sample orientation is parallel to the top edge of the specimen, there is a degree of rotation ($\alpha$) from ideal. To correct this, the FIB stage was rotated using the “XT-Align” function within the FEI software. This rotates the stage based on a line drawn across the sample by the user, to indicate the edge to make horizontal. This procedure can be seen in Figure 3.11.

Figure 3.11: Sample alignment (a) before and (b) after using the Xt-Align function in the FEI software.
3.6 Electron Back-Scatter Diffraction (EBSD) Collection and Analysis

The electron back-scattered diffraction (EBSD) data collection in this study includes the determination of coincident site lattice (CSL) deviation. This analysis was used to characterize annealing twin boundaries (CSL Σ3) before and after the cold-rolling process. Typical collection parameters utilized a 20 kV electron beam at 22 nA, with a 4x4 camera binning.

3.6.1 Coincident Site Lattice (CSL) Deviation

The calculation of the deviation from a coincident site lattice boundary character relies on the input of this special boundary into the OIM software. This analysis is based on what is known as Brandon’s Criterion, and can be manipulated to include boundaries close to CSL misorientations. The method developed by D. G. Brandon, enables the extension of a CSL boundary model to grain boundaries that deviate from the ideal coincidence. This relationship is defined in Equation 3.1, where \( \theta_m \) is the allowed deviation from the orientation of the CSL boundary and \( \Sigma \) is the CSL boundary type (i.e. Σ3).

\[
\theta_m < 15\sqrt{\Sigma}
\]

Equation 3.1

Annealing twins in the FCC system are defined as a CSL Σ3 boundary type, indicating perfect atomic matching with every third atom in the lattice. This boundary is crystallographically defined as a 60° rotation about the \([011]\), with the \{111\} being the habit plane between the matrix and twin, as shown in Figure 3.12. Based on this definition, and the values defined by Brandon’s Criterion, the OIM software can compare a set of pixels across a boundary, and calculate their deviation from the ideal orientation.

![Figure 3.12](image)

Figure 3.12: (a) Schematic representation of a CSL Σ3 boundary, explaining the origins of the CSL nomenclature. (b) A simulated SADP down the \(B=[011]\), where blue, red, and purple are the matrix, twin, and shared reflections, respectively.
3.7 Transmission Electron Microscopy (TEM)

A variety of S/TEM imaging and diffraction techniques were used in this study. A brief treatment of weak-beam dark-field (WBDF), centered dark-field (CDF), two-beam bright-field (BFTEM), and STEM energy dispersive spectroscopy (EDS) will be discussed here.

3.7.1 Dark-Field and Bright-Field Imaging

Several specific imaging techniques provide for useful, quantitative, and repeatable analyses in the TEM. Weak-beam dark-field (WBDF), centered dark-field (CDF), and bright-field TEM (BFTEM) techniques are the three primary imaging methods used that are based on specific crystallographic and diffracting conditions. The two-beam condition is an imaging condition that represents specific crystallographic information. This image consists of both mass/thickness and diffraction contrast, typically stemming from the transmitted beam and a single strongly diffracting reflection.

Weak-beam dark-field (WBDF) imaging is one of the primary methods used in defect analysis in the TEM. This technique is quite useful due to the fact that it allows you to more accurately image dislocation cores, among other defects. In this technique, as with centered dark-field and two-beam bright-field imaging techniques, it is important be in a two-beam condition, typically 5-6° away from a major zone axis.

While detailed descriptions of WBDF can be found in the literature, a brief treatment will be provided here. WBDF is performed by first forming a two-beam image with the desired g diffraction spot, shown schematically in Figure 3.13a. This results in the transmitted beam (O, in orange) and the desired g (G, in green) being highly excited and s equal to zero. Following this, the dark-field deflector coils are used to tilt the beam, and move the desired g to the original position of the transmitted beam (down the optic axis). At this point, the 3g should be at its Bragg condition, as shown schematically in Figure 3.13b, resulting in what is referred to a g/3g condition. Now, by inserting an appropriately size objective aperture to isolate the weakly diffracted beam to form an image with a large deviation parameter (s > 0), a weak-beam dark-field imaging condition has been achieved.
The collection of a centered dark-field (CDF) image is performed much like what was just described for the WBDF technique, and it is often useful to collect both images sequentially with minimal effort. Specifically, rather than tilting $+g$ to the optic axis, the beam is tilted such that $-g$ is brought to the optic axis and used to form the CDF image with $s_g=0$. Such images will have much higher intensities but without the fine detail that can be seen in WBDF images.

### 3.7.2 STEM Imaging and Energy Dispersive Spectroscopy (EDS)

STEM imaging in the FEI Talos F200X was performed primarily using the annular bright-field and high-angle annular dark field (HAADF) detectors. A camera length of 98 mm was determined to be sufficient for atomic number contrast with the HAADF detector, with camera lengths longer than this resulting in appreciable diffraction contrast.

For STEM-EDS measurements using the Bruker QUANTAX XFlash system, the manufacturer recommends a dead time of 5%. A HyperMap EDS collection saves the EDS spectrum at each pixel within the map, and allows for point and line scans to be analyzed in various ways. All EDS data was analyzed using a Cliff-Lorimer correction, allowing for a standardless quantification. The Cliff-Lorimer
method was originally developed for quantification of EDS spectra from binary systems, and has since been expanded to multi-component systems. This method compares the intensity of peaks simultaneously collected from the two elements (I_A and I_B), and in conjunction with the Cliff-Lorimer correction factor (k_{AB}), calculates the relative concentrations of each element. The basis for the Cliff-Lorimer analysis is defined by:\(^{42}\)

\[
\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}
\]

(Equation 3.2)

The basis for the Cliff-Lorimer correction factor (k_{AB}) is the assumption of a very thin foil, and thereby assuming no absorption or fluorescence effects, as in the case of bulk SEM-EDS examinations. However, it is important to note that this criterion is not always met in thin foils, and can result in errors in STEM-EDS measurements.\(^{98}\) If this assumption is valid, the sensitivity factor k_{AB}, is solely a function of atomic number, accelerating voltage and microscope.

### 3.8 Slow Strain Rate Testing (SSRT)

The susceptibility to SCC initiation of Alloy 690 was examined using the slow strain rate testing at the University of Michigan. Dr. Wenjun Kuang and Dr. Gary Was conducted these experiments, and the experimental details are discussed in the followed sections.

#### 3.8.1 Preparation for Testing

All samples were machined into tensile bars as shown in Figure 3.14. The gage section of each tensile bar was mechanically abraded up to #4000 grit and then electropolished for 30 s at 30 V in a solution of 10 volume percent perchloric acid in methanol, which was maintained at -30 °C. Several coupons measuring 8×8×4 mm were also prepared using the same procedure for grain boundary characterization and IG precipitate analysis. Slow strain rate testing (SSRT) was used to strain the samples at 1x10^-8 s^-1 in 360 °C high purity water containing 18 cc/kg H₂.

![Figure 3.14: Tensile specimen geometry for stress corrosion cracking (SCC) via slow strain rate tensile (SSRT) testing.](image-url)
3.8.2 Examination of SSRT Specimens

After the straining tests, a JEOL JSM-6480 SEM at the University of Michigan was used to image more than 40 equally spaced areas at 1000X along the gage section. The images were examined for intergranular cracks. Values of crack length per unit area, crack density and average crack length were calculated based on the crack number and measured crack length in the SEM micrographs. Among these three parameters, crack length per unit area provides the most complete description of SCC susceptibility, accounting for both the length and number of cracks in a sample’s area. A representative SEM micrograph showing the crack size and morphology in the CR-475-10k condition of Alloy 690 is shown in Figure 3.15a, with the crack length per area as a function of annealing parameters shown in Figure 3.15b.

![SEM micrograph of CR-475-10k alloy](image)

Figure 3.15: (a) Representative SEM micrograph of the crack morphology in a CR-475-10k alloy tested in 360 °C simulated PWR steam/water, with a strain rate of 1x10^{-8} s^{-1}. (b) The measured crack length per area (μm/mm²) as a function of annealing parameters.

It is worth noting that the presence of the large Ni/Fe rich spinel particles on the surface of the specimen is the result of cation contributions from the stainless steel autoclave body. Fournier et al. has shown that using a titanium-based autoclave greatly limits the formation of surface oxides. While it has been shown that in some cases these spinel particles can convolute the observation of shallow grain boundary cracks, it is not believed to be a concern for this study.

The susceptibility to crack initiation during SCC of Alloy 690 was examined in conditions aged at 350 and 475 °C for 10,000 hours, with the cold-rolled condition being examined up to 550 °C for 10,000 hours. This decision was made based on the increase in cracking behavior for the CR-475-10k condition, which was not observed for other TMP conditions. In addition to statistical cracking measurements, the stress-strain response (primarily yield stress) was examined.
In this chapter, the purported short-range order observed in Alloy 690, identified by the presence of diffuse scattering in SADPs, will be discussed. The diffuse scattering observed in a variety of TMP and annealing conditions of Alloy 690 will be presented in Section 4.1. A consideration of additional diffraction effects contributing to these intensities will be presented in Section 4.2. Similar observations in a variety of FCC materials will be discussed in Section 4.3. A consideration of higher-order Laue zone (HOLZ) diffraction will be provided in Section 4.4. Finally, theoretical considerations of diffuse scattering in TEM SADPs will be discussed in Section 4.5.

4.1 Diffuse Scattering in Alloy 690

The purported short-range order (SRO) in Alloy 690 has been suggested based on the observations of diffuse intensities at the $1/3\{422\}$ and $1/2\{311\}$ positions in $B=[111]$ and $B=[112]$ SADPs, respectively. These intensities have been observed in all TMP and annealing conditions of Alloy 690 examined in this study, as well as several additional cubic structures. Representative SADPs down the $B=[111]$ and $B=[112]$ zones in solution annealed Alloy 690 are presented in Figure 4.1, with arrows indicating the location of these diffuse intensities. In addition to the visual examination of these diffuse intensities, centered dark field (CDF) imaging utilizing the $1/3\{422\}$ reflections near the $B=[111]$ was performed. Unfortunately, no recognizable contrast was observed in Alloy 690 using this technique.

![Figure 4.1](image)

Figure 4.1: Observations in the as cold-rolled condition of Alloy 690 (CR-00-00). (a) The presence of $1/3\{422\}$ diffuse intensities in a $B=[111]$ SADP. (b) The presence of $1/2\{311\}$ diffuse intensities in a $B=[112]$ SADP.
4.2 Additional Diffraction Effects

The persistence of this diffuse scattering in various Alloy 690 conditions led to the examination of additional factors that might account for these extra diffraction intensities. As such, several diffraction effects were examined with regards to their contributions to diffuse scattering. Primarily, these factors include: (1) Kikuchi band intersections, (2) higher-order Laue zone (HOLZ) diffraction due to the thin foil effect, (3) thermal diffuse scattering (TDS), (4) sample preparation artifacts, and (5) the formation of surface oxides.

4.2.1 Kikuchi Bands and Higher-Order Laue Zone (HOLZ) Diffraction

The presence of Kikuchi band intersections and their effects on additional diffuse scattering in B=[111] and B=[112] zone axis patterns were examined in Alloy 690. Simulated Kikuchi band patterns, overlaid on experimental SADPs, are shown in Figure 4.2. In this instance, it is clear that the intersection of several Kikuchi bands correspond to the locations of 1/3{422} and 1/2{311} diffuse intensities when oriented exactly down zone. Additionally, simulations of higher-order Laue zone (HOLZ) diffraction also correlate well with the locations of these additional intensities, and are shown in Figure 4.4.

![Figure 4.2: Experimental selected area diffraction patterns overlaid with simulated Kikuchi bands for the (a) B=[111] and B=[112] zone axes.](image-url)
A careful tilting experiment was conducted in order to separate the effects of Kikuchi band intersections from the diffuse scattering and is presented in Figure 4.4. By tilting slightly off zone along a \{220\} band, it is clear that the 1/3\{422\} diffuse scattering deviates from the locations of Kikuchi band intersections. In Figure 4.4, the \{220\} Kikuchi bands are overlaid on the experimental SADP, showing the angular deviation off zone, yet these additional intensities remain in the same positions as when down zone. This observation indicates that the presence of 1/3\{422\} and 1/2\{311\} diffuse scattering is not due to the intersection of Kikuchi bands.

Figure 4.3: Experimental selected area diffraction patterns overlaid with the location of simulated HOLZ diffraction spots for the (a) B=[111] and B=[112] zone axes.

Figure 4.4: An examination of Kikuchi band intersections and their contribution to 1/3\{422\} diffuse scattering in B=[111] SADPs. (a) A Kikuchi band simulation overlaid on an experimental SADP, showing the (b) decoupling of the Kikuchi band intensities and diffuse scattering.
4.2.2 Thermal Diffuse Scattering (TDS)

The effects of lattice vibrations, or thermal diffuse scattering (TDS), can play a substantial role in the experimental observation of SADPs. These lattice vibrations can result in additional intensities present in SADPs, which would not be typically present otherwise.\textsuperscript{99,100} An examination TDS effects on 1/3\{422\} diffuse intensities in \textless 111\textgreater SADPs was conducted at Los Alamos National Laboratories. Using a double-tilt liquid nitrogen (LN2) cryostage, SADPs were taken at liquid nitrogen temperature (-196 °C) and compared to those taken at room temperature (~23 °C). As shown in Figure 4.5, the diffuse intensities are persistent at -196 °C, indicating their presence is not the result of TDS.

![Figure 4.5: Cryostage TEM down the B=[111] of Alloy 690 sample SA-475-3k at (a) -196 °C and (b) 23 °C, showing no obvious change in the 1/3\{422\} diffuse intensities.](image)

4.2.3 Sample Preparation and Surface Films

The presence of microstructural defects due to sample preparation and the formation of surface films (e.g. oxides) can result in additional reflections in SADPs. For example, during preparation of conventional foils via twin-jet electropolishing, the deposition of organics can occur on the foil surface. Additionally, during the storage of TEM foils, the formation of surface oxides will inevitably develop on Ni-Cr-base alloys. For Alloy 690 this would consist of Cr$_2$O$_3$, while for commercially pure nickel this would consist of NiO.

To determine if the presence of surface oxides or sample preparation artifacts is contributing to the additional diffuse scattering in SADPs, a FIB liftout of commercially pure (CP) nickel was taken. This process precludes the deposition of organics and the formation of oxides during traditional twin-jet electropolishing. Furthermore, while a thin layer of oxide is anticipated even for the short time between sample prep and TEM examination (<1 h), this oxide is unlikely to be substantial enough to result in
additional intensities in SADPS. The simulated B=[111] and B=[112] SADPs for the double diffraction of nanocrystalline NiO (a-b) and Cr₂O₃ (c-d) rings in the presence of FCC nickel are shown in Figure 4.6. While the intersection of these rings loosely corresponds to the locations of diffuse intensities for the NiO simulation, it is not the case for Cr₂O₃.

