Structural and Magnetic Studies of an Ex-service Cast Austenitic Steel Tube Used in Hydrogen Reformers

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THESIS
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This dissertation is dedicated to the memory of my beloved godmother Maruja; who taught me that life is better when is simple.
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SUMMARY

Direct reduction iron (DRI) is an alternative for the production of pure Iron. In this process, the reduction of iron ore (Fe₂O₃) by a reducing gas mixture (H₂ + CO) occurs without melting. The production of hydrogen is carried out by steam reforming of natural gas (CH₄) in catalyst-filled tubes. These tubes are Fe-Cr-Ni alloys and have an external diameter of 284 mm and wall thickness of 13 mm. This process takes place at an internal pressure of 0.2 MPa and temperatures of about 1030 °C. However, overheating caused by deficient reformer feed gas stream and other anomalies can bring up this temperature up to 1200 °C shortening its life expectancy.

In the present work, a retired centrifugally cast austenitic tube that underwent different levels of creep degradation along its length, was studied. The tube life was shortened to about 5 years due to overheating. The exposure temperatures were in the range of 750 – 1150 °C; from the top to the center of the tube; where a bulge developed as a result of excessive heat. Selected samples were extracted taking in consideration the location and exposure temperature. Rough magnetic studies were initially done on the bulk material of each selected sample using a scale-magnet fixture; revealing a progressive increase in the magnetic response with the degree of degradation. Consequently, these samples were studied metallographically using several analytical techniques in order to identify changes in the matrix composition, new phase formation or carbide transformation that can impart any magnetic response. Furthermore, magnetic and micro-magnetic studies were carried out to correlate quantitatively and qualitatively these microstructural changes with magnetic behavior. Moreover, microhardness measurements were
performed on the austenitic matrix of each selected sample to evaluate any change in mechanical properties caused by creep deterioration.

Our goal is to find a relationship between magnetic behavior and changes in microstructural morphology, mechanical properties, and creep degradation at different exposure temperatures along the tube length. Ultimately develop a non-destructive method based on changes in the magnetic response of samples with different degree of creep deterioration; that allow us to anticipate or signal the onset of critical damage, and calculate the remaining life of service-exposed samples; so that proper maintenance schedules can be arranged.
CHAPTER 1
INTRODUCTION

Direct reduction iron (DRI) is an alternative for the production of pure Iron. In this process, the reduction of iron ore (Fe₂O₃) by a reducing gas mixture (H₂ + CO) occurs without melting. The production of hydrogen is carried out by steam reforming of natural gas (CH₄) in catalyst-filled tubes. These tubes have an external diameter of 284 mm and wall thickness of 13 mm. This process takes place at an internal pressure of 0.2 MPa and temperatures of about 1030 °C [1]. However, overheating caused by deficient reformer feed gas stream and other anomalies can bring up this temperature up to 1200 °C shortening its life expectancy.

Reformer tubes are centrifugally cast manufactured and exhibit exceptional corrosion resistance at high temperatures. Owing to their high Fe, Cr and Ni contents; they possess an austenitic matrix which has paramagnetic properties at room temperature. However, it has been observed that as the alloy creeps it becomes ferromagnetic [2–4]. This shift in physical behavior has been addressed in the past [5], by studying the variation of ternary phase concentration (Fe-Cr-Ni) with Curie temperature. In particular; Stevens et al [2] made use of these previous results to study, by means of Magnetic Force Microscopy (MFM) measurements, the changes in the magnetic behavior of a highly carburized cast austenitic tube alloy (31 wt. % Fe, 37 wt. % Ni, 25 wt. % Cr, with molybdenum, titanium, zirconium and boron additions.). He found that this transformation is accompanied by depletion of Cr, due to the formation of Cr-rich carbides; and an enrichment of Fe and Ni in the matrix as the material is enriched in C from the inner tube atmosphere. These localized regions around the carbides increase with time of service creating a
chemical composition that is expected to induce magnetic behavior. Not many studies [6,7] took advantage of this phenomenon to correlate the degree of degradation with magnetic properties. However, at the University of Illinois at Chicago (UIC); there has been an extensive program in using magnetoelastic techniques to study the deterioration of materials due to corrosion or creep [8–10]. For instance, Polar et al [10] studied the microstructural changes caused by time-temperature-stress degradation (creep) in a ferromagnetic 410 stainless steel by means of magnetic hysteresis curves. He found a good correlation between the changes in coercivity and microstructural degradation under creep, and it was concluded that carbide precipitation and growth have a more significant impact on pinning the wall domains, which affect magnetic properties. Magnetoelastic techniques have been performed as a destructive test but, by working with ArcelorMittal R&D it was anticipated that magnetic measurements can be used as a non-destructive test to evaluate creep degradation.

