Microstructural Characterization of Magnetic Regions

in a Cast Austenitic Heat Resistant Steel

BY

GREGORY SPARKS
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THESIS

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Defense Committee:

J. Ernesto Indacochea, Chair and Advisor
Didem Ozevin, Civil and Materials Engineering
Craig Foster, Civil and Materials Engineering
This thesis is dedicated to my family, who have supported me throughout my academic career.
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GS
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Summary

The development of magnetic regions in an initially non-magnetic cast austenitic heat-resistant steel has been examined. Samples were extracted from different regions in a failed steam reformer tube. The samples had been exposed to different average temperatures over the 7-year life of the tube, resulting in different levels of damage. An as-cast sample of the material was also available as a control. After standard metallographic grinding and polishing of the samples, magnetic etching with ferrofluids was used to determine the presence and location of the magnetic zones. After locating these regions, energy-dispersive spectroscopy and electron backscatter diffraction in a scanning electron microscope were used to characterize the composition and structure of the magnetic regions. While not conclusive without further experimentation, results indicate that these magnetic regions are caused by localized chromium depletion from the Fe-Ni-Cr austenitic matrix. Unfortunately, due to experimental difficulties, the precise nature of the magnetic regions was not determined as intended, and further study is recommended.
1. INTRODUCTION

Steam reforming furnaces produce hydrogen from steam and natural gas for various uses. These steam reforming furnaces provide a chemically and thermally challenging environment for the furnace tubing. High-Ni-Cr cast austenitic steels are used to withstand the very high temperatures and oxidizing/carburizing atmosphere. The composition of the alloy used in this study is given below in Table I.

<table>
<thead>
<tr>
<th>Table I - CHEMICAL COMPOSITION OF THE ALLOY STUDIED (WT. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
</tr>
<tr>
<td>Bal.</td>
</tr>
</tbody>
</table>

Since this alloy is austenitic in the as-cast state, it is initially paramagnetic, but it has been discovered that during their service life the tubes become detectably ferromagnetic [1]. This study aims to examine this phenomenon in more detail and determine the precise nature of the transformation that occurs.

The interior of the tubing is exposed to a mixture of CH₄, H₂O, CO, CO₂, and H₂ as the steam reforming process proceeds. The relevant chemical reactions are as follows [1]:

\[
\begin{align*}
\text{CH}_4 + \text{H}_2 & \rightarrow \text{CO} + 3\text{H}_2 \quad (1.1) \\
\text{CH}_4 + \text{CO}_2 & \rightarrow 2\text{CO} + 2\text{H}_2 \quad (1.2) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad (1.3) \\
\text{CH}_4 + 2\text{H}_2\text{O} & \rightarrow \text{CO}_2 + 4\text{H}_2 \quad (1.4)
\end{align*}
\]
These reactions are highly endothermic. Even in the presence of a nickel-based catalyst to enhance the reaction rate, the furnace must be run at the extremely high temperatures, varying from 750-1150°C depending on location in the furnace tube [1], with localized short-term excursions to even higher temperatures. Said temperatures enable a variety of processes that affect the alloy and its microstructure. These processes include oxidation, carburization and nitridation from the gas mixture inside the tube and the air outside the tube (with accompanying phase precipitations and transformations) [2-11], coarsening of precipitates or localized compositional changes involving diffusion [12-15], creep [2], [4], [9-11], [16], and thermal stresses induced by temperature fluctuations during service or on furnace startup and shutdown [2], [6], [16]. Many of these damage mechanisms interact with or reinforce each other; fracture of the protective oxide scale by creep strain or thermal stress will encourage corrosion, while microstructural changes due to diffusion and corrosion can reduce creep resistance.

The results show that magnetic regions appear strongly in the most damaged sample tested, and less strongly in the second most damaged sample. No magnetic regions detectable with the technique used were found in the samples with less damage than the two previously mentioned ones, so those samples were not subjected to further characterization. The magnetic zones form around carbide or carbonitride precipitates in the metal.

Following this introduction, Chapter 2 provides a review of the literature on the processes active in the material that might be relevant to its transformation. Chapter 3 describes the experimental equipment and procedures used in this study. Chapter 4 presents the results and discusses them, while Chapter 5 gives the conclusions reached in this study.
2. LITERATURE REVIEW

2.1. Chemical Effects: Oxidation, Carburization, and Nitridation

Chemical reactions with the environment are a nearly ubiquitous source of damage in high-temperature metals. Various methods have been developed to combat this, with most focusing on the development of an adherent and continuous layer of highly stable oxide on the surface of the metal in question, said layer acting as a barrier to the diffusion of the reactive species from the environment into the material. However, this method rarely works perfectly. The precise effects of the subsequent reactions depend on the reactive species involved.