![Simulated SADPs of FCC nickel with the presence of double diffraction rings from nanocrystalline (a-b) NiO and (c-d) Cr₂O₃ down the B=[111] and B=[112] zone axes. Note that the presence of Cr₂O₃ in the B=[111] SADP does not correlate with the location of diffuse intensities.](image_url)
TEM examination of diffuse scattering in CP nickel, produced by FIB liftout, is shown in Figure 4.7. No rings from nanocrystalline NiO are present. A final cleaning of 2 kV was used on the FIB lamella to minimize curtaining and gallium implantation. The region used to produce the SADP is indicated in Figure 4.7b, and presented minimal damage due to FIB preparation. This examination shows that the presence of 1/3\{422\} diffuse scattering is unlikely to be the result of surface oxides or sample preparation artifacts, as NiO rings were not observed.

Figure 4.7: (a) BFTEM of the FIB liftout of commercially pure nickel, indicating where the diffraction was taken from. (b) B=\{111\} selected area diffraction pattern from the location indicated in (a), where the 1/3\{422\} diffuse intensities are clearly present.

4.3 Diffuse Scattering in Related Structures

Given the strong evidence that diffuse scattering in TEM SADP’s of Alloy 690 and CP nickel is not due to multiple diffraction artifacts, this study was extended to additional cubic systems. Several B=\{111\} SADPs from (a) Alloy 600, (b) Co-28.5Cr-6Mo, (c) IN945X, (d) CdTe,\(^{101}\) (e) Ni-55Cr, and (f) Ni-33Cr are shown in Figure 4.8. It is apparent that the 1/3\{422\} diffuse scattering occurs in all of these SADPs, suggesting that they are not the result of SRO. Note, that the additional sharp reflections in the IN945X alloy are due to the presence of \(\gamma’\)-Ni\(_3\)Al in the microstructure.
The presence of 1/3{422} diffuse scattering in B=[111] SADPs for (a) Alloy 600, (b) Co-28.5Cr-6Mo, (c) IN945X, (d) CdTe, (e) Ni-55Cr, and (f) Ni-33Cr.

The presence of 1/3{422} diffuse intensities in the <111> patterns in multiple systems indicates that SRO is unlikely the cause. Furthermore, the presence of nanocrystalline oxides, and the double diffraction of oxide rings, is unlikely the cause of these intensities. First, the presence of complete rings from the nanocrystalline oxide would likely be visible in addition to the intensities at locations where these rings intersect. Second, Alloy 690, Ni-Cr, Co-38.5Cr-6Mo and CdTe would form a variety of oxides, and are unlikely to result in additional intensities at these locations.

4.4 Higher-Order Laue Zone (HOLZ) Diffraction

Several higher-order zone axes containing {422} and {311} reflections were examined in an effort to see if the diffuse scattering persisted at the same locations, in hopes of further understanding the presence of the 1/3{422} and 1/2{311} intensities. In the event that the additional scattering is attributable to SRO, or an additional structure within the matrix, these intensities should fall at the same positions in zone axes containing {422} and {311} reflections (i.e. the 1/3{422} and 1/2{311} locations).
Conversely, if these intensities are the result of higher-order Laue zone diffraction due to relrod spiking, their locations should be easily accounted for, and are a function of foil normal. The additional zones examined include the [113], [114], [116], [012], [013] and [123], all of which contain either \{422\} or \{311\} reflections, and are shown on the stereographic triangle shown in Figure 4.9.

![Stereographic triangle showing the zone axes containing {422} and {311} reflections that were examined.](image)

**Figure 4.9:** Stereographic triangle showing the zone axes containing \{422\} and \{311\} reflections that were examined.

### 4.4.1 HOLZ Diffraction Simulations

A series of higher-order zone axis patterns were taken in a solution annealed and aged condition of Alloy 690 (SA-475-3k), and are presented in Figure 4.10 through Figure 4.17. For all zone axes examined, the presence of additional intensities correlates well with the predicted locations for HOLZ intensities, as shown in the JEMS simulations provided. Additionally, these intensities do not always fall at the 1/3\{422\} and 1/2\{311\} locations, as is the case for B=[111] and B=[112] zone axes. One such example is the B=[123] (Figure 4.15) zone axis, where the g=200 HOLZ reflection occurs parallel to the g = 5\overline{T}. These results indicate that the presence of additional diffuse scattering in TEM SADPs is not the result of SRO, but is consistent with the presence of higher-order Laue zone diffraction.
Figure 4.10: Comparison of experimental and simulated selected area diffraction patterns, assuming a \([111]\) foil normal, for the \(B=\[111\]\). Reflections in yellow (circle), blue (filled square), and red (open square) correspond to ZOLZ, +HOLZ, and –HOLZ, respectively.

Figure 4.11: Comparison of experimental and simulated selected area diffraction patterns, assuming a \([111]\) foil normal, for the \(B=\[112\]\). Reflections in yellow (circle), blue (filled square), and red (open square) correspond to ZOLZ, +HOLZ, and –HOLZ, respectively.
Figure 4.12: Comparison of experimental and simulated selected area diffraction patterns, assuming a [111] foil normal, for the B=[113]. Reflections in yellow (circle), blue (filled square), and red (open square) correspond to ZOLZ, +HOLZ, and –HOLZ, respectively.

Figure 4.13: Comparison of experimental and simulated selected area diffraction patterns, assuming a [111] foil normal, for the B=[114]. Reflections in yellow (circle), blue (filled square), and red (open square) correspond to ZOLZ, +HOLZ, and –HOLZ, respectively.
Figure 4.14: Comparison of experimental and simulated selected area diffraction patterns, assuming a [111] foil normal, for the $B=[116]$. Reflections in yellow (circle), blue (filled square), and red (open square) correspond to $ZOLZ$, $+HOLZ$, and $-HOLZ$, respectively.

Figure 4.15: Comparison of experimental and simulated selected area diffraction patterns, assuming a [111] foil normal, for the $B=[123]$. Reflections in yellow (circle), blue (filled square), and red (open square) correspond to $ZOLZ$, $+HOLZ$, and $-HOLZ$, respectively.
Figure 4.16: Comparison of experimental and simulated selected area diffraction patterns, assuming a [111] foil normal, for the B=[012]. Reflections in yellow (circle), blue (filled square), and red (open square) correspond to ZOLZ, +HOLZ, and −HOLZ, respectively.

Figure 4.17: Comparison of experimental and simulated selected area diffraction patterns, assuming a [111] foil normal, for the B=[013]. Reflections in yellow (circle), blue (filled square), and red (open square) correspond to ZOLZ, +HOLZ, and −HOLZ, respectively.
4.4.2 Tilting Experiment – Tracking the \{111\} Reflections

A systematic tilting experiment was conducted on Co-28.5Cr-6Mo and Alloy 690 in an effort to confirm that the diffuse intensities in the B=[111] SADPs are the result of the HOLZ effects previously mentioned. The initial experiment was conducted on an annealed Co-28.5Cr-6Mo alloy and consisted of tilting from a B=[112] zone axis along the \{220\} band towards the B=[111], and tracking the location and intensity of the \{111\} reflections. This is shown schematically in Figure 4.18, with a series of SADP’s and Kikuchi bands overlaid on a [111] electron backscatter diffraction (EBSD) Kikuchi map.

![Figure 4.18: Representation of the tilting experiment showing the <112> SADPs relative to the <111> (taken from Co-28.5Cr-6Mo) and overlaid on an EBSD Kikuchi map. The \{111\} reflections were tracked from the B=[112] into the B=[111] pattern.](image)

In an effort to provide more quantitative intensity information, microdensitometer measurements of the \{111\} reflections were made while keeping the beam parallel to the 220 planes. This experiment was reproduced on Alloy 690 in the thermally treated condition (TT-00-00) using convergent beam techniques to ensure symmetry about the \{220\} band, and therefore the relative intensities of the \{111\} reflections. This consisted of taking a CBED pattern at each incremental tilt, and utilizing the HOLZ lines to perform very fine alignments relative to the \{220\} band. A summary of this experiment is shown in Figure 4.19 and includes a BFTEM image taken parallel to the B=[112] from the region of interest, a B=[112] SADP with Kikuchi bands overlaid, a convergent beam pattern utilizing a short camera length, and a SADP/CBED pair taken at each incremental tilt.
Summary of results for the systematic tilting experiment, tilting from the \( B=[112] \) to the \( B=[111] \) zone axis while tracking the \{111\} reflections in the thermally treated condition of Alloy 690 (TT-00-00).

Microdensitometer measurements of the \{111\} intensities were taken at each incremental tilt, and are shown in Figure 4.20. Both the beam and camera conditions for each SADP were kept constant in order to minimize errors. The intensity measurements were taken using a line histogram across the two \{111\} reflections, and averaging their maximum intensities, as shown in Figure 4.20. For the data points highlighted in red, the intensity of the \{111\} reflections saturated the camera. These values were estimated by peak fitting the histogram using a Lorentzian peak fit, with an R-value of 0.95 or greater. As expected, the intensities of the \{111\} reflections are reduced when tilting away from the \( B=[112] \) zone axis, yet does not completely disappear in the \( B=[111] \) SADP. This observation indicates that the \{111\} intensities never completely disappear when tilting from the \( B=[112] \) to the \( B=[111] \), and is consistent with the additional diffuse scattering in \( B=[111] \) SADPs being the result of higher-order Laue zone diffraction as discussed previously.
Figure 4.20: (a) Location of the line histogram used to determine the \{111\} intensities, in this case for the B=[112]. (b) Summary of average intensities of the g=\(1\over 3\{422\}\) and g=\(\overline{1}\{111\}\) reflections as a function of tilt from the [112] to the [111] zone axis. Data points in red were determined using a Lorentzian curve fit with an R-value of 0.95 or greater.

### 4.4.3 Changes in Diffuse Intensities With Thickness

An investigation into the changes in diffuse intensities with foil thickness was performed on the TT-00-00 condition of Alloy 690. Foil thickness measurements were conducted at two locations, using the Kossel-Möllenstedt method.\(^{42}\) Additionally, SADPs were taken at these locations, as indicated in the BFTEM image in Figure 4.21a. These measurements indicated a foil thickness of \(\sim 105\) and \(\sim 374\) nm at locations 1 and 2, respectively. At location 1, the SADP (Figure 4.21b) clearly shows the presence of \(1/3\{422\}\) diffuse intensities. However, at location 2, the additional intensities appear weaker (Figure 4.21c). For the SADP taken at location 2, the pattern was taken slightly off zone in order to isolate the effects of HOLZ diffraction versus Kikuchi band intersections.
Figure 4.21: TEM examination of the effect of foil thickness on $1/3\{422\}$ diffuse scattering in the TT-00-00 condition of Alloy 690. (a) BFTEM from region of interest, showing the two locations where the thickness was measured, along with (b-c) the selected area diffraction patterns corresponding to these two locations. In (c) the SADP was specifically taken slightly off-axis, to ensure Kikuchi band intersections were not contributing to the $1/3\{422\}$ intensities.

4.5 Theoretical Simulations - Rocking Curve Analysis

To validate the experimental observations, a kinematical approach to modeling diffracting intensity as a function of deviation parameter was utilized. This theory assumes that the intensity due to multiple diffraction events (i.e. dynamical scattering) does not contribute to the observed intensity. This method calculates the diffracting intensity from a given plane as a function of the deviation parameter, or distance from the Ewald sphere, utilizing the following equation.\(^{97}\)
Equation 4.1

\[ I(s_g) = \left( \frac{\pi}{\xi_g} \right)^2 \sin^2 \left( \frac{\pi ts_g}{s_g^2} \right) \]

where \( \xi_g \) is the extinction distance, \( s_g \) is the deviation parameter of the given reflection, and \( t \) is the foil thickness. A rocking curve analysis was conducted for the \( B = [111] \) using the \( g = 11 \overline{1} \) reflection, using a 200 kV incident beam and assuming a pure nickel sample of 100 nm thickness. This condition was chosen to closely mimic the experimentally observed conditions in which diffuse scattering occurs. The calculated intensity for the \{111\} reflections with a deviation parameter of 0.1650 Å\(^{-1}\) is negligible, as indicated in Figure 4.22a. A second analysis was conducted using for the \( B = [113] \) using the \( g = \overline{1} \overline{1} \) reflection, with an accelerating voltage of 200 kV and assuming pure nickel with a 10 nm thickness. This condition was chosen to minimize required spiking distance (or deviation from Bragg) from the FOLZ to the Ewald sphere (\( s_g \)). Again, the relative intensity of the \( g = \overline{1} \overline{1} \) due to relrod spiking is negligible.

Figure 4.22: Rocking curve calculations for a nickel sample of (a) 100 nm thickness, oriented down the \( B = [111] \) using the \( g = 11 \overline{1} \), and (b) 10 nm thickness, oriented down the \( B = [113] \) using the \( g = \overline{1} \overline{1} \). The deviation parameter (distance from the HOLZ to the Ewald sphere) for the diffracting \( g \) in these two cases is 0.1650 Å\(^{-1}\) and 0.0990 Å\(^{-1}\), respectively.

The mathematical simulations for diffracting intensity presented above suggest that a kinematical approach does not fully predict the effects of HOLZ diffraction on the assumption that it stems from the thin foil effect. This kinematical theory assumes that the scattering intensity due to multiple diffraction events (i.e. dynamical scattering) is minimal, and does not contribute to the observed intensity. While this
assumption may be valid for very thin crystals, the extension to conventionally thick foils is not always accurate. Furthermore, this approach purely assumes these intensities are the result of the thin foil effect, and do not account for the possibility of atomic steps on the sample surface or dynamical diffraction effects contributing to the diffracting intensity.

4.6 Summary

The diffuse $1/3\{422\}$ intensities reported in $<111>$ selected area electron diffraction patterns (SADPs) in several FCC materials are consistent with scattering from higher-order Laue zones (HOLZ) rather than short range order (SRO), as has been proposed for alloys such as Alloy 690 (Ni-Cr-Fe). This diffuse scattering has been observed in a multitude of thermomechanical processing and annealing conditions of Alloy 690. Additionally, similar scattering has been shown to occur in the Ni-33Cr and Ni-55Cr binaries, commercially pure (CP) nickel, a Co-28.5Cr-6Mo alloy, IN945X, and CdTe.