In the present work, a retired centrifugally cast austenitic tube that underwent different levels of creep degradation along its length was studied. The tube life was shortened to about 5 years due to overheating. The exposure temperatures were in the range of 750 – 1150 °C; from the top to the center of the portion of the tube studied; where a bulge developed as a result of excessive heat. Selected samples were extracted taking in consideration the location and exposure temperature. Rough magnetic studies were initially done on the bulk material of each selected sample using a scale-magnet fixture; revealing a progressive increase in the magnetic response with the degree of degradation. Consequently, these samples were studied microstructurally; using several analytical techniques in order to identify changes in the matrix composition, new phase formation or carbide transformation that can impart any magnetic response. Furthermore,
magnetic and micromagnetic studies were carried out to correlate qualitatively these microstructural changes with magnetic behavior. Moreover, microhardness measurements were performed on the austenitic matrix of each selected sample to evaluate any change in mechanical properties caused by creep deterioration. Our objective is to find a relationship between this magnetic behavior with changes in microstructural morphology, mechanical properties, and creep degradation at different exposure temperatures along the tube length. Ultimately, develop a non-destructive method based on changes in the magnetic response of samples with different degree of creep deterioration; that allow us to anticipate or signal the onset of critical damage, and calculate the remaining life of service-exposed samples; so that proper maintenance schedules can be arranged.
CHAPTER 2
LITERATURE REVIEW

2.1. The MIDREX® Direct Reduced Iron (DRI) Process

Direct Reduction Iron (DRI) is the removal of oxygen from iron ore without melting. It is probably the most popular technology for converting iron ore into high purity iron for use in steel making applications. Midrex® DRI generally uses hydrogen as a reducing agent, and the chemical reactions that take place are as follow [11]:

\[
\begin{align*}
\text{Fe}_2\text{O}_3 + \text{H}_2 & \rightarrow 2\text{Fe} + 3\text{H}_2\text{O} \tag{2.1} \\
\text{Fe}_2\text{O}_3 + 3\text{CO} & \rightarrow 2\text{Fe} + 3\text{CO}_2 \tag{2.2}
\end{align*}
\]

Figure 1. Schematics of the Midrex® DRI process showing the hydrogen reformer section [11]
Figure 1 shows the schematic of the Midrex® DRI process where the main features are indicated. It is apparent from this figure that the reduction of iron ore takes place in the shaft furnace, where iron ore passes down through it; in the opposite direction to hydrogen. As the material moves downward, the oxygen content of the iron ore feed material is progressively removed by hydrogen gases that are passing up through the bed. It is evident, thus, that steam-methane reformer is crucial for this technology to exist.

The production of hydrogen is carried out in high alloy steel tubes where the following reactions more likely occur in the presence of a nickel catalyst [1]:

\[
\begin{align*}
    CH_4 + H_2O & \rightarrow CO + 3H_2 \\
    CH_4 + CO_2 & \rightarrow 2CO + 2H_2 \\
    CO + H_2O & \rightarrow CO_2 + H_2 \\
    CH_4 + 2H_2O & \rightarrow CO_2 + 4H_2
\end{align*}
\]

The hydrogen reforming process consists of catalyst-filled bank tubes; with an external diameter of 284 mm and wall thickness of 13 mm (see Figure 2). The chemical reactions taking place are highly endothermic; which means that the process is carried out at high temperatures (~1030 °C) at a pressure of about 0.2 MPa.