2.1.1. Oxidation

Oxidation is an extremely common form of chemical damage to a metal object at high temperatures, as oxygen from the atmosphere will be in contact with the metal unless special care is taken to exclude it. However, the fact that oxygen will almost always be present allows for the development of protective oxide scales from certain elements in the metal. For high temperature materials, these elements are primarily Cr → Cr₂O₃, Al → Al₂O₃, and Si → SiO₂. Unlike other metal oxides, such as iron oxide, these adhere tightly to the surface of the metal and act as a barrier to further diffusion of oxygen and other reactive species into the metal [17].

The primary scale-forming element in the alloy studied here is chromium, with a small amount of silicon present as well. The silicon can form a sub-layer of SiO₂ underneath the Cr₂O₃ scale, which acts as a barrier to outward diffusion of Cr metal and thus discourages excessive growth of the Cr₂O₃ scale at high temperatures. However, there is a substantial mismatch in coefficient of thermal expansion between the silica and the bulk metal [18]. Excessive amounts of silica can thus increase internal stresses during thermal cycling, encouraging spallation and loss of the protective oxide scale. The scale must then be rebuilt by oxidation of chromium in the
metal. If the cycle of spallation and scale healing continues, it will drain chromium out of the alloy until there is no longer sufficient chromium content to form a continuous oxide scale, at which point catastrophic internal corrosion will occur [6].

### 2.1.2. Carburization

Carburization is the process of carbon from the environment dissolving into a metal, where it acts as an interstitial solid solution element. Controlled carburization can actually have a beneficial effect, as the increased carbon content will increase the hardness of iron-based alloys, but excessive carburization is detrimental due to the accompanying increase in brittleness. Carbon-containing gases are not typically present in substantial concentrations in Earth’s atmosphere, so prevention of carburization is usually only a major issue in metals exposed to carbonaceous gases at high temperatures, such as in the methane reformer furnace tubes studied here.

Conveniently, the same chromium oxide scale that protects the alloy from oxidation is also an excellent barrier to carbon diffusion, with the solubility of carbon being under 0.01 ppm in the oxide [19]. However, carbon transport can still occur through flaws in the scale, including pores or cracks formed by thermal stresses, creep deformation, and various other mechanisms [5], [20]. In environments with extremely low oxygen activity and high carbon activity, the Cr₂O₃ scale can even be reduced to Cr₇C₃, destroying the protective oxide and allowing massive carburization of the metal [3], [7], [8], [21].

Carbon, in addition to simply dissolving in austenite, can also chemically react with some of the alloy components to form carbide precipitates. In the alloy studied here, carbide-forming elements that are present in the initial alloy include Cr, W, Ti, and Nb. Even in the as-cast state this alloy has a substantial amount of carbide precipitates, intended to increase the high-
temperature creep strength of the material. The precipitates most affected by introduction of additional carbon are the Cr-based precipitates, as substantial quantities of unreacted Cr are present in the as-cast alloy. Nb and Ti are present in very small quantities, and there is sufficient carbon in the initial alloy to fully react with them, while W is not a particularly strong carbide former by itself in austenitic Fe-Ni-Cr alloys and instead tends to remain in the austenitic matrix or dissolve in Cr-based carbides [22].

As such, addition of carbon causes the precipitation of carbides of various types. The chemical formulae for these carbides are often variable and are written with a generic “M” standing for various metal atoms. The primary carbides that form in similar alloys are MC, M_{23}C_6, and M_7C_3 [4], [11], [23]. MC type carbides in this alloy and similar alloys contain primarily Nb, Ti, or a mixture of the two [1], [9-11], along with small amounts of Fe/Cr/Ni [23]. The M_{23}C_6 carbides are primarily Cr (60-70 wt.%) and also have substantial enrichment of W (~14 wt.% versus overall ~4 wt.%), with roughly equal weights of Fe, Ni, and C making up the remainder of the precipitate mass [1]. M_7C_3 was not actually present in samples 9A and 15A (the two most damaged samples), despite being present in the as-cast state, as it transformed to M_{23}C_6. This is due to the presence of W in the alloy, which dissolves into the carbides and scavenges some C atoms, increasing the Cr/C ratio and promoting the transformation of M_7C_3 into M_{23}C_6 [24].

The precipitation of Cr-based carbides will reduce the concentration of Cr in the matrix immediately surrounding the carbide due to preferential uptake of Cr by the carbides [3], [15]. It is possible that this reduction in matrix Cr content is what causes the regions at the carbide/matrix interface to become ferromagnetic when removed from service and tested, as the Curie temperature of Fe-Ni-Cr alloys increases with decreasing Cr content [25]. Other proposed hypotheses include
the precipitation of a separate ferromagnetic phase at the interface, such as delta ferrite or stress-induced martensite.