Several diffraction artifacts, such as thermal diffuse scattering (TDS), surface oxides, sample preparation effects, and Kikuchi band intersections have been ruled out. Cryostage TEM at liquid nitrogen temperatures resulted in no change in diffuse scattering. A careful tilting experiment successfully isolated the effects of Kikuchi band intersections from diffuse scattering. A FIB liftout of CP nickel provided no evidence that sample preparation plays a role, nor that atomic ordering contributes to these intensities. Contrary to several hypotheses proposed in the literature, there was no observation of stacking faults or additional phases contributing to diffuse scattering.

All evidence in this study indicates the manifestation of $1/3\{422\}$ (and other) diffuse scattering events is consistent with higher-order Laue zone (HOLZ) diffraction, due to reciprocal lattice (rlrod) spiking from the HOLZ layer above and below the zero-order Laue zone (ZOLZ). A series of higher-order zone axis patterns, including the [111], [112], [113], [114], [116], [012], [013] and [123] zones, have been successfully indexed as presenting additional intensities consistent with higher-order Laue zone diffraction. A systematic tilting experiment has tracked the intensity of the \{111\} reflections from the B=[112] to the B=[111], further confirming a HOLZ diffraction and suggests that the presence of surface oxides does not play a role. Systematic measurements of foil thickness and the effects on diffuse scattering have shown that these intensities dissipate with sufficient thickness, albeit at thicknesses much greater than expected.

Theoretical simulations of the intensity HOLZ diffraction as a function of distance from the Ewald sphere (i.e. rocking curve) do not correlate with the empirical results in this study. This is suspected to be due to the kinematical nature of the rocking curve calculation, which does not fully account for the dynamical diffraction effects which occur in conventionally thick foils. Additionally, this
theoretical calculation does not account for various microscope parameters such as the size of the selected area aperture used or the convergence angle of the beam, both of which can affect the resultant diffracting intensities. Furthermore, these calculations do not account for the presence of atomic steps on the sample surface, which may possibly play a role in the diffuse scattering observed and have not been effectively ruled out in this study.
CHAPTER 5  PHASE STABILITY IN THE NI-CR SYSTEM

This chapter will discuss the phase stability of \( \gamma'\)-Ni\(_2\)Cr and \( \alpha\)-Cr in the Ni-Cr binary. The as-cast microstructure of a Ni-55Cr alloy will be presented in Section 5.1. The microstructural evolution and precipitation of \( \alpha\)-Cr will be discussed in Section 5.2. The precipitation behavior of \( \gamma'\)-Ni\(_2\)Cr will be discussed in Section 5.3. In Section 5.4, the effects of annealing at 900 °C followed by 500 °C will be discussed. Finally, a consideration of the Gibbs free energy of these phases and the thermodynamic stability will be discussed in Section 5.5.

5.1  As-Cast Ni-55Cr

The as-cast microstructure of the Ni-55Cr (wt. %) alloy, being slightly hypereutectic with respect to nickel, results in the formation of a Cr-rich dendritic structure with a partially divorced eutectic (Figure 5.1a). Cooling below \( \sim 1100 °C \) (below the shoulder of the \( \alpha\)-Cr solvus) results in the precipitation of a Widmanstätten \( \gamma\)-Ni structure within the Cr-rich dendrites, as observed in Figure 5.1b, due to the supersaturation of nickel within the chromium dendrite. It should be noted that the bright contrast of the Cr-rich regions in the SEM micrographs (Figure 5.1) is a result of the sample etching.

![SEM micrographs of the as-cast microstructure (etched), showing (a) Cr-rich dendrites with a partially divorced eutectic, where the majority phase is \( \gamma\)-Ni as expected from the phase diagram. (b) Upon cooling, the \( \alpha\)-Cr dendrites decompose into a \( \alpha + \gamma \) Widmanstätten structure.](image)

Figure 5.1:
SEM-EDS analysis of the as-cast microstructure shows dendritic and interdendritic compositions that fall well in line with the phase diagram solvi, which predicts a 66-68 wt. % chromium dendritic structure, and a ~47 wt. % chromium interdendritic structure. The SEM-EDS results (Figure 5.2) indicate an approximately 65 wt.% chromium dendritic composition, and a 48 wt.% chromium composition for the interdendritic γ-Ni solid solution, in good agreement with the binary phase diagram.

![SEM micrograph](image1)

**Figure 5.2:** (a) SEM micrograph of the as-cast microstructure, indicating the location of the (b) SEM-EDS line scan, i.e. across a primary dendrite. The average compositions of the dendritic and interdendritic regions are 65 and 48 wt. % Cr, respectively.

TEM analysis of the as-cast microstructure confirms the SEM findings, as shown in Figure 5.3. The Cr-rich dendritic structure has precipitated a fine γ-Ni Widmanstätten structure on cooling, as shown in the STEM-BF and STEM-HAADF micrographs in Figure 5.3(a-b). Note that the dendrites appear brighter in the STEM-HAADF micrograph due to thickness effects. The etchant used for sample preparation preferentially attacked the γ-Ni phase, resulting in the α-Cr dendrites being thicker and therefore providing more signal to the detector. Selected area diffraction patterns (SADPs) from the dendrite (Figure 5.3c) confirm a predominantly α-Cr structure, with fine, diffuse reflections stemming from the nanoscale γ-Ni precipitates. While a dedicated crystallographic analysis of this orientation relationship (O.R.) was not performed, it is consistent with a Kurdjumov-Sachs (K-S) type O.R. The interdendritic region is primarily γ-Ni, confirmed by the SADP shown in Figure 5.3d, and strain free. Additionally, the STEM-EDS analysis of this region (Figure 5.4) is consistent with the diffraction results.
Figure 5.3: TEM analysis of the as-cast microstructure. (a-b) STEM-BF and STEM-HAADF pair of an α-Cr dendrite with a γ-Ni Widmanstätten interior structure, and a predominantly γ-Ni interdendritic region. (c) SADP taken from the α-Cr dendrite, with fine reflections stemming from the nanoscale γ-Ni. (d) SADP taken from the interdendritic region confirming the γ-Ni structure.
Figure 5.4: STEM-EDS analysis of the dendritic/interdendritic regions, showing the presence of fine γ-Ni within the original α-Cr dendrite. (a) STEM-HAADF micrograph with the bright contrast stemming from Ni-rich precipitates, (b) nickel map and (c) chromium map.

The solidification behavior of the as-cast Ni-55Cr alloy is schematically shown in Figure 5.5. The initial formation of the Cr-rich dendrites occurs at approximately 1375 °C (neglecting the effects of undercooling), presumably resulting in a dendrite coring effect, with a composition range of 66-68 wt. % chromium. As mentioned previously, the ensuing eutectic solidification results in a partially divorced eutectic structure, producing mostly continuous γ-Ni with small pockets of α-Cr. Finally, upon adequate cooling below ~1100 °C, the α-Cr structure precipitates the fine γ-Ni Widmanstätten structure due to the supersaturation of nickel at lower temperatures.
Figure 5.5: Schematics detailing the solidification and precipitation sequence for the as-cast Ni-55Cr alloy, showing (a) the initial dendritic formation with minor dendrite coring, (b) the initial formation of eutectic α-Cr on the primary dendrite, (c) the interdendritic solidification of γ-Ni and α-Cr, and finally (d) the precipitation of Widmanstätten γ-Ni in α-Cr at temperatures below ~1100 °C.

### 5.2 Annealing at 900 °C – 4 h

Annealing the as-cast microstructure at 900 °C for 4 h resulted in the interdendritic precipitation of α-Cr, and the coarsening of the Widmanstätten structure, as shown in Figure 5.6(a-b). The interdendritic region exhibits a γ+α microstructure, with α-Cr occurring as both a continuous and discontinuous precipitate. SEM-EDS analysis indicates an interdendritic composition of ~45 wt.% chromium for γ-Ni, and 58 wt. % chromium for α-Cr. Given that the phase diagram would predict a 38
wt. % chromium for γ-Ni and 96 wt. % chromium for α-Cr, this error is attributed to the inadequate spatial resolution common at the 20 kV accelerating voltage used.

Figure 5.6: SEM analysis of Ni-55Cr after annealing at 900 °C for 4 h, showing (a-b) the precipitation of interdendritic α-Cr and the coarsening of the γ-Ni Widmanstätten structure. (c-d) SEM-EDS analysis of the interdendritic lamellar structure.
TEM analysis confirmed the SEM findings above, as presented in Figure 5.7. The interdendritic regions of γ-Ni have transformed into an α+γ microstructure, with two primary morphologies of α-Cr precipitation. A centered dark-field image (CDF) of the interdendritic lamellar structure is shown in Figure 5.6a, taken near B=[011] using g=200 of γ-Ni. A similar examination of the eutectic α-Cr and coarsened γ-Ni Widmanstätten is shown in Figure 5.6b, taken near B=[113] using $g = 1\overline{1}0$ of α-Cr.

![TEM images of Ni-55Cr alloy](image)

**Figure 5.7:** TEM analysis of the Ni-55Cr alloy after annealing at 900 °C for 4 h. (a) Centered dark-field (CDF) image of the interdendritic γ-Ni, taken near B=[011] using g=200 of γ-Ni. (b) CDF of a eutectic α–Cr particle, with a coarsened γ-Ni Widmanstätten structure in the interior. Taken near B=[113] using $g = 1\overline{1}0$ of α-Cr.

The evolution of the as-cast microstructure after annealing at 900 °C for 4 h is presented schematically in Figure 5.8. Annealing results in two primary transformations. First, the γ-Ni Widmanstätten structure within the Cr-rich dendrite coarsens to reduce the overall surface area of the fine structure. Second, the precipitation of α-Cr within the γ-Ni interdendritic regions occurs in two morphologies, as a continuous and discontinuous precipitate. Further discussion of this morphology is presented in Section 5.2.1.
Figure 5.8: Schematic of the precipitation behavior observed after annealing at 900 °C for 4 h. The interdendritic precipitation of α-Cr occurs in two morphologies, and the γ-Ni Widmanstätten structure coarsens to reduce the surface area of the fine structure. Compositions are in wt. % chromium and based on the phase diagram.

5.2.1 Crystallography of α-Cr Precipitation

TEM diffraction analysis of the interdendritic precipitation of α-Cr was performed, and a representative STEM-BF micrograph of the regions of interest is presented in Figure 5.9a. An orientation relationship (O.R.) analysis of α/γ at locations 1 and 2 are presented in Figure 5.9(b-c). In the case of discontinuous precipitation of α-Cr, it was determined that this formed with a Nishiyama-Wasserman (N-W) type O.R. Conversely, the continuous precipitation of α-Cr (location 2) occurs in a Kurdjumov-Sachs (K-S) type O.R. These orientation relationships are defined as:

\[
\begin{align*}
\text{Kurdjumov – Sachs} & : & \langle 111 \rangle_{\gamma} & \parallel \langle 011 \rangle_{\alpha} \\
& & \langle 10 \bar{1} \rangle_{\gamma} & \parallel \langle 11 \bar{1} \rangle_{\alpha} \\
\text{Nishiyama – Wasserman} & : & \langle 0 \bar{1} 1 \rangle_{\gamma} & \parallel \langle 001 \rangle_{\alpha} \\
& & \langle \bar{T}11 \rangle_{\gamma} & \parallel \langle T10 \rangle_{\alpha}
\end{align*}
\]
Figure 5.9: (a) STEM-BF micrograph of a representative region of the 900 °C – 4 h alloy, showing two primary morphologies of α-Cr. (b) The discontinuous precipitation of α-Cr (location 1) exhibits a Nishiyama-Wasserman (N-W) type orientation relationship, while (c) the continuous precipitation of α-Cr (location 2) is a Kurdjumov-Sachs (K-S) type orientation relationship.
5.3 Annealing at 500 °C – 1,000 h

Annealing the as-cast microstructure at 500 °C for 1,000 hours resulted in little change within the interdendritic regions, but considerable coarsening of the γ-Ni Widmanstätten structure, as seen in Figure 5.10. In addition to this coarsening, the dendritic/interdendritic interfacial regions underwent considerable coarsening thereby producing relatively large pockets of α-Cr and γ-Ni + γ′-Ni₂Cr, as seen in Figure 5.10b. This occurs at the dendritic/interdendritic interface for two reasons. First, this boundary provides a heterogeneous nucleation site, requiring less energy for nucleation. Second, the interdendritic region is supersaturated in chromium, and rejects this solute at the dendritic/interdendritic interface.

![SEM micrograph of Ni-55Cr alloy annealed at 500 °C for 1,000 h, showing the evolution of α-Cr (dark) and γ-Ni + γ′-Ni₂Cr (light) precipitation at the dendrite/interdendritic interface.](image)

Figure 5.10: SEM micrographs (BSE) of the Ni-55Cr alloy annealed at 500 °C for 1,000 h, showing the evolution of α-Cr (dark) and γ-Ni + γ′-Ni₂Cr (light) precipitation at the dendrite/interdendritic interface.

SEM-EDS analysis of the precipitation at this interface (Figure 5.11) provides further insight into the local composition and precipitation events occurring during the 500 °C anneal. In this case, the SEM-BSE micrograph shows a region of eutectic α-Cr which has transformed into pockets of α-Cr and γ-Ni + γ′-Ni₂Cr. These pockets of transformed γ-Ni have rejected chromium solute to the α-Cr particles, and enables the precipitation of γ′-Ni₂Cr within the nickel rich γ-Ni.
Figure 5.11: SEM-EDS of the Ni-55Cr alloy, taken across a region of eutectic α-Cr, after annealing at 500 °C for 1,000 hours, showing the distribution of α-Cr and γ-Ni. The light regions consist of γ-Ni + γ'-Ni$_2$Cr and are enriched in nickel relative to the interdendritic γ-Ni which appears to remain untransformed.

A region similar to that shown above was chosen for S/TEM examination, and is presented in Figure 5.12a. Locations 1 and 2, as indicated in the STEM micrograph, are a single continuous grain of γ-Ni, determined by translating the beam (in diffraction) across their interface. However, the presence of γ'-Ni$_2$Cr was only observed within the Ni-rich pockets of γ-Ni, as shown in the SADP in Figure 5.12b. The SADP taken from location 2 (Figure 5.12c) confirms a consistent crystallographic orientation (continuous grain) between the two locations, yet the lack of γ'-Ni$_2$Cr precipitation. Finally, the regions of dark contrast in the STEM-HAADF (location 3) are shown to be α-Cr, with the diffraction pattern shown in Figure 5.12d being consistent with the BCC structure having a lattice parameter of 2.87 Å.
Figure 5.12: (a) STEM-HAADF micrograph of the Ni-55Cr alloy annealed at 900 °C for 4 h, showing an interdendritic α-Cr particle which has transformed into pockets of γ-Ni and α-Cr, with the presence of γ'-Ni$_2$Cr at location 1. (b) SADP taken from location 1, confirming the presence of γ'. (c) SADP taken from location two, which is a continuous grain with location 1, showing no presence of γ'. (d) SADP taken from location 3, consistent with the BCC α-Cr structure (a$_0$ ≈ 2.87 Å).
A STEM-EDS analysis of the regions of $\gamma$ and $\gamma+\gamma'$, as shown in Figure 5.13(a-b), exhibits a composition gradient between the dendritic and interdendritic regions of $\gamma$-Ni. The interdendritic composition of $\gamma$-Ni is approximately 55 wt. % chromium. Conversely, the dendritic pockets of $\gamma$-Ni are ~60 wt.% nickel, enriched due to the rejection of chromium from the interdendritic nickel when annealed at 500 °C for 1,000 h. The interdendritic $\gamma$-Ni at the dendritic/interdendritic interface can reject chromium to the $\alpha$-Cr dendrite, and during this rejection the formation of $\gamma'$-$\text{Ni}_2\text{Cr}$ occurs, resulting in pockets of $\alpha$-Cr and $\gamma'$-$\text{Ni}_2\text{Cr} + \gamma$-Ni.