In addition to this type of deterioration, there is a series of other anomalies, such as uneven heat distribution inside the reformer tube bank, and overheating caused by deficient reformer feed gas stream that may compromise the integrity of reformer tubes [12–15].
Reformer tubes play an important role in the performance of DRI process. The tube life is limited by creep, which is driven by a combination of the stability of the alloy properties at high temperature and service conditions. Although reformer tubes are designed to last no less than 100,000 hours (~11 years), premature failure occurs if either the microstructure of the alloy at the intended service conditions is unstable, or service conditions exceed the alloy limitation. The most common plant conditions influencing the tube alloy microstructure destabilization are the following [16–21]:
• Service temperature:

Continuous fluctuation of the service temperature causes acceleration of the microstructural changes in the tube. Despite short-term variations, when the temperature increases beyond the alloy limit; the microstructure changes are so drastic that intense creep or remelting of dendrite spaces take place instantaneously. Moreover, short-term variations in temperature generate thermal stresses in the tube wall.

• Atmosphere conditions inside and outside the tube:

Reformer tubes are high alloy steels where a protective chromium oxide layer builds-up on the surface and keep oxygen from reaching the actual alloy. The tube deterioration starts when this oxide layer breaks down and oxidizing or carburizing atmosphere invades the alloy grain boundaries (GBs). Consequently, Cr-oxides or Cr-carbides form in the subsurface regions; impoverishing the surrounding matrix.

• Mechanical and thermal stresses:

Pressure, load and vibrations during the process cause breakdowns of the protective Cr-oxide layer on the tube surface. This facilitates the invasion of the aggressive atmosphere into the alloy, accelerating the creep deterioration.

Therefore, it is paramount that appropriate operating conditions are maintained in order to extend the average reformer tube life. Furthermore, it is also important to implement suitable monitoring methods to prevent catastrophic failures and unplanned shutdowns.
2.2. Metallurgical Studies of Reformer Tubes

Hydrogen reformer tubes are subjected to extremely harsh working environments; involving high temperatures, stresses, and corrosion. Owing to these severe operation conditions, they are generally fabricated from centrifugally cast creep-resistant high C austenitic steels, as contemplated in the standard ASTM A297 [22,23]. Table 1 shows the chemical composition of some grades of alloys extracted from this standard, highlighting the alloys type HP and HK; which are the most commonly used for this application. This standard provides complete information, e.g. mechanical properties, manufacturing, chemical composition, etc, on different series of alloys. We can also observe that the maximum amount of Ni (~ 68.0 wt. %) corresponds to the alloy type HX, while the highest Cr content (~ 30.0 wt. %) belongs to the alloy type HD. Although alloy type HP is generally taken as a benchmark for further development of heat resistant steels [23], continuous research and development, using modern computational science-based tools have been applied to improve the physical and mechanical properties of alloys used for these applications [24–28]. However, the main elements for all heat resistant alloys are Ni and Cr; which enhance a series of properties as discussed next.

<table>
<thead>
<tr>
<th>Grade</th>
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<th>Composition, % (max. except when range is given)</th>
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<tr>
<td></td>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>HK</td>
<td>25 Chromium, 20 Nickel</td>
<td>0.2-0.6</td>
</tr>
<tr>
<td>HX</td>
<td>17 Chromium, 66 Nickel</td>
<td>0.35-0.75</td>
</tr>
<tr>
<td>HD</td>
<td>28 Chromium, 5.0 Nickel</td>
<td>0.5 max</td>
</tr>
<tr>
<td>HP</td>
<td>26 Chromium, 35 Nickel</td>
<td>0.35-0.75</td>
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</table>
Sufficient Ni content plays an important role by improving the carburizing resistance since it decreases the carbon solubility in the alloy [29]. On the other hand, the oxidation resistance is guaranteed by sufficiently high Cr content (≥ 20 wt.%) [30]. Under most conditions a slow-growing scale of Cr₂O₃ and spinel (Mn,Fe) Cr₂O₄ is formed. Additional protection is possible by the incorporation of elements having a higher oxygen affinity than that of Cr, e.g. Silicon or Aluminum. If these elements are present in a content of 1.5 wt. % or more, they may form a more or less continuous sublayer of oxides beneath the Cr₂O₃ layer. Reactive elements such as Cerium, Yttrium or Niobium can be added in small amount (about 0.1 wt.%) and have beneficial effects on the adherence and protectiveness of the scales [12,14,15,30–32]. A thorough overview of the effects of other alloying elements on centrifugally cast austenitic steels will be discussed further in the next chapter.