### 2.1.3. Nitridation

Nitridation is similar to carburization in that it is the dissolution of nitrogen into a metal as an interstitial solid solution element. Nitrogen is not present in the process gas on the inside of the furnace tubing, but it is present in the ambient atmosphere outside of the tubes. In the work done by O. Quintana [1], both sample 9A and sample 15A (the two most damaged samples) showed signs of nitridation in zones near the outer diameter, while less-damaged samples taken from regions of lower temperature did not appear to have undergone nitridation to any detectable degree.

Nitrogen uptake results in another set of transformations and precipitation reactions, with the precise results depending on the alloy composition. The strong carbide-forming elements Ti and Nb can both also form isostructural nitrides or carbonitrides separately or in solid solution with each other [26-29], for an overall chemical formula of (Ti,Nb)(C,N). Chromium forms a hexagonal close-packed nitride or carbonitride Cr$_2$N or Cr$_2$(C,N) [8], [30], [31], and this was observed in samples 9A and 15A by O. Quintana with some minor substitutions of W/Fe/Ni for Cr [1]. M$_{23}$C$_6$ carbide has near zero solubility for nitrogen [32], and the presence of nitrogen thus tends to destabilize M$_{23}$C$_6$ while promoting the formation of the η-carbide structure with general formula M$_6$C. A wide range of metal atoms can be substituted into this crystal structure, but nitrogen tends to promote the formation of an otherwise rare composition, this being Cr$_3$Ni$_2$Si$_X$ (with X being C or N) [27], [33]. This matches well with the composition of the M$_6$(C,N) carbonitrides observed in samples 9A and 15A by O. Quintana, except for the presence of a substantial amount of W (11-13 wt%) in said carbonitrides. However, it is known that this
precipitate does not strictly follow its chemical formula, and a W/Cr/Ni/Si-based M6C carbide has been described in the literature by M. Mostafaei et al [34].

2.2. Diffusion and Coarsening of Precipitates

Diffusion is the movement of atoms through a solution, in this case a solid solution. Overall motion is produced by concentration gradients- if the atoms are equally likely to move in any given direction, but there are more of those atoms in one region, then it will be more likely for one of the atoms to move away from the region than to move towards it, and a net flux of atoms is produced. A certain energy is required for an atom to jump to a different position, and increased temperature thus dramatically increases the diffusion rate by increasing the number of atoms with sufficient energy to do so [13]. Diffusion along grain boundaries rather than through the volume of the material reacts differently to temperature, as the energy needed for an atom to move along a grain boundary is less than for it to move through the bulk of the material. This tends to cause grain boundary diffusion to dominate at lower temperatures, as it falls off more slowly with decreasing temperature, while volume diffusion dominates at high temperatures due to the fact that grain boundaries are only a small fraction of the material [14].

The diffusion of carbon (an interstitial component of the alloy) is very rapid compared to the diffusion of chromium (a substitutional component of the alloy). This means that in the precipitation of chromium carbides, carbon can easily move to the location of the growing carbide and maintain fairly even levels throughout the remaining matrix. However, chromium is instead taken from the matrix immediately adjacent to the growing carbide, resulting in the development of chromium-depleted regions around the carbide precipitates [15]. This is known as “sensitization” due to the fact that it can make the alloy vulnerable to corrosion in the chromium-depleted regions. However, if the carbide precipitates stabilize at a given size, over time chromium
from the bulk matrix will diffuse towards the depleted zones, restoring a nearly homogeneous
distribution ("desensitization").

Coarsening of precipitates (also referred to as “Ostwald ripening” [12]) consists of the
tendency for smaller precipitates to shrink and larger precipitates to grow over time. Atoms on
the interface between the precipitate and the matrix are in a higher energy state than atoms in the
interior of the precipitate. Smaller precipitates have a larger fraction of their particles on the
interface, and are thus less stable overall than larger precipitates. Statistics will favor atoms
leaving the smaller precipitates to enter the matrix, and leaving the matrix to enter the larger
precipitates, resulting in growth of the larger precipitates at the expense of the smaller precipitates
[13]. At a constant fraction of precipitate, this results in fewer, more widely spaced precipitate
particles, reducing the strengthening effect caused by the particles interfering with dislocation
motion. This affects both short-term strength and creep resistance of the material.

2.3. Creep

Creep is another ubiquitous damage mechanism for high-temperature structural materials
consisting of permanent deformation occurring over time while under stress at high temperatures,
eventually leading to failure of the material. The critical temperature above which creep is an
important factor is typically 30%-50% of the absolute melting temperature of the material [16].
As the melting temperature for Fe-Ni-Cr alloys of this type is around 1400 °C [35], the service
temperature range of 750-1150 °C is well above the critical temperature for creep, and the reformer
tube studied here failed by severe creep deformation in the highest-temperature section.

Creep in crystalline materials such as the metal alloy studied here occurs through multiple
mechanisms grouped in several broad classes, these being diffusional flow, grain boundary sliding,
and dislocation creep [16]. All of these mechanisms are thermally activated, hence the strong effect of temperature on rate of creep and the lack of significant creep at lower temperatures.