Figure 5.13: (a) STEM-HAADF micrograph of the Ni-55Cr alloy annealed at 900 °C for 4 h, showing a decomposed eutectic $\alpha$-Cr particle, indicating the region of interest chosen for the (b) STEM-EDS line scan. Also included are STEM-EDS maps for (c) nickel and (d) chromium.
A schematic representation of the microstructural evolution after annealing at 500 °C for 1,000 h is shown in Figure 5.14, and will be discussed here. During annealing, the interdendritic \( \gamma \)-Ni rejects chromium to the dendrite, resulting in pockets of \( \alpha \)-Cr and \( \gamma \)-Ni + \( \gamma' \)-Ni\(_2\)Cr at the perimeter of the \( \alpha \)-Cr dendrite. Additionally, a coarsening of the interior Widmanstätten \( \gamma \)-Ni structure is observed. Further consideration of this behavior, and examination of the Gibbs free energy of this process, will be discussed in Section 5.5.

Figure 5.14: Schematic of the microstructural evolution after annealing the Ni-55Cr alloy at 500 °C for 1,000 h. The dotted grey line indicates a continuous grain between \( \gamma + \gamma' \) and \( \gamma \) with varying nickel concentration.

5.4 Annealing at 900 °C – 4 h + 500 °C – 1,000 h

The microstructural evolution after annealing at 900 °C for 4 h followed by 500 °C for 1,000 h can be seen in Figure 5.15. The presence of interdendritic \( \alpha \)-Cr, both as a discontinuous and continuous precipitate, is ubiquitous throughout the microstructure and occurs during the 900 °C – 4 h anneal. Additionally, a coarsening of the \( \gamma \)-Ni Widmanstätten structure occurs. Subsequent annealing at 500 °C for 1,000 h results in a slight coarsening of these structures, but no precipitation of \( \gamma' \)-Ni\(_2\)Cr is observed.
Figure 5.15: (a-b) SEM BSE micrographs of Ni-55Cr annealed at 900 °C for 4 h, followed by 500 °C for 1,000 h, showing the coarsening of the γ-Ni Widmanstätten structure, and the interdendritic precipitation of α-Cr. (c-d) SEM-EDS line scan across an interdendritic/dendritic region.

TEM examination of the material in this latter condition confirmed the SEM findings, and is presented in Figure 5.16. Again, the initial anneal at 900 °C for 4 h resulted in α-Cr precipitation within the interdendritic regions, and no precipitation at the dendritic/interdendritic interfaces. Additionally, as shown in the TEM SADP (Figure 5.16b), the interdendritic γ-Ni contains no γ'-Ni₂Cr precipitation.
Figure 5.16: (a) STEM-BF micrograph of Ni-55Cr annealed at 900 °C for 4 h, followed by 500 °C for 1,000 h, showing the interface between a transformed Cr-rich dendrite and the transformed interdendritic α+γ region. (b) TEM SADP taken from the γ-Ni within the interdendritic region, showing no presence of γ'-Ni$_2$Cr.

5.5 Gibbs Free Energy and Thermodynamic Equilibrium

A consideration of schematic Gibbs free energy curves is useful for explaining the relative phase stabilities during the various stages of annealing in the Ni-55Cr binary. Schematic Gibbs free energy curves for the Ni-Cr binary at 500 °C are shown in Figure 5.17, assuming the γ'-Ni$_2$Cr precipitate to be stable. The as-cast microstructure of the Ni-55Cr alloy should result in a eutectic γ-Ni composition of ~47 wt.% chromium. Subsequent annealing of this microstructure at 500 °C should result in the dissolution of γ-Ni, and result in a two-phase microstructure of γ'-Ni$_2$Cr + α-Cr, as indicated by the schematic Gibbs free energy diagram below.

Annealing of the as-cast Ni-55Cr alloy at 900 °C – 4 h would result in a two-phase interdendritic microstructure of γ-Ni and α-Cr, with a γ-Ni composition of ~38 wt.% chromium. Subsequent annealing of this alloy at 500 °C for 1,000 hours should still result in the precipitation of γ'-Ni$_2$Cr at the expense of γ-Ni, again resulting in a two-phase microstructure of γ'-Ni$_2$Cr and α-Cr. While this is what would be expected based on the equilibrium Ni-Cr binary phase diagram and the schematic Gibbs free energy curves in Figure 5.17, this is not experimentally observed. It appears that the 900 °C – 4 h anneal, and the resultant α-Cr precipitation within the interdendritic, reduces the driving force for γ'-Ni$_2$Cr precipitation during subsequent annealing at 500 °C.
The microstructural evaluation of the Ni-55Cr condition annealed at 900 °C – 4 h followed by 500 °C – 1,000 h indicates an inconsistency with the Gibbs free energy diagram shown in Figure 5.17. The γ+α structure, precipitating during the 900 °C anneal, should readily transform into a γ’+α microstructure during subsequent annealing at 500 °C. This should occur at any α/γ interface, and the γ-Ni should be consumed as a result. However, the lack of this precipitation suggests that γ’-Ni$_2$Cr is a metastable precipitate, contrary to what the phase diagram suggests. Schematic Gibbs free energy curves for the Ni-Cr binary at 500 °C, assuming γ’-Ni$_2$Cr to be metastable, are shown in Figure 5.18. In this diagram, it is clear that the system can lower its free energy by precipitating γ’-Ni$_2$Cr, and that this structure should eventually transform into a γ-Ni + α-Cr structure at equilibrium. While the mechanism of this behavior is not entirely clear, it appears that the presence of α-Cr after annealing at 900 °C precludes the precipitation of γ’-Ni$_2$Cr during subsequent annealing at 500 °C.
5.6 Summary

The as-cast microstructure of the Ni-55Cr binary exhibits a Cr-rich dendritic structure surrounded by a partially divorced eutectic. During cooling, the α-Cr dendritic precipitates a Widmanstätten γ-Ni structure due to the supersaturation of nickel in α-Cr at lower temperatures. Annealing this microstructure at 500 °C for 1,000 hours results in the formation of γ-Ni and α-Cr pockets at the dendritic/interdendritic interface. The γ-Ni pockets also contain fine γ’-Ni$_2$Cr precipitates, on the order of 5-10 nm. The 900 °C – 4 h anneal results in the precipitation of α-Cr within the interdendritic regions, both by continuous and discontinuous precipitation. Subsequent annealing of this microstructure at 500 °C for 1,000 hours does not result in the precipitation of γ’-Ni$_2$Cr within the microstructure, and suggests that the γ’-Ni$_2$Cr precipitate is metastable in contradiction to what the phase diagram suggests. The precipitation of α-Cr during the 900 °C anneal reduces the driving force for the formation of metastable γ’-Ni$_2$Cr during annealing at 500 °C.

Examination of schematic Gibbs free energy curves at 500 °C, assuming γ’-Ni$_2$Cr to be stable, would suggest that γ’ should form regardless of previous annealing treatments, resulting in a γ’+α microstructure and the dissolution of γ-Ni. However, annealing at 900 °C followed by annealing at 500 °C did not result in γ’ formation. Again, while the mechanism of this behavior is not entirely clear, it appears that the presence of α-Cr after annealing at 900 °C precludes the precipitation of γ’-Ni$_2$Cr during subsequent annealing at 500 °C.
CHAPTER 6  STRESS CORROSION CRACKING OF ALLOY 690

This chapter will detail the microstructural evolution of Alloy 690 during thermomechanical processing and long-term aging, and its effects on stress corrosion crack initiation. The as-received microstructures will be discussed in Section 6.1, with a focus on the effects of cold-rolling in Section 6.2 and the $\text{M}_2\text{C}_6$ precipitation behavior in Section 6.3. The precipitation of $\alpha$-Cr during the long-term aging of cold-rolled and thermally treated plus cold-rolled microstructures, both as a continuous and discontinuous precipitate, will be discussed in Section 6.4. The observed SCC initiation behavior as a function of microstructure will be discussed in Section 6.5. Finally, a discussion of the effects of microstructural evolution on the SCC behavior of Alloy 690 will be discussed in Section 6.6.

6.1  The As-Received Microstructures of Alloy 690

The as-received condition of Alloy 690 consists of an average grain size between 100-200 µm, with a high density of annealing twins (CSL $\Sigma3$). In the solution-annealed (SA-00-00) condition (Figure 6.1a), the microstructure is primarily single-phase FCC with an occasional transgranular (TG) or intergranular (IG) titanium nitride (TiN) particle. The application of a 20% cold reduction (CR-00-00) results in a high dislocation density with a mixture of dislocation tangles, slip bands, and deformation twins. The general microstructure of the as-rolled condition is shown in Figure 6.1b. During this cold-rolling process, the coherent annealing twin boundaries are deformed, often losing coherency and effectively becoming more like high angle boundaries. These boundaries are referred to as previously coherent twin boundaries, or PCTBs, in the following text. The application of a thermal treatment of 700 °C for 17 h (TT-00-00) results in a high density of Cr-rich, $\text{M}_2\text{C}_6$-type carbides at high-angle boundaries (HABs) and incoherent twin boundaries, as shown in Figure 6.1c. These $\text{M}_2\text{C}_6$ carbides occur as both regular HAB precipitates, and as cellular precipitates. The combination of a 700 °C anneal for 17 h followed by a 20% cold reduction (TTCR-00-00) produces both the deformation substructure expected for the cold-rolled (CR) condition along with the pre-existing network of grain boundary carbides seen in the thermally-treated (TT) condition. The general microstructure of the TTCR-00-00 condition is shown in Figure 6.1d.
Figure 6.1: SEM micrographs of as-received Alloy 690 in the (a) solution annealed (SA-00-00), (b) cold-rolled (CR-00-00) (c) thermally treated (TT-00-00), and (d) thermally treated plus cold-rolled (TTCR-00-00) conditions.

As stated above, the 20% cold reduction results in a mix of slip bands and deformation twinning. Figure 6.2(a-b) is a BFTEM/WBDF pair of the general dislocation substructure, showing the presence of dislocation tangles. The presence of fine deformation twins, localized to regions of high strain and ranging from 10’s to 100’s of nm’s, are also common in the microstructure, as seen in the CDF image and SADP in Figure 6.2(c-d). This substructure is unsurprising given the high level of deformation for this low SFE (~20 mJ/m² for Ni-29Cr-10Fe) alloy, and has been observed by other investigators.71,87,88,103–105
Figure 6.2: TEM analysis of the deformation substructure of the CR-00-00 alloy. (a-b) BFTEM and weak-beam dark-field (WBDF) pair taken near $B=[011]$ using $g = 11\overline{1}$. (c-d) Centered dark-field (CDF) and selected area diffraction pattern (SADP) of nanoscale deformation twins, taken near $B=[011]$ using $g = 11\overline{1}$. 
In addition to the presence of planar slip, slip bands, and deformation twins, a degree of grain boundary damage occurs in the TTCR-00-00 alloy due to the presence of brittle $M_{23}C_6$ carbides. As shown in Figure 6.3, this damage is in the form of cracked carbides, in addition to the formation of occasional voids that are related to the slip incompatibility of this phase. This grain boundary damage has also been observed by Bruemmer et al., and has been suggested to result in crack tip blunting during SCC testing of Alloy 690.71

Figure 6.3: SEM micrographs of the grain boundary damage occurring due to a 20% cold reduction following the 700 °C – 17 h heat treatment (TTCR-00-00), showing (a) void formation and carbide cracking in a cellular region of $M_{23}C_6$, and (b) a cracked $M_{23}C_6$ particle at a high-angle boundary.

6.2 The Effects of Cold Rolling on Annealing Twins

As expected for a low stacking fault energy (SFE) FCC alloy, Alloy 690 contains a high density of annealing twins. To analyze the degree of misorientation away from the coherent CSL $\Sigma 3$ boundary character due to cold-rolling, and the influence on carbide precipitation, three techniques were used: (1) convergent beam electron diffraction (CBED) parallel to the $\{111\}$ habit plane, to observe the angular rotation across the boundary, (2) selected area diffraction (SAD) to characterize the nature of precipitation and, in several cases, show the splitting of the habit plane reflections, and (3) electron backscatter diffraction (EBSD) to quantify on a larger scale, the degree of deviation from the CSL $\Sigma 3$ boundary character.
TEM analysis of the SA-00-00 and SA-475-10k alloys is presented in Figure 6.4 for reference. As expected, there is no deviation from the CSL $\Sigma 3$ boundary character, nor the precipitation of $M_{23}C_6$ at the coherent twin boundaries upon aging. The precipitation of $M_{23}C_6$ at the incoherent face of annealing twins occurs upon aging at 475 °C (not presented here), and has been reported by other authors.\textsuperscript{106}

![Figure 6.4: TEM examination of an annealing twin boundary in the (a-b) SA-00-00 and (c-d) SA-475-10k alloys. (a+c) BFTEM image of the annealing twin taken near $B=[011]$ with three inset CBED patterns down the $B=[011]$. (b+d) SADP down the $B=[011]$, taken across the matrix/twin interface, showing the absence of any $M_{23}C_6$ reflections.]

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The CR-00-00 alloy exhibits a highly-strained microstructure, and the loss of coherency at annealing twin boundaries. For example, the BFTEM/CBED analysis presented in Figure 6.5a shows an annealing twin that was deformed during cold-rolling. The SADP taken across the twin/matrix boundary (Figure 6.5b) shows no reflections from M$_{23}$C$_6$ carbides, but a splitting of the habit plane reflections consistent with a loss of coherency of the twin boundary.