### 2.2.1 Effect of Alloying Elements

As mentioned earlier; centrifugally cast austenitic stainless steels with Cr/Ni ratios of 25/20 (Type HK) and 26/35 (Type HP) are generally used for tubes in steam reforming furnaces. The typical microstructure of these as-cast alloys is an austenite matrix with intergranular eutectic-like primary rich carbides such as; M₇C₃ or M₂₃C₆ [33–39]. As the alloys are exposed to high service temperatures; fine secondary carbides are formed interdendritically while at the same time primary carbides dissolve. Creep resistance basically depends on the distribution of fine, strong, and stable particles [23]. However, the propensity for particle coarsening increases at high temperature, due to surface energy minimization [40,41]. This process occurs as a diffusion process, consequently, the higher the temperature the faster the diffusion. Thus, it is paramount
to stabilize the fine dispersion of particles. This is carried out by adding carbide stabilizing elements such as; Nb, Ti, Y, W, Zr, Si and other rare-earths (RE) elements (Ce+La+Hf) [33,40,42–50].

Among all these elements, Nb is probably the most important one in all heat resistant materials, produced as centrifugally cast tubes. Additions of Nb, or Nb+Ti, to HP steels were found to promote the fragmentation of the as-cast microstructure and the partial replacement of chromium carbides by more stable ones [47,51]. These carbides, as shown in Figure 3, are MC-type carbides (NbC, TiC or (Nb,Ti)C), which are more resistant to coarsening; have high melting temperature, and are prone to remain in their position without changing their crystalline volume during exposure to high temperatures [52].

Figure 3. Back Scattered Electron (BSE) image showing the microstructure of a Fe-Cr-Ni-Nb-W alloy. MC-type carbides and chromium carbides are pointed out.
However, it has been reported that when adding only Nb (2.5 wt. %) to a 25Cr-35Ni cast austenitic alloy; there is an in-situ transformation of NbC into a silicide known as G-phase [46–48,53,54]. This phase was first identified by Soares et al [42] at temperatures between 700 and 1000 °C, and has been found to be an intermetallic topologically close-packed (TCP) phase with stoichiometry; Ni$_{16}$Nb$_6$Si$_7$ [42]. Piekarski et al [45] found that when adding Nb+Ti+Si to a 0.3C-20Ni-18Cr cast steel; the G-phase had the following stoichiometry; Ni$_{16}$(Nb,Ti)$_6$Si$_7$. Nevertheless, it has been observed that interfaces G-phase/matrix are preferential sites for creep crack nucleation [47,55]. Thus, it is important to control or restrain the transformation of (Nb,Ti)C into G-phase. According to Almeida et al [47], since G-phase does not dissolve Ti, this element would control this transformation process. Moreover, when adding Ti, finer and more evenly distributed secondary carbides, and smaller fraction of G-phase were found, thus superior creep properties were obtained. In addition, it is also widely believed that the G-phase precipitation tends to increase with increasing the content of Si in cast steels [56]. Ibanez et al [57] reported that when adding 2.62 wt. % of Si to a centrifugally cast modified-HP steel with 1.97 wt. % Nb; NbC precipitates were almost completely transformed to G-phase. Not to mention, the detrimental effects of high Si contents, such as; risk of ferrite and sigma phase ($\sigma$) formation.