Diffusional flow consists of vacancy diffusion either through the crystal lattice or along grain boundaries. Grain boundary sliding is movement of grains relative to one another, accommodated by diffusional flow (this mechanism is sometimes considered a subset of diffusional flow). Both of these mechanisms are promoted by a decrease in the average grain size and thus an increase in the number of grains and grain boundaries. The last category, dislocation creep, consists of dislocation movement (similar to ordinary plastic deformation, but at stresses well below the room-temperature yield strength), which is mostly unaffected by grain size but is strongly promoted by stress in the material [16].

Creep also has an effect on other damage mechanisms. Creep strain can open cracks in the protective chromium oxide layer, allowing carburization by carbon ingress through the cracks [4], [20], [21]. The necessary oxidation to re-establish the protective oxide layer also drains chromium out of the austenite matrix near the surface, hastening the failure of the material by lack of sufficient chromium to form a continuous protective scale.

2.4. **Thermal Stress**

Thermal stress is an issue that occurs due to differential strain caused by thermal expansion. If two materials are joined to one another but have different coefficients of thermal expansion, changing the temperature of the joint structure will cause internal stresses to develop that maintain equal strain in the components [16]. Alternately, similar stresses can develop if different sections of an otherwise homogeneous material are at different temperatures. The material in this study must deal with both versions; the protective chromium oxide scale has a different coefficient of thermal expansion than the underlying metal, and temperature gradients form through the metal
both in service and during furnace startup and shutdown. Maintaining significant ductility at low temperatures such that the furnace tubes can be shut down without shattering is a significant design problem, especially when combined with the equally important requirement of high strength and creep resistance at high temperatures [2]. The thermal stresses themselves can also contribute to creep in the material.
3. EXPERIMENTAL WORK

3.1. Experimental Plan

The experimental plan was to first identify and locate the magnetic zones in the material using magnetic etching with ferrofluids, reproducing and continuing work initially done by O. Quintana [1]. Four aged samples were used along with an as-cast sample for a control; the sample titles and their approximate service temperatures are given below in Table II. A depiction of the sample extraction process (performed prior to this work) is given below in Figure 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Approximate Service Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Cast</td>
<td>N/A</td>
</tr>
<tr>
<td>1A</td>
<td>750</td>
</tr>
<tr>
<td>4A</td>
<td>850 to 950</td>
</tr>
<tr>
<td>9A</td>
<td>1000 to 1150</td>
</tr>
<tr>
<td>15A</td>
<td>≥ 1150</td>
</tr>
</tbody>
</table>

After locating the magnetic regions, their structure and composition were to be analyzed so as to identify the phase present. Electron backscatter diffraction and energy-dispersive spectroscopy were chosen as the analysis methods used.
Figure 1 - Diagram of sample extraction process taken from work by O. Quintana [1]
3.2. **Sample Preparation**

The samples were first ground with increasingly fine SiC grinding paper (up to 1200 grit) and then polished using 1 µm and 0.05 µm alumina. Chemical etching was performed using glyceregia (10 mL glycerol + 15 mL HCl + 5 mL HNO₃) to show the carbide precipitates.

3.3. **Magnetic Etching with Ferrofluids**

3.3.1. **Background**

Magnetic etching with ferrofluids is a technique used to reveal magnetic regions and domains in a sample, first developed by Francis Bitter in 1932 [36]. His original method used 1 µm diameter magnetic Fe₂O₃ particles suspended in ethyl acetate. More modern ferrofluids use 10 nm diameter magnetic nanoparticles, coated with surfactants to prevent settling and agglomeration in the chosen solvent [37]. The magnetic-particle-containing suspension or colloid is placed on the surface of a sample and the particles are drawn to magnetic regions and outline magnetic domains [38]. Applying an external magnetic field with an electromagnet will enhance the contrast between ferromagnetic regions and paramagnetic regions, as the strength of the local magnetic field will be greatly increased by the energized ferromagnetic material. This method was used in the present study.

3.3.2. **Equipment Used**

The metallographic microscope (a Leco 300 metallograph with attached digital camera), electromagnet, and power supply used for magnetic etching in this study are shown below in Figure 2. A support stand was constructed for the electromagnet to avoid putting excessive stress on the specimen traversal table. For magnetic etching, one drop of ferrofluid was placed on the sample surface using a pipette, then a 35x50mm No. 1 cover slip was placed on top of the fluid to spread it out in a thin layer, hold it onto the surface when inverted, and prevent the fluid from
contacting the objective lens of the microscope. The electromagnet and power supply had been used by O. Quintana previously [1]. The magnet characteristics are given below in Table III. DC power was provided by a Shenzen-Mastech HY 3005-3 digital power supply at 30 V, resulting in a current of ~4.0 A (the current would slowly decrease during runtime due to resistive heating and the subsequent increase in resistivity of the wire). The large inner diameter of the solenoid ensures that there is a large area where the field lines will be normal to the sample surface and that the field strength will drop off slowly past the end of the electromagnet.