![Figure 6.5: TEM examination of the CR-00-00 alloy. (a) BFTEM of an annealing twin taken near B=[011] using $g=\overline{1}11$, with two inset CBED patterns down the B=[011], showing the distortion of the boundary. (b) B=[011] SADP, showing no presence of M$_{23}$C$_6$ but the splitting of the habit plane reflections, indicating a deviation from the ideal CSL $\Sigma 3$ boundary character.](image)

Analysis of the CR-475-10k condition (Figure 6.6) also shows evidence of the loss of coherency of these special boundaries. The BFTEM image presented in a shows a high degree of strain, indicated by the presence of fine deformation twins parallel to the twin boundary (Figure 6.6a). The three B=[011] CBED patterns (inset) show a significant deviation across this boundary. Not surprisingly, aging at 475 °C for 10,000 hours resulted in the precipitation of M$_{23}$C$_6$ at this PCTB due to the increased boundary energy, as shown by the presence of M$_{23}$C$_6$ carbide reflections in the B=[011] SADP (Figure 6.6b).
Figure 6.6: TEM examination of the CR-475-10k alloy. (a) BFTEM of an annealing twin taken near B=[011] using $g=\overline{11}1$, with three inset CBED patterns down the B=[011], showing the distortion of the boundary. (b) B=[011] SADP, showing the presence of $M_2\text{C}_6$ at the twin/matrix boundary.

EBSD analysis of the SA-00-00, SA-475-10k, CR-00-00, and CR-475-10k alloys provides a more holistic representation of the deformation occurring at these special boundaries, and the resultant change in boundary energy and precipitation behavior. A series of orientation imaging microscopy (OIM) maps, showing the parent/twin relationship in blue/red respectively, is shown in Figure 6.9. This analysis is accompanied with a series of CSL $\Sigma3$ deviation measurements of the boundary. These measurements are based on two adjacent pixels across the annealing twin boundary, and represent the minimum angular rotation from a CSL $\Sigma3$ boundary character. Note that for the cold-rolled specimens, Brandon’s criterion was relaxed in order to still identify annealing twins with significant deviation from the ideal boundary nature. The undeformed (SA-00-00 and SA-475-10k) conditions showed no deviation from the ideal boundary character, while the deformed (CR-00-00 and CR-475-10k) conditions showed a deviation of up to tens of degrees in some instances.
Figure 6.7: EBSD analysis of (a+e) SA-00-00, (b+f) CR-00-00, (c+g) SA-475-10k, and (d+h) CR-475-10k conditions of Alloy 690, showing the deviation from the ideal CSL Σ3 annealing twin character.
As discussed in Chapter 2, the deformation of both high-angle and special boundaries have been examined by a number of authors. As deformation proceeds, there is a mixture of lattice rotation and slip offsets (e.g. Figure 6.8). As shown in Figure 6.8a, the BFTEM/WBDF pair shows the accumulation of strain at the annealing twin boundary after cold-rolling, while in the SEM micrograph (Figure 6.8c), a slip offset is apparent due to the intersection of a planar slip band with the coherent twin boundary.

Figure 6.8: Annealing twin damage in the CR-00-00 alloy. (a-b) BFTEM/WBDF pair taken near B=[011] using g=111, showing the accumulation of strain at the PCTB. (b) SEM micrograph of a slip band interacting with a coherent twin boundary.
6.2.1 Deformation of Annealing Twins in CR vs. TTCR Alloys

As discussed in Section 6.1, the application of a 700 °C − 17 h thermal treatment followed by a 20% cold reduction results in a high degree of grain boundary deformation, in the form of cracked carbides and grain boundary voids. Due to the higher strain accumulation at the grain boundary in the TTCR alloy, the destruction of annealing twin boundaries is not as prevalent. A comparison of the deviation from the CSL Σ3 boundary character for the CR-00-00 and TTCR-00-00 alloys is shown in Figure 6.9.

Figure 6.9: EBSD analysis of the (a+c) CR-00-00 and (b+d) TTCR-00-00 alloys, showing an increased deviation of the annealing twin boundary in the CR-00-00 alloy compared to the TTCR-00-00 alloy.
6.3 Cellular Precipitation of M$_{23}$C$_6$ in Alloy 690

The cellular precipitation of M$_{23}$C$_6$-type carbides is a well-documented phenomenon in Ni-base superalloys such as Alloy 690.$^{71,79,107}$ In addition to the cellular precipitation of M$_{23}$C$_6$ during annealing, a concurrent recrystallization of the matrix and precipitation of lamellar α-Cr was observed in cold-rolled Alloy 690 aged at 550 °C, and appears morphologically similar to classical cellular precipitation colonies. To distinguish between these two, the latter will be referred to as recrystallization of γ-Ni and precipitation of α-Cr.

All instances of cellular precipitation in Alloy 690 examined in this study were determined to be Cr-rich M$_{23}$C$_6$-type carbides. This precipitation behavior was observed in thermally treated conditions, and conditions aged at or above 475 °C. The typical size and morphology for the TT-00-00 alloy is shown in Figure 6.10a. Confirmation of the M$_{23}$C$_6$-type structure by TEM diffraction is shown in Figure 6.10b, and confirms the cube-cube orientation relationship with the adjacent γ-Ni, with a lattice parameter of approximately 10.6 Å.

Figure 6.10: (a) SEM micrograph showing the cellular precipitation of M$_{23}$C$_6$ in the TT-00-00 alloy, and (b) BFTEM and SADP of a FIB liftout confirming the M$_{23}$C$_6$ structure.
STEM-EDS mapping (Figure 6.11) was performed to examine the elemental distribution in the cellular regions. In all cases, these carbides were identified as Cr-rich and are consistent with the ThermoCalc predictions presented in Section 6.4.3. In the examination of a FIB liftout, the carbon-rich signature at the sample surface in Figure 6.11d is the result of the platinum deposition used during the liftout process, which uses a carbon-containing precursor as a carrier gas.

![STEM-BF](image1)

![Ni](image2)

![Cr](image3)

![C](image4)

Figure 6.11: STEM-EDS mapping of cellular precipitation in the TT-00-00 alloy, showing these carbides to be Cr-rich M$_{23}$C$_6$-type.

The SA-350-10k and CR-350-10k alloys contained negligible grain boundary precipitation, with no cellular product, as shown in the SEM micrographs in Figure 6.12(a-b). This is not surprising given the limited kinetics at 350 °C, even after 10,000 hours of aging. Likewise, the TT-350-10k and TTCR-350-10k conditions showed no evidence of coarsening during annealing, either with regards to typical HAB precipitates or cellular regions (Figure 6.12c-d). Note that in Figure 6.12d, the bright transgranular particles are an artifact from the etching process.
Figure 6.12: SEM micrographs showing the effects of annealing Alloy 690 at 350 °C for 10,000 h. (a) SA-350-10k, (b) CR-350-10k, (c) TT-350-10k, and (d) TTCR-350-10k conditions.

Annealing at 475 °C for 10,000 h (Figure 6.13) resulted in an increase in both continuous and discontinuous precipitation of M$_{23}$C$_6$ at HABs and PCTBs in the SA and CR conditions, and is explained by the increased kinetics in this temperature regime compared with 350 °C. In the case of SA and CR conditions, the size of these cellular regions was small, and typically less than 1 μm in size. With regards to the TT and TTCR conditions (TT-475-10k and TTCR-475-10k), little change was observed regarding the size and distribution of these cellular regions, with no observable coarsening of GB precipitates.
Figure 6.13: SEM micrographs showing the precipitation of $M_{23}C_6$ at high-angle boundaries after annealing Alloy 690 at 475 °C for 10,000 h. (a) SA-475-10k, (b) CR-475-10k, (c) TT-475-10k and (d) TTCR-475-10k conditions.

Finally, annealing at 550 °C for 10,000 h resulted in a change in precipitation behavior. First, for the SA-550-10k condition in Figure 6.14, large colonies of cellular $M_{23}C_6$ (on the order of 5-15 μm) were observed. STEM-EDS and diffraction analysis confirmed these regions to be Cr-rich carbides as opposed to $\alpha$-Cr, based on the structure identification in (b) and the carbon signature in (d).
Likewise, annealing the cold-rolled condition of Alloy 690 at 550 °C resulted in M$_{23}C_6$ precipitation at HABs with limited cellular precipitation, as observed in Figure 6.15a. Furthermore, large (~10-50 μm) regions of what appear to be the cellular precipitation of M$_{23}C_6$ are also present. However, as seen in Figure 6.15b, these regions are significantly larger than those observed in other conditions of Alloy 690. Closer examination of these regions reveals that rather than the cellular precipitation of M$_{23}C_6$,
these features appear to be the result of recrystallization of the matrix and precipitation of α-Cr. A more detailed treatment of this recrystallization and precipitation is addressed in Section 6.4.

![SEM micrographs of the CR-550-10k alloy, showing (a) negligible cellular precipitation of Cr$_2$C$_6$ and (b) the concurrent recrystallization of the matrix and precipitation of α-Cr.](image)

Figure 6.15: SEM micrographs of the CR-550-10k alloy, showing (a) negligible cellular precipitation of Cr$_2$C$_6$ and (b) the concurrent recrystallization of the matrix and precipitation of α-Cr.

The TT-550-10k alloy contained cellular regions of M$_{23}$C$_6$, originating from the initial heat treatment at 700 °C for 17 h, as shown in Figure 6.16. The 550 °C anneal resulted in slight coarsening of the pre-existing grain boundary carbides, shown in the SEM micrograph in Figure 6.16a. TEM diffraction again confirmed these cellular precipitates to be M$_{23}$C$_6$, as indicated by the STEM-BF and SADP image in Figure 6.16b.

The TTCR-550-10k alloy exhibited a slight coarsening of the carbides originally produced by the thermal treatment at 700 °C for 17 h, as shown in Figure 6.17a. This coarsening occurred both for the continuous and discontinuous carbides. Furthermore, while a high degree of precipitation also occurred at slip bands, there appears to be limited precipitation occurring at PCTBs (Figure 6.17b). Additionally, a concurrent recrystallization of the matrix and precipitation of α-Cr that morphologically resembles the cellular reaction was observed in Figure 6.17b.
Figure 6.16: The effects of annealing thermally treated Alloy 690 at 550 °C for 10,000 h. (a) SEM micrograph of a cellular region of M_{23}C_6. (b) STEM-BF and SADP of a cellular region, confirming it to be Cr-rich M_{23}C_6.

Figure 6.17: The effects of annealing thermally treated and cold-rolled Alloy 690 at 550 °C for 10,000 h. (a) SEM micrograph showing a slight coarsening of grain boundary carbides. (b) SEM micrograph showing the precipitation at slip bands, as well as the concurrent recrystallization of γ-Ni and precipitation of α-Cr.
6.4 Precipitation of α-Cr in CR and TTCR Conditions at 550 °C

Closer examination of the CR and TTCR conditions of Alloy 690 aged at 550 °C showed the presence of recrystallized γ-Ni grains, with concurrent α-Cr lamellar precipitation. Conversely, this precipitation behavior and recrystallization was not observed in the 350 and 475 °C conditions, and is suspected to be related to the limited recrystallization kinetics of γ-Ni at these lower temperatures, and the sluggish precipitation behavior of α-Cr. In addition to this pseudo-recrystallization phenomenon, the precipitation of α-Cr was observed occasionally at HABs and PCTBs. Given the creation of new, strain-free grains, as well as the presence of an additional precipitating species at HABs, this precipitation behavior was examined in greater detail. Finally, an examination of SA and TT conditions aged at 550 °C for 10,000 h showed no clear presence of α-Cr at HABs.

6.4.1 Cold-Rolled Alloy 690 Annealed at 550 °C

The cold-rolled condition of Alloy 690 annealed at 550 °C for 10,000 hours (CR-550-10k) contained isolated regions of recrystallized matrix grains that contain α-Cr precipitates that were frequently lamellar or rod-like in nature (see arrows in Figure 6.18a and the higher magnification micrograph in Figure 6.18b). Furthermore, a high density of α-Cr and M23C6 was present at slip bands, PCTBs, and HABs (Figure 6.18(c+d)). The α-Cr at the HABs were considerably larger than the M23C6 precipitates, and their structures were confirmed by diffraction analysis in the TEM. It appears that the recrystallized regions, although morphologically similar to cellular precipitation, are in reality the result of recrystallization of the matrix with solute chromium rejection leading to the “concurrent” precipitation of α-Cr. This precipitation behavior first requires the nucleation of a recrystallized γ-Ni grain, which typically occurs near a grain boundary where the localized strain is highest. The formation of this recrystallized grain enables the precipitation of α-Cr, which proceeds to grow in a cellular fashion.
Figure 6.18: SEM examination of the CR-550-10k alloy, showing in (a-b) the size, distribution, and morphology of recrystallized γ-Ni plus α-Cr precipitation, as well as the precipitation of α-Cr and Cr$_2$3C$_6$ at (c-d) HABs and slip bands. The identification of α-Cr at HABs in SEM micrographs was based on precipitate size, as these particles are consistently larger than their carbide counterpart.

S/TEM observations confirmed the presence of α-Cr and recrystallized γ–Ni, and are detailed in Figure 6.19. The B=[001] CBED pattern can be indexed as coming from a BCC phase (i.e. α-Cr) with a 2.87 Å lattice parameter that is consistent with the structure. Likewise, the recrystallized region of γ-Ni
appears to be essentially strain free, and the presence of annealing twins is consistent with a recrystallization mechanism. Finally, STEM-EDS mapping (Figure 6.19(b-d)) confirms the high concentration of chromium and the absence of carbon.

Figure 6.19: S/TEM analysis of the CR-550-10k alloy, showing the recrystallized γ-Ni containing α-Cr precipitates. (a) STEM-BF micrograph, with accompanying diffraction consistent with each structure. (b-d) STEM-EDS maps showing the distribution of α-Cr, and the lack of $M_{23}C_6$ precipitation.
Electron back-scattered diffraction (EBSD) measurements confirmed that these regions of $\gamma+\alpha$ occurred by recrystallization rather than cellular precipitation in spite of their appearance morphologically. An image quality (IQ) map and an inverse pole figure (IPF) map from one such region is shown in Figure 6.20. The annotation in (a) shows an approximate 40-45° misorientation across the boundary, and the IPF in (b) shows no rational orientation relationship between the recrystallized grain and the surrounding matrix grains. This boundary character differs from the cellular precipitation regions, where the cellular colonies are epitaxial with the initiating grain and confirms that this is a recrystallization phenomenon rather than classical cellular precipitation. For the case of cellular precipitation, the migrated boundary would result in a strain free region along with the precipitation of a second phase. This strain free region would be continuous with the grain in which the boundary migrated away from. Conversely, during the formation of a recrystallized grain, which would also be strain free, the initial grain boundary would be maintained.

Figure 6.20: EBSD micrographs of a $\alpha+\gamma$ region in the CR-550-10k alloy, showing (a) the misorientation across a HAB overlaid on an IQ map. (b) The IPF of the region indicates no rational orientation relationship.