Nunes et al [48] studied the addition of Yttrium (Y) to a centrifugally cast NbTi-modified HP steel. He found that, owing to the high reactivity of Y with C, and the early solidification of yttrium carbides, these particles served as heterogeneous nucleation sites for primary chromium carbides; promoting fragmentation of carbides thus resulting in improved creep properties. Furthermore, Yan et al [44] reported that Y played also an important role in the refinement of
impurity, which has a positive effect on the ductility of the alloy. Yan et al also investigated the
effect of W when added to an yttrium modified-HP40Nb steel, showing that W additions refine
the microstructure during solidification. In addition, W was found to restrain the phase
transformation of NbC into G-phase, which resulted in improved stability of mechanical
properties during aging. Other authors addressed that, even though W is not a strong MC-type
carbide former, it has a profound effect on the distribution of MC carbides [58], and has also
been reported to dissolve into the secondary $\text{M}_{23}\text{C}_6$ carbides thus increasing the thermal stability
of the carbides and high temperature long-term creep rupture strength [59–61].

Additions of Zr and rare-earth (RE) have been studied in combination with other elements
such as; Nb and Ti. Wen-Tai and Honeycombe [50] investigated the microstructural effects of
adding combinations of Nb+Zr and Nb+Ti+Zr to HK40 and IN519 steels in order to confer
additional creep rupture strength. The most effective combination was Nb+Ti+Zr, which
modified the NbC microstructure from a lamellar to a granular morphology. Moreover, it was
also reported that secondary (Nb,Ti,Zr)C precipitates possessed greater resistance to coarsening
during creep.

Following Wen-Tai and Honeycombe findings, further investigations were made to add these
elements to modified-HP40Nb steels; combined with rare-earths as additional carbide forming
and refining elements. Kirchheiner and Woelpert [52], at Schmidt and Clemens GmbH, found
that a combination of Ce+La+Hf was the most effective and economic addition of RE. In fact, a
modified-HP40Nb steel alloyed with these RE combination (HP-Micro grade) showed higher
creep strength at temperatures up to 1100 °C (See Figure 4), due to a subtle carbide distribution,
NbC mixed with chromium carbides along the grain boundaries, and Ti+Zr+RE mainly dispersed in the matrix. Moreover, it was also reported a better carburization resistance and creep ductility. Despite improvements in alloying technology; other routes have been explored in order to improve creep properties [37,38,62–65]. In recent years, many researchers have been improving the fabrication of reformer tubes through a new process that consist of a regular centrifugally cast process coupled with an electromagnet. The introduction of magnetic forces during this stage greatly improved the creep properties of centrifugally cast stainless steel tubes by modifying the direction of solidification, which causes the refinement of the grains and promotes the increment of chromium carbide along the grain boundaries [37].

Figure 4. Ranking in creep resistance of micro alloyed materials, showing with a red bar the difference between the HP40 mod. Nb steel and the same alloy but modified with RE (redrawn from [52]).
Centrifugally cast austenitic stainless steels exhibit two different microstructures, basically because of the fast cooling rate in the metallic moulds. Columnar or elongated grains near the outer wall, and equiaxed grains close to the inner wall (Figure 5). Generally, creep cavities and cracks initiate within the inner surface; where thermal and hoop stresses combine synergically [52]. However, cracks would propagate slower in equiaxed grains compared to columnar structures, which ultimately improve creep properties.

![Figure 5. Macro-etched image of a Fe-Cr-Ni-Nb-W alloy showing the dual microstructure through the tube wall.](image-url)
2.3. Creep Degradation

Creep deformation is an unrecoverable plastic deformation that takes place when materials are exposed to high temperatures ($> 0.4 \ T_m$, where $T_m$ is the absolute melting temperature of the material); and at a constant applied stress over an extended period of time. This process is diffusion-controlled thus, it becomes of particular importance in materials experiencing extensive periods of time at elevated temperatures [66], such as the conditions that reformer tubes undergo. Creep occurs because dislocations in the crystal structure are able to diffuse across grain boundaries and other discontinuities which normally inhibit plastic flow [21].