Figure 2 - (A) Microscope, electromagnet on stand, and power supply, (B) Close-up of electromagnet with sample in position
Table III - ELECTROMAGNET CHARACTERISTICS

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner coil diameter</td>
<td>109 mm</td>
</tr>
<tr>
<td>Outer coil diameter</td>
<td>144 mm</td>
</tr>
<tr>
<td>Length</td>
<td>75 mm</td>
</tr>
<tr>
<td>Wire Diameter</td>
<td>1 mm</td>
</tr>
<tr>
<td>Turns</td>
<td>800</td>
</tr>
<tr>
<td>Drive voltage</td>
<td>30 V</td>
</tr>
<tr>
<td>Approximate drive current</td>
<td>4 A</td>
</tr>
<tr>
<td>Approximate magnetic field</td>
<td>6 mT</td>
</tr>
<tr>
<td>(at end of electromagnet)</td>
<td></td>
</tr>
</tbody>
</table>

The ferrofluid used was purchased from Ferrotec Corporation. Initially a water-based ferrofluid (EMG 805) was used, diluted at a 3:1 ratio of water to ferrofluid with additional distilled water. This lower concentration helped prevent the ferrofluid particles from obscuring the sample features, while still leaving sufficient particles to outline the magnetic regions. However, the water in this ferrofluid tended to evaporate fairly quickly, depositing the particles on the sample surface and preventing further particle motion. As the most powerful detection method for the ferromagnetic regions was migration of the ferrofluid particles toward said regions in response to electromagnet activation, this interfered with efficient examination of the sample. Only a few good images could be taken before the sample needed to be removed and cleaned, which actually required re-grinding and polishing the sample to fully remove the particles adhered to the surface (even ultrasonic cleaning failed to remove the particles). An oil-based ferrofluid (EMG 911) was substituted, as it evaporated much more slowly. However, this ferrofluid had to be used undiluted, as additional oil of identical composition was unavailable, causing the details of the sample to be
more obscured by the ferrofluid particles. Both fluids yielded some usable images. Details of the fluids used are given below in Table IV.

<table>
<thead>
<tr>
<th>Name</th>
<th>Solvent</th>
<th>Saturation magnetization</th>
<th>Viscosity at 27°C</th>
<th>Density at 25°C</th>
<th>Magnetic particle concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMG 805</td>
<td>Water</td>
<td>22 mT</td>
<td>3 mPa·s</td>
<td>1.19 g/cc</td>
<td>3.6% by volume</td>
</tr>
<tr>
<td>EMG 911</td>
<td>Oil</td>
<td>11 mT</td>
<td>2 mPa·s</td>
<td>0.89 g/cc</td>
<td>2% by volume</td>
</tr>
</tbody>
</table>

3.4. **Electron Backscatter Diffraction**

3.4.1. **Background**

Electron backscatter diffraction (EBSD) is a scanning electron microscope-based diffraction technique. A beam of electrons produced by the SEM strikes the sample at an angle (typically the sample surface is held at 70° to the horizontal [23], [39]) and diffracts off atoms in the sample surface. The diffracted electrons produce paired diffraction cones for each diffraction plane in the material. These cones are intercepted by a fluorescent screen and the pattern of lines thus formed is interpreted to determine the crystal structure of the material [23], [39]. A good surface finish with very little damage is required for good results. In the case of hard materials like the steels examined in this study, a thorough mechanical polish can be sufficient, but otherwise electropolishing or an acid etch can be used to remove the remaining damaged layer after mechanical polishing [39].
3.4.2. **Sample Preparation**

Samples 9A and 15A were prepared for EBSD by hand polishing with 0.02 µm colloidal silica for 1 hour per sample after the initial metallographic polish that had been applied to all samples (see Section 3.2). Initial experiments showed that this was sufficient to get acceptable diffraction patterns from the hard precipitates, but diffraction from the austenite matrix was worse, especially very near the edges of the precipitates where the matrix had been shielded from polishing. An acid etch with glyceregia (10 mL glycerol + 15 mL HCl + 5 mL HNO₃) was applied after re-rubbing the samples with 0.05 µm alumina for 15 seconds to prevent flashing (a phenomenon where a heavy pattern of microscopic cracks appears in the surface of a nickel-based alloy that was polished with colloidal silica and then etched with a reagent containing Cl⁻ ions [40]). Unfortunately, this proved similarly unsuccessful. As previous efforts had managed to get good diffraction patterns off this material, further experimentation after improvement of the surface finish was planned, but the available time was insufficient. Data from previous work on these samples will be used in addition to the incomplete data gathered during these more recent attempts.