In addition to the recrystallization in the CR-550-10k alloy, $\alpha$-Cr and $M_{23}C_6$ precipitated at HABs, PCTBs, and slip bands (Figure 6.22). The $B=[001]$ CBED pattern, taken from the large chromium particle along the PCTB in Figure 6.22b confirms the presence of $\alpha$-Cr adjacent to smaller $M_{23}C_6$ precipitates. Furthermore, $\alpha$-Cr and $M_{23}C_6$ were also observed at HABs (Figure 6.21(c+d)), where it is noted that the $\alpha$-Cr particles are significantly larger than their carbide counterparts.
Figure 6.21: The precipitation of α-Cr and M23C6 in the CR-550-10k alloy. (a) STEM-BF micrograph of α-Cr and Cr23C6 precipitation at a previously coherent annealing twin boundary, with a higher magnification in (b). (c) A BFTEM image of α-Cr and M23C6 precipitation at a HAB, with (d) a B=[011] SADP taken from the α-Cr particle in (c).

In order to confirm the relative size and distribution of the α–Cr and M23C6 phases, a long-term STEM-EDS map was taken of a PCTB (Figure 6.22). Based on the difference in carbon content predicted by ThermoCalc (Section 6.4.3), the delineation between Cr-rich M23C6 and α-Cr can be determined, although in this case SADPs from both particles were obtained to confirm the STEM-EDS analysis.
Figure 6.22: STEM-EDS analysis of the precipitation behavior at a previously coherent annealing twin boundary in the CR-550-10k alloy. (a) STEM-BF with a B=[011] convergent beam pattern taken from a large chromium particle. STEM-EDS maps of (b) nickel, (c) chromium, and (d) carbon used to identify α-Cr vs. $M_23C_6$. 
6.4.2 Thermally Treated and Cold Rolled Alloy 690 Annealed at 550 °C

The precipitation behavior, and specifically the occurrence of α-Cr, was examined in the TTCR-550-10k condition of Alloy 690. Even with a high density of M\textsubscript{23}C\textsubscript{6} due to the initial thermal treatment at 700 °C, there is a degree of α-Cr and M\textsubscript{23}C\textsubscript{6} precipitation occurring during long-term annealing at 550 °C. This precipitation occurs at HABs, PCTBs, and slip bands, in addition to several pockets of recrystallized γ-Ni, as seen in Figure 6.23. Additionally, because of the larger carbides produced by the original 700 °C heat treatment, the identification of α-Cr vs. M\textsubscript{23}C\textsubscript{6} at HABs by SEM imaging proved more difficult.

![Figure 6.23: SEM micrographs of the recrystallization and precipitation behavior in the TTCR-550-10k alloy. (a) The precipitation of M\textsubscript{23}C\textsubscript{6} and α-Cr at HABs and slip bands, with pockets of recrystallized Ni and α-Cr. (b) SEM micrograph at higher magnification, showing a large region of recrystallized Ni and α-Cr.](image)

TEM investigation of the TTCR-550-10k alloy confirmed that the recrystallized γ-Ni regions again contained α-Cr. Additionally, as in the case of the CR-550-10k condition, several large particles of α-Cr were observed at HAB’s in conjunction with M\textsubscript{23}C\textsubscript{6}. STEM-BF micrographs of the concurrent recrystallization and precipitation, as well as the HAB precipitation of α-Cr, are shown in Figure 6.24.
Figure 6.24: STEM-BF micrographs of the TTCR-550-10k condition, showing (a) the concurrent recrystallization of the matrix and precipitation of α-Cr, as well as (b) the precipitation of α-Cr at a HAB.

Diffraction analysis of an α-Cr particle at a HAB was performed in the TTCR-550-10k alloy. The BFTEM image in Figure 6.25a shows the presence of α-Cr, M$_{23}$C$_6$, and TiN at a HAB. The diffraction work on the α-Cr particle determined it formed with a Kurdjumov-Sachs orientation relationship with the matrix, and is shown in Figure 6.25b. STEM-EDS measurements of this region (Figure 6.26) indicate the α-Cr particle nucleated around a pre-existing TiN particle, and confirms the identification of α-Cr.

Figure 6.25: TEM examination of the precipitation of α-Cr at a HAB in the TTCR-550-10k alloy. (a) BFTEM of α-Cr, TiN, and M$_{23}$C$_6$ at the boundary and (b) SADP indicating that the α-Cr particle has a Kurdjumov-Sachs orientation relationship with the adjacent FCC matrix.
Figure 6.26: STEM-EDS mapping of the grain boundary α-Cr and TiN particles showing the (a) Ni, (b) Cr, (c) C, (d) Fe, (e) Ti and (f) N distributions.

6.4.3 ThermoCalc Predictions and Phase Stability

In an effort to examine the relative phase stabilities and the expected compositions of M_{23}C_6, α-Cr, and the γ-Ni matrix, a thermodynamic equilibrium analysis was performed using ThermoCalc (with the TCNi7 database). As presented in Figure 6.27, the expected volume fraction of M_{23}C_6 (~0.005%) remains relatively constant over the experimental temperature regime (350 – 700 °C). Conversely, the volume fraction of α-Cr varies considerably with temperature. The predicted composition of M_{23}C_6 indicates chromium solubility in the carbide of ~95 wt. % and the α-Cr predictions show a relative chromium solubility of ~98 wt. %, and limited solubility of carbon. These predictions have enabled the phase identification of Cr-rich M_{23}C_6 vs. α-Cr to be determined by STEM-EDS measurements in addition to TEM diffraction techniques, and provided insight to the phase stabilities for these alloy conditions.
Figure 6.27: ThermoCalc predictions for Alloy 690 using the TCNi7 database for (a) equilibrium volume fraction of γ-Ni, α-Cr, and M_{23}C_6, with (b) a magnified view of the M_{23}C_6 volume fraction. Compositions of (c) Cr-rich M_{23}C_6 and (d) α-Cr.

Several conclusions regarding the relative kinetics and phase stabilities of Cr_{23}C_6 and α-Cr can be drawn from the microstructural observations and ThermoCalc predictions. The ThermoCalc prediction of α-Cr precipitation at lower temperatures, yet the microstructural observation of only Cr_{23}C_6, indicates a nucleation barrier with regards to α-Cr. This is considered reasonable due to the sluggish kinetics of α-Cr at these temperatures. On this basis, we can explain the lack of α-Cr precipitation at temperatures below 550 °C, in spite of a significant driving force.

6.5 Stress Corrosion Cracking (SCC) Results

In this section, the SCC initiation behavior of Alloy 690 will be discussed and related to the
microstructural evolution of this alloy. All of the mechanical tests were conducted at the University of Michigan by Dr. Wenjun Kuang and Dr. Gary Was.

6.5.1 Considerations of Testing Methodology

A consideration of the slow strain rate test (SSRT) methodology is crucial in explaining the stress corrosion cracking (SCC) initiation behavior of Alloy 690 in this study. Primarily, the comparison of alloys with different yield stresses is of concern due to the displacement-control nature of the test. In this study, all alloys were taken to ~4% plastic strain during slow strain rate testing. Representative stress-strain curves for the as-received conditions of Alloy 690 are shown in Figure 6.28, with the stress-strain curves from additional conditions of Alloy 690 presented in Appendix D. Note that the unloading of the CR and TTCR conditions at ~2% strain is the result of a temporary power outage during testing. Given the significant difference in yield stress for the SA/TT and CR/TTCR conditions (200 and 800 MPa, respectively), these alloys experience very different stresses during SSR testing. In this context, two alloys (SA and CR) taken to 4% plastic strain, will see a ~4x difference in applied stress. Therefore, the cold-rolled (CR) and thermally treated plus cold rolled (TTCR) conditions of Alloy 690 will experience a much more aggressive test, resulting in increased SCC initiation, when compared to solution annealed (SA) or thermally treated (TT) conditions. As a result, a comparison between SA/TT and CR/TTCR conditions of Alloy 690 requires careful interpretation.

Figure 6.28: Stress-strain curves of the four as-received conditions of Alloy 690 during slow strain rate testing at $1 \times 10^{-8}$ s$^{-1}$ in 360 °C high purity water containing 18 cc/kg H$_2$.

6.5.2 CR and TTCR: Summary of Microstructural Evolution

A summary of the microstructural evolution of the CR and TTCR conditions on aging will be presented in this section and correlated with the observed stress corrosion cracking behavior. The cold-
rolled (CR) condition of Alloy 690, as depicted in Figure 6.29a, is primarily free of precipitation. As discussed in Section 6.2, the cold rolling process transforms the majority of annealing twins into essentially high angle boundaries. Aging the CR alloy at 350 °C for 10,000 hours (Figure 6.29b) results in a negligible degree of M$_{23}$C$_6$ precipitation at HABs and PCTBs due to the limited transport kinetics at this temperature. Conversely, aging the CR alloy at 475 °C for 10,000 hours (Figure 6.29c) results in an increase in carbide precipitation at these locations, on the order of ~100 nm in size. Finally, aging the CR alloy at 550 °C for 10,000 hours (Figure 6.29d) results in three primary changes from the 475 °C condition. First, there is a coarsening of M$_{23}$C$_6$ carbides at HABs and PCTBs with a size of ~200 nm. Second, the precipitation of α-Cr occurs at these locations, with particles typically much larger than the carbide counterparts. Finally, the concurrent recrystallization of the matrix and precipitation of lamellar α-Cr occurs at multiple regions throughout the microstructure.

Annealing of the TTCR condition resulted in a relatively small change in the microstructure for temperatures below 550 °C. The initial thermal treatment at 700 °C for 17 h (Figure 6.30a) resulted in a high density of grain boundary Cr$_{23}$C$_6$ precipitation. The application of a 20% cold reduction following this thermal treatment results in deformation of coherent twin boundaries, but to a lesser extent compared with the SACR material; this is believed to be due to the more heterogeneous deformation of the TTCR material due to the presence of the brittle GB carbides that formed during the TT. Subsequent annealing of this microstructure at 350 °C for 10,000 hours (Figure 6.30b) results in a negligible change in the microstructure, with the exception of a few very fine carbides at HABs and PCTBs. Further annealing at 475 °C for 10,000 hours (Figure 6.30c) results in limited coarsening of the existing carbides, and a negligible increase in carbide precipitation at PCTBs. Finally, the 550 °C for 10,000 h anneal (Figure 6.30d) results in a similar evolution as with the CR-550-10k condition. The precipitation of large α-Cr particles at HABs occurs, as well as the concurrent recrystallization and precipitation behavior.
Figure 6.30: Schematic microstructural evolution for the (a) TTCR-00-00 condition annealed at (b) 350 °C, (c) 475 °C, and (d) 550 °C for 10,000 hours.

6.5.3 Stress Corrosion Crack Initiation and Morphology

The stress corrosion cracking (SCC) susceptibility of Alloy 690 was performed via SEM image analysis of specimens tested to similar plastic strain levels (~4%). Two representative micrographs of the cracking behavior at (a) high-angle boundaries and (b) previously coherent annealing twins, in this case for the CR-475-10k condition, are presented in Figure 6.31. It should be noted that the large spinel oxide particles on the surface are an artifact stemming from the stainless-steel autoclave.

Figure 6.31: SEM micrographs of the typical crack morphology after SCC testing in 360 °C simulated PWR water at a strain rate of $1 \times 10^{-8}$ s$^{-1}$. In this instance, we observe (a) cracking at a random high-angle boundary, as well as at (b) previously coherent annealing twin boundaries. Note that the large spinel oxides on the surface are an artifact from the autoclave.
The cracking behavior in this study was primarily intergranular (IG) in nature, with the occasional transgranular (TG) crack. Given the rarity of TG crack propagation, only IG cracking behavior was analyzed here. Additionally, given the susceptibility of PCTBs to cracking in the CR and TTCR conditions of Alloy 690, a statistical boundary-type distribution and cracking susceptibility study was performed at the University of Michigan. The relative length fraction of high-angle boundaries (HABs), annealing twin boundaries, and other coincident site lattice (CSL) boundaries, as determined by EBSD, is shown in Figure 6.32a. The relatively low fraction of coherent annealing twin boundaries in the CR-00-00 and CR-475-10k conditions is due to their transformation to PCTBs during the rolling process, as discussed in Section 6.2. After SCC testing, these conditions were then examined for cracking at coherent annealing twin boundaries (in the case of SA-00-00/SA-475-10k), and PCTBs (in the case of CR-00-00/CR-475-10k). As expected, the SA-00-00 and SA-475-10k conditions exhibit no cracking susceptibility at annealing twin boundaries. Conversely, for the CR-00-00 and CR-475-10k conditions, the PCTBs are highly susceptible to cracking.

Figure 6.32: Analysis of the SA and CR conditions annealed at 475 °C for 10,000, showing the (a) grain boundary character distribution, and (b) the degree of cracking at coherent and previously coherent annealing twin boundaries.

While the examination of SCC susceptibility of Alloy 690 was measured using the three cracking metrics discussed previously, only the measurement of crack length per unit area will be presented here. This measurement provides the most holistic representation of cracking behavior, and most definitively shows the trends among TMP conditions. A full presentation of all SCC statistics for all TMP conditions is provided in Appendix D.

The SCC susceptibility and cracking statistics for the cold rolled and aged conditions of Alloy 690 is presented in Figure 6.33. As discussed in previous sections, the CR+aged conditions show a trend
of recovery with increased annealing time and temperature, as expected. The maximum drop in yield stress occurs after annealing at 550 °C for 10,000 hours, resulting in approximately a 200 MPa recovery. Examination of the cracking statistics (Figure 6.33b) shows an increase in the SCC susceptibility for the CR-475-10k condition. Interestingly, this trend does not continue with the CR-550-10k condition. It is expected that the reduced SCC susceptibility of the CR-550-10k condition may be the result of the large pockets of recrystallized matrix that may accommodate more strain during testing, thereby lowering the overall cracking susceptibility.

![Figure 6.33: Stress corrosion cracking (SCC) results for CR and CR+Aged conditions of Alloy 690, showing (a) Yield stress and (b) crack length per area as a function of aging.](image)

Annealing of the TTCR condition resulted in a similar degree of recovery as observed in the CR+Aged condition, as presented in Figure 6.34a. However, examination of the SCC statistics presented in Figure 6.34b show a negligible increase in cracking behavior for the TTCR-475-10k condition. On this basis, SCC testing of the TTCR-550-10k condition was not conducted.
6.6 Discussion of Stress Corrosion Cracking (SCC) Initiation

The observed SCC behavior of cold-rolled (CR) and thermally treated plus cold-rolled (TTCR) conditions of Alloy 690 annealed at various temperatures for up to 10,000 clearly exhibits a complicated dependence on the microstructure. These factors primarily include: (1) the presence and size of M$_{23}$C$_6$ carbides at grain boundaries, (2) the degree of chromium depletion adjacent to the boundary due to carbide precipitation, (3) the applied stress during testing, affected by recovery during annealing, (4) the presence of large, strain free, recrystallized grains of nickel, (5) the presence of grain boundary damage due to cold-rolling, and (6) the amount of susceptible boundary area.