Many investigation have been published in this subject [67–72] in order to elucidate the creep behavior of a wide range of metals and metallic alloys. In particular; Nabarro [67] categorized creep in commercially pure polycrystalline metals under constant stress into four stages. An instantaneous initial elastic strain, followed by Stage I; a decelerating creep region called Andrade $\beta$, Stage II; which denotes that portion where almost a steady-state Andrade $\kappa$ creep takes place, and Stage III; where the strain rate ($\dot{\varepsilon}$) increases leading to fracture. All these stages are shown in Figure 6, however; attention is usually focused on steady-state creep in stage II, which often dominates the creep behavior.
There are two broad mechanisms by which steady-state creep takes place in metals; diffusion 
creep and dislocation creep [66,71]. Diffusion creep, as its name implies; occurs by transport of 
vacancies via diffusion within the grain. This process is driven by a gradient of free energy; 
created in this case by the applied stress. Figure 7a illustrates the principle of Nabarro-Herring 
(N-H) diffusion creep; where depletion of vacancies take place along grain boundaries that 
undergo compressive stress; while a corresponding excess of vacancies occur along those grains 
experiencing tensile stress [66]. The movements of these vacancies produce an increase in length 
of the grain along the direction of the applied stress. Moreover, diffusion creep can also take 
place along the grain boundaries, in the so-called Coble diffusion creep (C). As Figure 7b shows, 
in this process there is a build-up of particles along the grain boundaries that are nearly parallel.
to the tensile axis, while depletion of these particles takes place in areas closely perpendicular to the tensile axis.

Both N-H and C creep have been found to be proportional to the applied stress, nonetheless, they both are sensitive to grain size; having that N-H creep strain-rate is proportional to the inverse square root of the grain size, whereas; C creep strain-rate is proportional to the inverse cube root of the grain size [72–74].

Conversely, *Dislocation creep* involves the movement of dislocations, which requires higher stresses but relatively low temperatures. This process occurs intragranularly and the sequential

![Figure 7. Illustration of the principal of diffusion creep showing the (a) Nabarro-Herring diffusion creep taking place through the grains, and (b) Coble diffusion creep, taking place along the grain boundaries (redrawn from [73]).](image-url)
mechanisms that take place are; dislocation glide creep and dislocation climb creep. Figure 8 shows the schematics of these mechanisms.

Since diffusion is required for dislocations to climb; the process is temperature-dependent. Furthermore, this is the basic controlling mechanism in steady-state creep of solid solution alloys. There are two other creep mechanisms that occur at relatively low stresses and involve a combination of both; diffusional and dislocation creep; they are Harper-Dorn (H-D) creep and Grain boundary sliding (GBS). Unlike other creep processes, in H-D creep there is still no
consensus regarding the understanding of the phenomenon and its microstructural characteristics [75]. Nevertheless, there are some characteristics of its behavior that appear inconsistent with conventional N-H creep. The most important are described as follows [75,76]:

(i) First, the steady-state creep strain rate is significantly higher, by more than two orders of magnitude, than those expected for bulk or grain-boundary diffusion controlled creep.

(ii) The steady-state creep strain is independent of the grain size and it is the same for pure metals and solid solutions.

(iii) H-D creep is suppressed by the presence of small grains, precipitates or most importantly; initial high dislocation density.

(iv) It is characterized by a dislocation density that is independent of the applied stress; and is the same for pure metals and solid solutions.

In contrast, GBS is perhaps the least understood low-rate creep mechanism that usually occurs at high temperatures. Sliding is a grain displacement mode in which grains shear relative to each other at grain boundaries. The strain produced by GBS can range from a few percent up to 90% of the total strain; depending on the material and testing conditions [77]. As shown in Figure 9, the displacements can be easily recorded by using marker lines scratched on the actual surface of the sample. After creep test, GBS is observed by the shear separation of the lines where they cross the grain boundaries. According to Cannon and Nix [78]; there are two types of sliding processes identified as:
(i) Lifshitz sliding. This sliding is associated with the accommodation of diffusion creep such that when the grains become elongated; there is no net increase in the number of grains following the direction of the applied stress.

(ii) Whereas Rachinger sliding accounts for the relative displacement of grains during high-temperature creep such that they retain substantially their original shape. In this case; the number of grains lying along the direction of the applied stress, increases.

Figure 9. Schematic of the GBS mechanism showing a marker line scratched on the polished surface of the sample (a) before creep test and (b) after creep test (redrawn from [77]).