3.4.3. **Equipment Used**

Initial electron backscatter diffraction experiments were performed using the FEI Quanta ESEM with Oxford AZtec EBSD/EDS system at Northwestern University’s Electron Probe Instrumentation Center (EPIC). Later experiments were performed using a JEOL-JSM 5900LV SEM with Oxford AZtec EBSD/EDS system at Illinois Institute of Technology.
3.5. **Energy-Dispersive Spectroscopy**

3.5.1. **Background**

Energy-dispersive spectroscopy (EDS) is a form of elemental analysis commonly used in scanning electron microscopes. As the beam of electrons impacts the sample, electrons are ejected from atoms in the sample, generating characteristic x-rays as other electrons drop to lower energy levels. Different atoms produce distinctive characteristic x-rays, allowing qualitative elemental analysis of the sample [23]. Some quantitative analysis is also possible through comparison of the relative intensities of the various characteristic x-rays. In bulk samples, scattering of the electron beam within the material results in x-ray generation from a teardrop-shaped volume approximately 1 µm in size; this puts a limit on the spatial resolution achievable for such samples [23], [41]. Sample preparation specifically for EDS was not necessary, as any surface finish sufficient for good results from EBSD will also give good results from EDS.

3.5.2. **Equipment Used**

Both SEMs used for EBSD were also capable of performing EDS. As EBSD was given priority over energy dispersive spectroscopy, and efforts to produce good diffraction data within the available time were unsuccessful, no new energy dispersive spectroscopy was performed. However, some data is available from previous work on these samples, including some wavelength dispersive spectroscopy.
4. RESULTS AND DISCUSSION

The results from experiments done during this study are presented and discussed here, along with results from previous studies on these samples when current experimental results were unavailable or insufficient. First the results from magnetic etching with ferrofluids are given, with discussion of the location and size of the detected magnetic regions and comparison to earlier results. Then the results from electron backscatter diffraction are shown. As mentioned earlier in the Experimental Work section, difficulties with achieving the required surface finish prevented the acquisition of the desired data, but some of the results are nevertheless presented and compared with earlier results using the same technique. Finally, as was also mentioned in the Experimental Work section, no new results were obtained using energy dispersive spectroscopy, but results using the same or similar techniques on the same samples are presented and related to the other data shown here.

4.1. Magnetic Etching with Ferrofluids

Magnetic etching of the as-cast sample provides an example of the behavior of the ferrofluid on a paramagnetic material. As shown below in Figure 3 and Figure 4, the magnetic nanoparticles are visible only as an overall darkening of the sample surface with the electromagnet off (being far too small to be individually observable in an optical microscope), but they form into randomly distributed visible clusters under the influence of an external magnetic field. This clustering is typical behavior for the ferrofluid in such a situation, and is not an indication that the sample is ferromagnetic [38]. This confirms that the as-cast material is paramagnetic.
Figure 3 - As-cast sample with ferrofluid, electromagnet off

Figure 4 - As-cast sample with ferrofluid, electromagnet on
Examination of sample 15A using the water-based ferrofluid showed that the magnetic particles were weakly attracted to the carbide-matrix interfaces with the external magnetic field off, and very strongly attracted to said interfaces when the field was turned on. Figure 5 and Figure 6 below show this behavior. This implies that there is ferromagnetic material present at the carbide-matrix interfaces. Further examination of this sample showed that these areas were present on almost every carbide throughout the entire thickness of the sample. As these areas did not exist in the undamaged material, it is clear that one or more of the high-temperature damage processes was responsible for their creation. This sample was taken from the highest-temperature region of the failed furnace tube, with the most visible creep damage. It is known that creep strain can damage the protective chromium oxide layer on the surface of the material, allowing ingress of gas-phase carbon from the carburizing atmosphere present in the furnace tube [4]. In this particular sample, it is also known that the precipitates were not pure carbides but rather carbonitrides, the material having picked up nitrogen from the atmosphere outside the furnace tubing [1]. Normally, chromium-depleted regions initially form around these chromium-rich precipitates, but once all the carbon or nitrogen in the material has been incorporated into precipitates time at high temperature allows chromium from the bulk matrix to diffuse towards the depleted zone, restoring more even levels [15]. However, this material had a continuous source of additional carbon and nitrogen from the atmosphere inside and outside the tube, which would result in continuous precipitate growth. Thus, chromium-depleted regions adjacent to the carbides could persist even with the material held at high temperatures for long periods of time. It is known that Fe-Ni-Cr alloys become increasingly magnetic as the Cr content drops below 15% [25], so such chromium-depleted zones could be the cause of these magnetic regions.
Figure 5 - Sample 15A with ferrofluid, electromagnet off