Kai$^{63}$ and Was$^{62}$ have shown that the precipitation of Cr-rich M$_{23}$C$_6$ in Alloy 690 results in significant chromium depletion adjacent to the boundary, on the order of 10 wt. %. This degree of chromium depletion has been shown by Mishima to result in approximately a 120 MPa reduction in yield strength. Lee et al. have shown that the presence of carbides at the boundary result in a deterioration in mechanical properties, and this behavior tracks with carbide size. Furthermore, Bruemmer and coworkers have observed cracking to occur at the carbide/matrix interface in Alloy 600 and Alloy 690.
6.6.1 Cold-Rolled Condition of Alloy 690

The CR-00-00 and CR-350-10k conditions of Alloy 690 exhibit very little SCC susceptibility in this study. This is primarily attributed to two factors: (1) the lack of pre-existing grain boundary M_{23}C_6, and therefore (2) the lack of chromium depletion adjacent to the boundary. Schematic microstructures for CR-00-00 and CR-350-10k are shown in Figure 6.35(a-b), with schematic chromium profiles adjacent to the boundary in Figure 6.35(e-f). Conversely, annealing at 475 °C for 10,000 hours results in significant carbide precipitation at HABs (Figure 6.35c), and a degree of chromium depletion as a result (Figure 6.35g). These two factors can be used to explain the significantly increased SCC susceptibility for the CR-475-10k condition. The CR-550-10k condition exhibits a larger carbide size than CR-475-10k condition (Figure 6.35d), and possibly an increased degree of chromium depletion (Figure 6.35h). While this would be expected to result in even greater SCC initiation, the presence of large recrystallized nickel grains allows for the CR-550-10k condition to accommodate more deformation during SCC testing, and reduces the degree of cracking as well as the imposed stress during testing.

6.6.2 Thermally Treated and Cold-Rolled Condition of Alloy 690

The as-received condition of thermally treated and cold rolled Alloy 690 (TTCR-00-00) contains M_{23}C_6 at HABs throughout the microstructure, shown schematically in Figure 6.35i. While this would be expected to increase the degree of SCC, Bruemmer et al. have shown that the application of a 20% cold reduction following thermal treatment results in the formation of grain boundary voids and cracked carbides, and suggested that both blunt the crack tip and reduce propagation. Furthermore, the reduced deformation of coherent annealing twin boundaries (discussed in Section 6.2) results in less susceptible boundary area for carbide precipitation and SCC initiation. Subsequent annealing of the TTCR-00-00 condition at 350 and 475 °C results in minimal coarsening of the carbides (Figure 6.35(j-k)), and would suggest a reduction in the degree of chromium depletion adjacent to the boundary (Figure 6.35(f-g)). Finally, the TTCR-550-10k condition exhibits a coarsening of the carbide structure, in addition to the formation of the recrystallized grains of nickel. Again, these strain-free grains are expected to accommodate more strain during SCC testing, and therefore reduce SCC susceptibility.
Figure 6.35: Schematic microstructures for (a) CR-00-00, (b) CR-350-10k, (c) CR-475-10k, and (d) CR-550-10k. Expected chromium composition profiles during annealing (e) CR/TTCR at (f) 350 °C, (g) 475 °C, and (h) 550 °C. Schematic microstructures for (i) TTCR-00-00, (j) TTCR-350-10k, (k) TTCR-475-10k, and (l) TTCR-550-10k.
6.7 Summary

The microstructural evolution due to long-term aging Alloy 690, and the resultant SCC behavior as determined by SSRT testing, have been established. These summative results are as follows:

1. The cold-rolling process of Alloy 690 results in the deformation of annealing twin boundaries (CSL Σ3), and effectively transforms these boundaries into high angle boundaries (HABs). This transformation results in additional nucleation sites for $\text{M}_{23}\text{C}_6$ and $\alpha$-Cr upon subsequent annealing, and adds susceptible boundary area to the microstructure.

2. The long-term aging of cold-rolled Alloy 690 at 550 °C results in the precipitation of $\alpha$-Cr and the concurrent recrystallization and precipitation of $\gamma$-Ni and $\alpha$-Cr respectively. This behavior is not observed in solution annealed (SA) or thermally treated (TT) conditions, or conditions aged below 550 °C, and is explained in terms of reduced atomic mobility and the nucleation barrier for $\alpha$-Cr precipitation.

3. A consideration of the slow strain rate testing methodology and the different strengths of the SA/TT and CR/TTCR alloys has made it clear that comparison of these conditions should be made with caution. Due to the difference in strengths, where the SA/TT material has a yield strength of ~200 MPa and the CR/TTCR material has a yield strength of ~800 MPa, these materials will see stresses that correlate with the flow stress. As such, the slow strain rate test will be much more aggressive for the cold-rolled conditions of Alloy 690, and result in an increase in SCC initiation.

4. The CR-475-10k condition of Alloy 690 has been shown to be the condition most susceptible to SCC of those examined. The presence of grain boundary voids and cracked carbides in the TTCR and TTCR+Aged conditions of Alloy 690 reduces the amount of deformation at annealing twins, and results in less overall susceptible boundaries. The higher susceptibility of the CR-475-10k condition is attributed to the presence of a greater density of boundaries where the brittle $\text{Cr}_{23}\text{C}_6$ carbides will form and lead to crack initiation.
The main research objectives in this study were (1) to examine the diffuse scattering in TEM selected area diffraction patterns (SADPs) attributed to short-range order in Alloy 690, (2) to examine the precipitation behavior and stability of $\gamma'$-Ni$_2$Cr in the Ni-Cr binary, (3) to examine the microstructural evolution of Alloy 690 in the solution annealed (SA), 20% cold-rolled (CR), thermally treated (TT), and thermally treated plus cold-rolled (TTCR) conditions after long-term aging at 350, 475, and 550 °C for 10,000 hours, and (4) to evaluate the stress corrosion cracking (SCC) susceptibility of these conditions of Alloy 690 during slow strain rate tensile (SSRT) testing in simulated primary water reactor (PWR) conditions at 360 °C, using a strain rate of $1 \times 10^{-8} \text{ s}^{-1}$. A summary of the significant findings is provided in the following sections.

7.1 Atomic Ordering and Diffuse Scattering in Alloy 690

- The presence of $1/3\{422\}$ and $1/2\{311\}$ diffuse scattering in $B=[111]$ and $B=[112]$ SADPs of Alloy 690 is not caused by SRO, but rather appears to be due to the presence of higher-order Laue zone (HOLZ) scattering into the zero layer.
- Similar diffuse intensities were observed in Alloy 690, Alloy 600, IN945X, Ni-55Cr, Ni-33Cr, CdTe, Co-28.5Cr-6Mo and commercially pure nickel, indicating this is a general observation in FCC materials.
- A tilting experiment conducted on Alloy 690, tracking the strong $\{111\}$ reflections from the $B=[112]$ to the $B=[111]$ zone axis, confirmed that these intensities never fully disappear and are present in the $1/3\{422\}$ positions in the $<111>$ zones.
- A series of zone axes containing $\{422\}$ and $\{311\}$ reflections were examined for diffuse scattering. The additional diffuse intensities were not always at the $1/3\{422\}$ and $1/2\{311\}$ positions, but could be consistently correlated with the projections of HOLZ reflections into the zero layer.

7.2 Phase Stability in the Ni-Cr System

- Annealing a cast Ni-55Cr binary alloy at 500 °C for 1,000 h resulted in the precipitation of $\alpha$-Cr and $\gamma$-Ni + $\gamma'$-Ni$_2$Cr pockets at the dendritic/interdendritic interface. Annealing at 900 °C for 4 h resulted in the precipitation of interdendritic $\alpha$-Cr. Annealing at 900 °C followed by 500 °C resulted in the interdendritic precipitation of $\alpha$-Cr during the 900 °C treatment, but no $\gamma'$-Ni$_2$Cr precipitation was observed during subsequent annealing at 500 °C.
- The lack of $\gamma'$-Ni$_2$Cr precipitation when annealing at 900 °C followed by 500 °C suggests an
inconsistency in the Ni-Cr binary phase diagram, and indicates that the \( \gamma' \)-Ni\(_2\)Cr phase is not an equilibrium phase. Rather, this study indicates \( \gamma' \)-Ni\(_2\)Cr is a metastable precipitate that only forms as coherent precipitates in the \( \gamma \)-Ni matrix and only for certain compositions of g-Ni and certain temperatures.

7.3 Stress Corrosion Cracking of Alloy 690

- The 20% cold-reduction of Alloy 690 resulted in the deformation of coherent annealing twin boundaries, and an increased SCC susceptibility of these boundaries. Subsequent annealing resulted in the precipitation of Cr-rich M\(_{23}\)C\(_6\) (at 475 and 550 °C) and \( \alpha \)-Cr (at 550 °C) at both previously coherent twin boundaries and high angle boundaries.

- The 20% cold-reduction of thermally treated Alloy 690 (TTCR) results in the formation of grain boundary voids and cracked M\(_{23}\)C\(_6\) carbides; this has been suggested by Bruemmer et al. to blunt the crack tip during SCC testing and reduce propagation.\(^{12}\)

- Due to the increased strain accumulation and grain boundary damage during rolling of the TTCR alloy, the previously coherent annealing twins receive less damage during rolling than in the SACR material. This results in less susceptible boundary area for precipitation during subsequent aging, and a reduced SCC susceptibility for the alloy in all annealing conditions.

- Annealing the CR and TTCR conditions of Alloy 690 at 550 °C for 10,000 h resulted in colonies of recrystallized \( \gamma \)-Ni containing \( \alpha \)-Cr precipitates, which morphologically appear similar to cellular or eutectoid precipitation. These soft pockets are believed to account for the higher SCC resistance of 690 after these anneals. It is speculated that these strain free regions allow for more strain accommodation during SCC testing and reduce SCC susceptibility.

- Stress corrosion cracking (SCC) testing of Alloy 690 indicates an increased susceptibility for the CR alloy annealed at 475 °C but not for the TTCR alloy.

- The SCC resistance of the as-rolled (CR) Alloy 690, and that annealed at 350 °C, is attributed to the lack of grain boundary carbides and no chromium depletion at the boundary.

- The SCC resistance of the TTCR alloy, both in the as received and annealed at 350 and 475 °C conditions, is attributed to the presence of grain boundary voids and cracked carbides acting to blunt the crack tip and thus reducing crack propagation during SCC testing.\(^{12}\)

- The long-term concerns by industry of SCC initiation in Alloy 690 in the thermally-treated condition can probably be ignored unless there are regions where the alloy has been significantly hardened mechanically and the material will undergo some type of dynamic loading.
CHAPTER 8  FUTURE WORK

This body of work has focused on three primary investigations, namely, (1) the atomic ordering and diffuse scattering of Alloy 690, (2) the phase stability of the Ni-Cr system, and (3) the stress corrosion cracking of Alloy 690. Each of these subjects contains aspects that can be further expanded upon to provide insight into their behavior. This suggested work is as follows:

- In-situ ion sputtering of CP nickel or Alloy 690, in order to observe possible changes in diffuse scattering as a result of surface oxides. While the current work suggests that the presence of surface oxides does not contribute to diffuse scattering, this experiment could further validate these observations. This would consist of the collection of a B=[111] SADP, before and after in-situ ion sputtering in the TEM, followed by microdensitometer measurements across the 1/3\{422\} positions.

- Examination of atomic steps present in TEM thin-films using an alloy with well-defined cleavage planes. Examination of an alloy such as MgO, with specific \{100\} cleavage planes, could enable the study of higher-order Laue zone diffraction as a function of atomic steps. Likely, these atomic steps would occur on the \{100\} surface, and result in rerod spiking normal to this surface. A recreation of the systematic tilting experiment conducted in this study on MgO could further ascertain if these intensities stem from atomic steps on the foil surface, as they should be well predicted based on the thin-foil effect.

- Theoretical simulations of diffracting intensities in this body have work do not correlate with the experimental observations. An expansion on this theory, using the dynamical multislice theory, could better explain the presence of additional intensities in TEM SADPs. This theory, developed by Cowley et al.,\textsuperscript{108} has been successfully used to predict diffracting intensities in TEM SADPs of Al-Cu, exhibiting streaking due to the thin-feature effects of nanoscale precipitates. These simulations could be used for further explain the presence of diffuse scattering in Alloy 690 and similar FCC materials, and account for a variety of other factors, such as the presence of atomic steps on the foil, surface oxides, etc.

- Annealing of the as-cast Ni-55Cr binary alloy for extended times could further elucidate the phase stability of the \(\gamma\)-Ni\(_2\)Cr precipitate. Annealing the binary alloy at 500 °C for tens of thousands of hours should show the progression of \(\gamma\)-Ni\(_2\)Cr precipitation, followed by the dissolution of \(\gamma\), resulting in a two-phase \(\gamma\)-Ni + \(\alpha\)-Cr microstructure. Examination of this microstructure using a combined SEM/TEM/EDS approach could further expand on the work presented here.
• In-situ TEM tensile straining of Alloy 690, with varying sizes of $M_{23}C_6$, and therefore chromium profiles adjacent to the grain boundary, could provide crucial insight into the deformation mechanisms of this alloy. While previous work in Alloy 600 has suggested that fracture occurs at the carbide/matrix interface, no such work has been performed in Alloy 690. The in-situ tensile testing of Alloy 690 in the TEM could provide insight regarding the mechanisms of deformation in this alloy. This work should be correlated with a systematic evaluation of carbide size, and measurements of chromium depletion adjacent to the boundary. Furthermore, the in-situ observation of crack propagation would provide insight into the mechanisms of crack-tip interactions with grain boundary voids and cracked carbides that are present in the TTCR condition of Alloy 690.