Figure 6 - Sample 15A with ferrofluid, electromagnet on
Examination of sample 9A with the same ferrofluid found only a few carbides with magnetic regions. All of these were close to the inner diameter of the sample. The vast majority of the material displayed a similar response to magnetic etching as the as-cast sample (i.e., sample 9A was almost wholly paramagnetic). Figure 7 and Figure 8 show an area containing some of the few carbides with magnetic regions, along with many carbides that have no associated magnetic regions. Consistency with the hypothesis that localized chromium depletion is responsible for the formation of magnetic regions would require that the rate of carbon/nitrogen intake is limited in this sample compared to sample 15A. The rate is not zero, as this sample (like sample 15A) contains carbonitrides as well as carbides, implying that the protective oxide scale has at times been damaged enough to allow absorption of nitrogen from atmosphere outside the furnace tube. However, supporting evidence for the rate being lower is present in the fact that the precipitates in this sample are visibly smaller and have a lower volume fraction than those in sample 15A. This could be explained by the fact that creep strain in the original furnace tube was visibly less for sample 9A (see Figure 1), which would reduce the relative rate of gas ingress through reduced damage to the oxide scale from said creep strain. The average chromium content of the austenite matrix was also higher in sample 9A compared to sample 15A (~20 wt% versus ~13 wt%) [1], which would allow for easier healing of the oxide scale after damage.
Figure 7 - Sample 9A with ferrofluid, electromagnet off

Figure 8 – Sample 9A with ferrofluid, electromagnet on
The oil-based ferrofluid was used to do a full-thickness survey of both sample 9A and sample 15A, starting at the outer diameter and taking pictures at approximately 1mm intervals. As mentioned earlier in the Experimental Work section on magnetic etching, the oil-based ferrofluid was used for this survey because the water-based ferrofluid evaporated too quickly to take more than a few pictures before the solvent evaporated and deposited the ferrofluid particles on the surface, which would significantly reduce the effectiveness of the technique for detecting small ferromagnetic regions.

This survey of sample 9A found no detectably magnetic regions in the bulk of the sample, giving additional confirmation that only a few specific locations in said sample contained magnetic regions. However, metal adjacent to regions of corrosion-product scale on the outer diameter of both sample 9A and sample 15A showed strong magnetism. This is shown below in Figure 9, Figure 10, Figure 11, and Figure 12. Note the distinctive “coral” patterns typical of ferrofluid particles attracted to individual magnetic domains on the metal, along with regions of densely packed magnetic particles at the metal-scale interface. The former supports the hypothesis that chromium depletion results in the metal matrix becoming magnetic, as it is well known that chromium depletion occurs in the matrix underneath the chromium oxide scale [20]. The latter is consistent with the discovery of magnetite (Fe₃O₄) in the oxide scale of sample 15A by O. Quintana using X-ray diffraction [1], as well as others in the literature in similar samples [42]. However, in the study by Quintana, mechanical removal of the oxide scale from sample 15A only reduced the sample’s overall magnetic susceptibility by approximately 21.5%, indicating that the majority of the magnetic response actually came from the internal regions of magnetic metal [1].
Figure 9 – Sample 15A outer diameter with ferrofluid, electromagnet off

Figure 10 – Sample 15A outer diameter with ferrofluid, electromagnet on
Figure 11 – Sample 9A outer diameter with ferrofluid, electromagnet off

Figure 12 – Sample 9A outer diameter with ferrofluid, electromagnet on
Image-Pro® Plus 4.5 image analysis software was used to measure the thickness of the magnetic regions as indicated by the bands of particles for three carbides in both sample 9A and 15A. The results of this analysis are shown in Figure 13 and Figure 14. The average width for sample 15A is 3.9 µm, which disagrees with magnetic force microscopy data from O. Quintana [1] showing the magnetic carbide-matrix interface to be 1.5 µm wide at most (see Figure 15). I suspect this is caused by the magnetic particles in the ferrofluid gathering as closely as possible towards the magnetic region, with more particles close enough to be affected by the magnetic field from the energized ferromagnetic material than can be packed into the region directly above the material, increasing the apparent width of the magnetic region. The few magnetic regions detected in sample 9A had an average measured width of 1.8 µm. This width is not directly comparable to MFM results, as no interfacial magnetic regions were detected in sample 9A using such [1]. That lack is consistent with the magnetic etching results above showing that the vast majority of sample 9A does not contain interfacial magnetic regions. The few such regions that were found (see Figure 8) are mostly a result of the fact that the magnetic etching technique works well at low magnifications, allowing large fields of view for more effective searching.

The primary purpose of these measurements was to determine the level of magnification and resolution necessary to accurately image the regions of interest using EBSD and EDS. It might also be possible to analyze the volume fraction of magnetic regions and correlate it with various damage parameters (the hardness of the matrix, Larson-Miller parameter, etc) in order to use it as a method of damage measurement, but this seems slow, destructive and inefficient compared to non-destructive measurement by overall magnetic response already considered by O. Quintana [1].
Figure 13 – Three carbides in sample 15A with magnetic region width measurements
Figure 14 – Three carbides in sample 9A with magnetic region width measurements
4.2. **Electron Backscatter Diffraction**

Electron backscatter diffraction was intended to be used to identify the crystal structure of the area of interest. Unfortunately, the technique requires an extremely good surface finish on the area of interest, and I was unable to achieve such in the time available. The best phase image obtained is shown below in Figure 16. The blue area was successfully indexed as Mz(C,N). The white area is where the software was unable to successfully index the crystal structure, typically because there was no distinct pattern at all (any residual surface damage can severely degrade diffraction pattern quality, as the technique samples only the surface layer of the material [39]). The scattered points inside the non-indexed area are too few and far apart to be treated as reliable
data, and are more likely matches to statistical noise from the vague patterns obtained in that region (Martin Detrois, personal communication, August 4, 2014). The unindexed diagonal line in the area of $M_2$(C,N) was matched to an interface between two adjacent carbide particles. The scale is different in the x and y directions because the sample was held at 70° to the horizontal (see Experimental Procedure), and thus 1 µm along the sample surface appears longer in one direction when viewed as a two-dimensional image taken from a direction not parallel to the surface.

Further experimentation is needed to properly index the areas of interest at the carbide-matrix interface in this sample. A more successful large-area EBSD indexing image from work by O. Quintana is given below in Figure 17 for contrast. This image demonstrates that good diffraction patterns are possible from the austenite matrix, so long as the surface is sufficiently well prepared. It also seems to show that, at least in sample 9A, the austenite matrix’s crystal structure is maintained near the interface between the matrix and the carbide, although the magnification and resolution is lower than I would like in order to state this conclusively.
An EBSD image of this quality focused on the carbide-matrix interface would be very useful in conclusively determining whether the appearance of the magnetic regions is a true phase transformation with accompanying crystal structure changes, or simply a result of compositional changes in the austenite matrix.

Figure 17 – (a) EBSD phase map superimposed over the left half of (b) SE image near the outer diameter of sample 9A. (c) and (d) are diffraction patterns from small M_{23}C_6 carbides at points 1 and 2 respectively in (b). Taken from work by O. Quintana [1].
4.3. **Energy-Dispersive Spectroscopy**

As mentioned earlier, no new EDS was performed on these samples, as it was planned to be done after EBSD to aid in characterization in case the crystal structure was not sufficient by itself (e.g. characterizing the composition of the austenite matrix at the carbide-matrix interface if it was determined that no phase transformation had occurred at said interface). However, the localization of the magnetic regions with magnetic etching strongly suggests that the chromium content in the magnetic regions was much lower than average for the matrix. It is well known that chromium depletion occurs both near the protective oxide scale (with chromium being oxidized to replace damage to the scale [6]) and near chromium-rich carbides (with chromium being taken up into the carbides [43-45]), and both of these locations are where we find the magnetic regions. Previous work by O. Quintana on these samples has also confirmed that the average chromium content of the bulk austenitic matrix decreases with increasing damage, to a minimum of 12-13 wt% in sample 15A [1], which is already substantially lower than the overall as-cast chromium content of 28.8%, and just barely above the minimum required to form a continuous oxide scale. The hypothesis of chromium depletion being responsible for the magnetic regions in the austenite matrix is consistent with data from Stevens et al [25] showing that as the Cr content of a Fe-Ni-Cr alloy decreases, the ferromagnetic character of the alloy increases, particularly once under 15 wt% Cr.
5. CONCLUSIONS

1. Magnetic etching with ferrofluids is a very useful technique for qualitative detection of small ferromagnetic regions embedded in a paramagnetic material, due to effectiveness at low magnification allowing for large fields of view.

2. Magnetic etching does not give perfect quantitative results. While the qualitative location of the region will be accurate, the exact size can be inaccurate when compared with more sensitive techniques like magnetic force microscopy. This appears to be because excess colloidal particles gather around the edges of the magnetic region. In larger magnetic regions, the domains will be outlined by the particles and only the very edges of the region will have the excess particles, but for small regions such as encountered near internal precipitates in this study, the domains are too small to be seen and only these “edge regions” are visible. These clusters of ferrofluid particles extend further outward than the true extent of the magnetic region. This extra size is actually part of what allows the technique to be useful for detecting very small magnetic regions at low magnifications, at least in this case.

3. Sample preparation for electron backscatter diffraction was difficult, as it requires a very good surface finish, and the area of interest was a very small region of austenite (likely softened by chromium depletion) immediately adjacent to a hard carbide or carbonitride precipitate.
4. Magnetic regions form over time in regions of the sample usually associated with chromium depletion from the Fe-Ni-Cr matrix. However, this depletion was not confirmed by spectroscopy, and further study is recommended to provide conclusive evidence.

5. Only the sample taken from the highest-temperature region of the furnace tubing had the severe degree of damage required for massive and continuous carburization/nitridation, resulting in the development of persistent chromium-depleted zones around internal precipitates despite the high service temperature allowing for diffusion of chromium from the bulk matrix towards said depleted zones.
6. CITED LITERATURE