• A post-mortem examination of the conditions of Alloy 690 tested for stress corrosion cracking would provide valuable insight into the deformation, oxidation, and cracking mechanisms at play. This work would focus on crack tip interactions with recrystallized matrix grains, regions of cellular carbides, and the defect population in the microstructure. This post-mortem evaluation, combined with the current work on Alloy 690, could further elucidate the mechanisms of SCC in this alloy.
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### APPENDIX A ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>BFTEM</td>
<td>Bright Field Transmission Electron Microscopy</td>
</tr>
<tr>
<td>CBED</td>
<td>Convergent Beam Electron Diffraction</td>
</tr>
<tr>
<td>CDF</td>
<td>Centered Dark-Field</td>
</tr>
<tr>
<td>CP</td>
<td>Commercially Pure</td>
</tr>
<tr>
<td>CSL</td>
<td>Coincident Site Lattice</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Back-Scattered Diffraction</td>
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<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
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<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
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<td>FOLZ</td>
<td>First-Order Laue Zone</td>
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<tr>
<td>FRRI</td>
<td>Forbidden Reflection Lattice Imaging</td>
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<tr>
<td>GB</td>
<td>Grain Boundary</td>
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<tr>
<td>HAB</td>
<td>(Random) High Angle Boundary</td>
</tr>
<tr>
<td>HOLZ</td>
<td>Higher-Order Laue Zone</td>
</tr>
<tr>
<td>HRSEM</td>
<td>High-Resolution Scanning Electron Microscopy</td>
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<tr>
<td>KAM</td>
<td>Kernel Average Misorientation</td>
</tr>
<tr>
<td>OIM</td>
<td>Orientation Imaging Microscopy</td>
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<tr>
<td>PCTB</td>
<td>Previously Coherent Annealing Twin Boundary</td>
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<tr>
<td>Relrod</td>
<td>Reciprocal Lattice Rod</td>
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<tr>
<td>SADP</td>
<td>Selected Area Diffraction Pattern</td>
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## APPENDIX B EXPERIMENTAL MATRIX

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<tr>
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<td>TT-00-00</td>
<td>700 °C – 17 h</td>
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</tr>
<tr>
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<td>TTCR-00-00</td>
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<td>350 °C – 3,000 h</td>
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<td>CR-475-10k</td>
<td>20 % Cold Reduction</td>
<td>475 °C – 10,000 h</td>
</tr>
<tr>
<td>31</td>
<td>TT-475-10k</td>
<td>700 °C – 17 h</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>TTCR-475-10k</td>
<td>700 °C – 17 h then 20% Cold Reduction</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>SA-550-10k</td>
<td>1100 °C – 1 h</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>CR-550-10k</td>
<td>20 % Cold Reduction</td>
<td>550 °C – 10,000 h</td>
</tr>
<tr>
<td>35</td>
<td>TT-550-10k</td>
<td>700 °C – 17 h</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>TTCR-550-10k</td>
<td>700 °C – 17 h then 20% Cold Reduction</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX C MATLAB ROCKING CURVE CODE

%% ALL UNITS IN ANGSTROMS UNLESS OTHERWISE NOTED
%% EXPERIMENTAL RELROD CALCULATIONS
clc; clear all; close all;

disp('All inputs are space delimited');

%% USER INPUTS
prompt = 'Accelerating Voltage (kV): ';
AccV = input(prompt);

prompt = 'System: 
  (1) FCC-Ni 
  (2) DC-Silicon 
  (3) ZnBlende-GaN: 
  ';
ans = input(prompt);

if ans == 1 % FCC-Nickel
    p(1,1)=0;  p(1,2)=0;  p(1,3)=0;
p(2,1)=0.5;  p(2,2)=0.5;  p(2,3)=0;
p(3,1)=0.5;  p(3,2)=0;   p(3,3)=0.5;
p(4,1)=0;   p(4,2)=0.5;  p(4,3)=0.5;
a=3.5;
    AN=28;
else if ans == 2 % DC Silicon
    p(1,1)=0;  p(1,2)=0;  p(1,3)=0;
p(2,1)=0.5;  p(2,2)=0.5;  p(2,3)=0;
p(3,1)=0.5;  p(3,2)=0;   p(3,3)=0.5;
p(4,1)=0;   p(4,2)=0.5;  p(4,3)=0.5;
p(5,1)=0.25; p(5,2)=0.25; p(5,3)=0.25;
p(6,1)=0.75; p(6,2)=0.75; p(6,3)=0.25;
p(7,1)=0.75; p(7,2)=0.25; p(7,3)=0.75;
p(8,1)=0.25; p(8,2)=0.75; p(8,3)=0.75;
a=5.431;    % Pearson's Handbook
    AN=14;
else if ans == 3 % GaN
    p(1,1)=0;  p(1,2)=0;  p(1,3)=0;
p(2,1)=0.5;  p(2,2)=0.5;  p(2,3)=0;
p(3,1)=0.5;  p(3,2)=0;   p(3,3)=0.5;
p(4,1)=0;   p(4,2)=0.5;  p(4,3)=0.5;
p(5,1)=0.25; p(5,2)=0.25; p(5,3)=0.25;
p(6,1)=0.75; p(6,2)=0.75; p(6,3)=0.25;
p(7,1)=0.75; p(7,2)=0.25; p(7,3)=0.75;
p(8,1)=0.25; p(8,2)=0.75; p(8,3)=0.75;
a=4.52;
    AN=19; % average of Ga (31) and N (7)
end
% Number of atom positions
m=size(p,1);

% Zone Axis
prompt = 'Zone Axis: ';
str = input(prompt,'s');
ZA = strread(str);

% Foil Normal
prompt = 'Foil Normal: ';
str = input(prompt,'s');
FN = strread(str);

% User Input g Vector (Spiking g)
prompt = 'Spiking g: ';
str = input(prompt,'s');
g = strread(str);

ZA_mag = norm(ZA)^2;
FN_mag = norm(FN)^2;
g_mag  = norm(g)^2;

% Foil Thickness
prompt = 'Thickness (≈): ';
t = input(prompt);

%% RELATIVISTIC WAVELENGTH
% Used in Loretto's Calculation via extinction distance
kV=AccV*1000;       % ACCELERATING VOLTAGE (eV)
c=2.998e8;          % SPEED OF LIGHT (m/s)
mo=9.1095e-31;      % MASS OF ELECTRON (kg)
h=6.6261e-34;       % PLANCK'S CONSTANT (kg-m2/s2)
e=1.6022e-19;       % ELECTRON ENERGY (kg-m2/s2)
lambda = (h/sqrt((2*mo*kV*e*(1+(e*kV)/(2*mo*c^2)))))*10^10; % RELATIVISTIC WAVELENGTH

%% STRUCTURE FACTOR CALCULATION
% DOT PRODUCT (hU + kV + IW)
i=1;
while i <= m
    mag(i) = 2*pi()*(p(i,1)*g(1) + p(i,2)*g(2) + p(i,3)*g(3));
    i=i+1;
end
% REAL & IMAGINARY PARTS
i=1;
while i <= m
  real_part(i) = cos(mag(i));
  imag_part(i) = sin(mag(i));
  i=i+1;
end

real_part = sum(real_part);
imag_part = sum(imag_part);

% STRUCTURE FACTOR
F_form = complex(real_part,imag_part);

% ACCOUNTING FOR SCATTERING FACTOR
F_val = F_form*AN;

% STRUCTURE FACTOR CONJUGATE
F_form_conj = conj(F_form);
F_val_conj = conj(F_val);

% INTENSITY (FORM)
I_form = abs(F_form*F_form_conj);

% INTENSITY (NUMERICAL)
I_val = abs(F_val*F_val_conj);

%% G SPACING AND SPIKING DISTANCE (DEVIATION PARAMETER) CALCULATION
% How long would a relrod need to be to intersect the Ewald's sphere and
% what would the projected spacing be in your diffraction pattern as a
% function of unit cell and beam parameters, including foil normal.

% g dot ZA
g_dot_ZA = dot(g,ZA);

% Angle between g-vector and Zone Axis
g_ZA_cos = ((g_dot_ZA)/(sqrt(g_mag)*sqrt(ZA_mag)));
g_ZA_Ang = acosd(g_ZA_cos);

% FN dot ZA
FN_dot_ZA = dot(FN,ZA);

% Angle between Foil Normal and Zone Axis
FN_ZA_cos = (FN_dot_ZA)/(sqrt(FN_mag)*sqrt(ZA_mag));
FN_ZA_Ang = real(acosd(FN_ZA_cos));

ZA_mag_norm = (sqrt(g_mag)*g_ZA_cos)^2;
FN_mag_norm = (sqrt(ZA_mag_norm)/FN_ZA_cos)^2;

ZA_f = sqrt(ZA_mag_norm/ZA_mag);
FN_f = sqrt(FN_mag_norm/FN_mag);

% Normalized Values
i = 1;
while i <= 3
    ZA_norm(i) = ZA(i)*ZA_f;
    FN_norm(i) = FN(i)*FN_f;
    if g_dot_ZA > 0
        g_proj(i) = g(i) - FN_norm(i);
    elseif g_dot_ZA < 0
        g_proj(i) = g(i) + FN_norm(i);
    else
        disp('ERROR');
    end
end
i=i+1;
end

ZA_norm_mag = ZA_norm(1)^2 + ZA_norm(2)^2 + ZA_norm(3)^2;
FN_norm_mag = FN_norm(1)^2 + FN_norm(2)^2 + FN_norm(3)^2;
g_proj_mag = g_proj(1)^2 + g_proj(2)^2 + g_proj(3)^2;

% TRUE D-SPACING OF G-VECTOR
d_g = a/sqrt(g_mag);

% PROJECTED D-SPACING OF G-VECTOR
d_g_proj = a/sqrt(g_proj_mag);

% SPIKING MAGNITUDE (DEVIATION PARAMETER) 1/≈
sg = sqrt(FN_norm_mag)/a;
theta_g=asind(lambda*2*sg);

%%% EXTINCTION DISTANCE CALCULATION by Fultz & Howe, p.343 eq. 7.17
V=a^3; % CUBIC UNIT CELL VOLUME
ex=(pi()*V)/(lambda*real(F_val)); % EXTINCTION DISTANCE

%%% INTENSITY vs. DEVIATION PARAMETER CALCULATION
% D-SPACING DOWN ZONE
d=a/sqrt(ZA_mag);
% NUMBER OF UNIT CELLS
N_z_exact = t/d;

% PROMPT DERIVATION TYPE
prompt = 'Which derivation would you like to plot? 
  (1) Reimer: Accounts for Structure Factor 
  (2) Loretto: Accounts for Extinction Distance\n';
ans = input(prompt);
i=1;  % Initialize Counter

if ans == 1
    s(i,1)= -sg;
    while s(i,1) <= sg
        K(i) = s(i,1);
        Relrod_Intensity(i,1) = I_val*(sin(pi()*N_z*s(i,1)*d).^2)/(pi()*s(i,1)*d).^2;
        plot(s(i,1),Relrod_Intensity(i,1))
        hold all;
        s(i+1,1)=s(i,1)+0.00005;
        i=i+1;
    end
    Relative = (I_val*(sin(pi()*N_z*sg*d).^2)/(pi()*sg*d).^2)/max(Relrod_Intensity)
    title('Reimer Rocking Curve');
end

if ans == 2
    s(i,1)= -sg;
    while s(i,1) <= sg
        K(i,1) = s(i,1);
        Relrod_Intensity(i,1) = ((pi()/ex)^2)*((sin(pi()*t*s(i,1))^2)/(pi()^2*s(i,1)^2));
        plot(s(i,1),Relrod_Intensity(i,1))
        hold all;
        s(i+1,1)=s(i,1)+0.00005;
        i=i+1;
    end
    title('Loretto Rocking Curve');
    Relative=((pi()/ex)^2)*((sin(pi()*t*sg)^2)/(pi()^2*sg^2))/max(Relrod_Intensity)
end

xlabel('Deviation Parameter (1/≈)');
ylabel('Intensity (arb. units)');
I_{sg} = 1_val*(\sin(pi()^N_z*sg*d).^2)/(pi()^sg*d).^2;

prompt = 'Output Results? Y or N';
ans = input(prompt, 's');

if ans == 'Y'
    Relrod_Intensity(i, 1) = ((pi()/ex)^2)*((\sin(pi()^t*s(i))^2)/(pi()^2*s(i)^2));
    output = horzcat(Relrod_Intensity, s); % Combine input and output data to a single matrix
    prompt = 'File Name?';
    file = input(prompt, 's');
    output_name = strcat(file, '.csv'); % Dictate the output file name (add output.csv)
    csvwrite(output_name, output, 1, 0); % Export to .csv file
end
APPENDIX D STRESS CORROSION CRACKING (SCC) RESULTS

Figure D.1: Stress corrosion cracking (SCC) results for SA and SA+Aged conditions of Alloy 690, showing (a) Yield stress, (b) crack length per area, (c) crack density, and (d) average crack length. Error bars (95% CI) are associated with the deviation in crack measurement.
Figure D.2: Stress corrosion cracking (SCC) results for CR and CR+Aged conditions of Alloy 690, showing (a) Yield stress, (b) crack length per area, (c) crack density, and (d) average crack length. Error bars (95% CI) are associated with the deviation in crack measurement.
Figure D.3: Stress corrosion cracking (SCC) results for TT and TT+Aged conditions of Alloy 690, showing (a) Yield stress, (b) crack length per area, (c) crack density, and (d) average crack length. Error bars (95% CI) are associated with the deviation in crack measurement.
Figure D.4: Stress corrosion cracking (SCC) results for TTCR and TTCR+Aged conditions of Alloy 690, showing (a) Yield stress, (b) crack length per area, (c) crack density, and (d) average crack length. Error bars (95% CI) are associated with the deviation in crack measurement.
Figure D.5: The yield strength of Alloy 690, as a function of thermomechanical processing and annealing temperature (for 10,000 hours), during stress corrosion cracking testing at $1 \times 10^{-8}$ s$^{-1}$ in 360 °C high purity water containing 18 cc/kg H$_2$.

Figure D.6: Stress-strain curves of the as-received conditions of Alloy 690 during stress corrosion cracking testing at $1 \times 10^{-8}$ s$^{-1}$ in 360 °C high purity water containing 18 cc/kg H$_2$. 
Figure D.7: Stress-strain curves of solution annealed Alloy 690, aged at 350 and 475 °C, during stress corrosion cracking testing at $1 \times 10^{-8}$ s$^{-1}$ in 360 °C high purity water containing 18 cc/kg H$_2$.

Figure D.8: Stress-strain curves of cold-rolled Alloy 690, aged at 350 °C, during slow strain rate testing at $1 \times 10^{-8}$ s$^{-1}$ in 360 °C pressurized steam/water.
Figure D.9: Stress-strain curves of cold-rolled Alloy 690, aged at 475 °C, during slow strain rate testing at $1 \times 10^{-8}$ s$^{-1}$ in 360 °C pressurized steam/water.

Figure D.10: Stress-strain curves of solution annealed Alloy 690, aged at 350 and 475 °C, during slow strain rate testing at $1 \times 10^{-8}$ s$^{-1}$ in 360 °C pressurized steam/water.
Figure D.11: Stress-strain curves of solution annealed Alloy 690, aged at 350 and 475 °C, during slow strain rate testing at $1 \times 10^{-8} \text{ s}^{-1}$ in 360 °C pressurized steam/water.