It is well established that under Rachinger sliding at high-temperature creep; nucleation, growth, and subsequent interlinkage of grain boundary cavities lead to the premature failure of the material [79–81]. Cavities are frequently observed to nucleate at the grain boundaries normal
to the applied stresses [69,82,83], and there have been proposed various theories that fall into the categories shown in Figure 10 [69]. Once cavities nucleate, creep deterioration takes place through cavity growth; being the main mechanisms:

- by diffusion-controlled cavity growth, which occurs at elevated temperatures; thus favoring diffusion on the cavity surface, and ultimately causing migration and transport along the grain boundary. In contrast, when low temperatures are present, creep void growth takes place through plasticity, where one of the mechanisms could be dislocation-glide controlled.

- Another mechanism is grain boundary sliding; where cavities would generally grow in the plane of the boundaries. This mechanism is more likely to occur at high strain rates and closely spaced cavities, characteristics of the later stages of creep. Moreover, the fact that cavities are rather spherical instead of plate-like or lenticular, suggests that cavity growth does not essentially involve sliding, having that diffusive cavity growth rates are larger than growth rates by grain boundary sliding [69].

- Constrained diffusional cavity growth is another mechanism for which some cavities are present only on isolated grain boundaries. These uncavitated areas can constrain those areas undergoing elongation due to the additional influence of cavitation, in this case, coalescence of cavities may be controlled by plastic creep rate [69,84].
Cavities can also grow by plasticity, this occurs as a result of creep deformation of the material surrounding the grain boundary cavities in the absence of a vacancy flux. This mechanism becomes of great importance in systems under high strain conditions.

Figure 10. Cavity formation mechanisms (a) showing the sliding of grains leading to cavitation from ledges and triple points, (b) a high strength cavity nucleation from vacancy condensation, (c) by cavity nucleation from a Zener-Stroh mechanism and finally (d) by the formation of a cavity when a particle-obstacle is present, along with a combination of the previous mechanisms (redrawn from [69]).

- Cavities can also grow by plasticity, this occurs as a result of creep deformation of the material surrounding the grain boundary cavities in the absence of a vacancy flux.

This mechanism becomes of great importance in systems under high strain conditions.
where significant strain is achieved. It has been also suggested that void growth during creep plasticity can be accompanied by other diffusion controlling mechanisms. Consequently, material from the cavity is deposited on the grain boundary by grain boundary diffusion; causing an increment in the length of the specimen due to the deposition of atoms over the diffusion length. Furthermore, in the presence of creep plasticity in regions ahead of the cavity; this deposition distance increases further. Figure 11 shows an illustration of the coupled mechanism for cavity growth.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{coupled_cavity_growth.png}
\caption{Schematic of the coupled diffusion-plasticity creep-controlling mechanism (redrawn from [69]).}
\end{figure}

Ultimately, creep rupture occurs as intergranular fracture and it takes place when cracks and voids form and coalesce along grain boundaries. Fracture may develop as wedge-like cracks
(“w” voids) when high stresses are present, instead of spherical shaped voids (“r” voids). However, it is believed that wedge crack can also occur as a consequence of spherical voids accumulation.

In hydrogen reformer tubes, with low condition stresses and high temperatures (~0.8 $T_m$), failure is believed to occur due to stresses caused by the temperature gradient through the tube wall; which is an order of magnitude greater that the stress caused by the pressure in the tubes [21]. Furthermore, start-up and shut-downs result in cycles of alternate tension and compression, which will eventually cause the failure of the component. In addition, service related carburization/oxidation also contribute to the premature failure [41].

2.4. Correlation Between Microhardness and Creep Degradation

Nearly half a century has passed since the introduction of the parameter that correlates temperature and time for the extrapolation of creep data. The first study was done by Larson and Miller, who introduced the concept of a parametric function ($\varnothing$) that included stress and temperature as variables. The function has the following form [85]:

$$\varnothing = f(\sigma, t)T(C + \log t) \quad (2.9)$$

Where; $\sigma$ is the applied stress, $t$ is the rupture time, $T$ the absolute temperature and $C$ is a constant. However, in order to apply this method for the estimation of the remaining life during
routine inspections in industrial plants, it is indispensable to test extracted samples under conditions of accelerated creep [85]. This process can be time consuming and may involve uncertain results. In contrast, hardness measurements can also indicate the resistance of the material to deformation thus; it can provide an estimate of the degree of damage in a material previously exposed to temperature and stress for long periods of time. Moreover, its simplicity, economy (of space, time and material), portability and its virtually non-destructive characteristics make of this technique a potential non-destructive test method to estimate loss of mechanical properties and creep resistance [85,86]. Initial studies to correlate hardness measurements with creep resistance were done by Kohlhofer and Penny [86] however, recently other efforts have been done in order to correlate hardness and Larson-Miller parameter (LMP) in 9Cr–1Mo–V–Nb [87], 1Cr–1Mo-0.25 V [88–90], and 2.25Cr-1Mo steels [85].

Figure 12 (a) shows that the LMP follows a linear correlation with the hardness of crept 2.25Cr-1Mo steel. Moreover, Masuyama [87] also found a linear correlation with the hardness of an aged and crept 9Cr–1Mo–V–Nb steel. As we expected; hardness decreases as the materials deteriorate, however, in the case of the aged materials almost a bilinear behavior was found, as shown with dashed lines in Figure 12 (b). It was observed that the amount of reduction in hardness in the case of the aged materials was lower compared to the softening of crept materials. Therefore, this technique is sensitive enough to associate the microstructural changes in the material such as; carbide coalescence and contribution of solid solution, with creep resistance (LMP) for any particular steel.
Figure 12. LMP plotted against (a) Hardness on crept specimens of 2.25Cr-1Mo steel tested at different stresses and temperatures (redrawn from [85]), and (b) Hardness on a series of crept and aged specimens of a welded 9Cr–1Mo–V–Nb steel (redrawn from [87]).
It is anticipated that this work will present a new way to calculate the remaining life of ex-
service reformer tubes by correlating the degree of degradation, by means of LMP calculations,
with hardness measurements. However, in addition we will take advantage of the changes in the
magnetic behavior of the materials as it deteriorates to further predict the remaining life of ex-
service reformer tubes [91]. The next section will go into the details of the magnetic behavior of
centrifugally cast austenitic stainless steels.

2.5. Magnetic Behavior of Cast Austenitic Steel Alloys

When a material is placed in a magnetic field \( \mathbf{H} \), this is magnetized. This magnetization is
described as magnetization vector \( \mathbf{M} \). Since the magnetization is induced by the field; we can
assume that \( \mathbf{M} \) is proportional to \( \mathbf{H} \).

\[
\mathbf{M} = \chi \mathbf{H}
\]  \hspace{1cm} (2.10)

Where \( \chi \) is the proportionality constant; known as the magnetic susceptibility of the medium.
Depending on the response to the influence of a magnetic field; magnetic materials may be
classified as diamagnetic, \textbf{paramagnetic}, antiferromagnetic, \textbf{ferromagnetic}, and ferrimagnetic.
A more detailed discussion about these classes of materials can be found in texts [92,93]. We
will limit our discussion to the phenomena that occurs in our study by defining paramagnetic and
ferromagnetic materials.
In paramagnetic materials some of the atoms or ions have a net magnetic moment because of the unpaired electrons in partially filled orbitals. These magnetic moments have insignificant interaction with each other and can orient themselves without any restriction (Figure 13a). Thus, the magnetization is zero when the field is removed. However, in the presence of a field, there is a partial alignment of the atomic magnetic moments in the direction of the field, therefore, they posses a positive magnetic susceptibility ($\chi > 0$). Pierre Curie investigated the magnetic properties of various paramagnetic materials, finding that at finite temperatures the particles in the material are thermally excited and free to take random orientations. Consequently, he formulated that for a given temperature; the magnetization, $M$, is directly proportional to the applied field, $H$. Equation 2.11 defines the law of paramagnetism of Curie; which states that the susceptibility is inversely proportional to the absolute temperature.

\[
\chi = \frac{C}{T} \tag{2.11}
\]

Where $C$ is a constant known as the Curie constant, and $T$ is the absolute temperature. $\chi$ is positive and becomes infinite at absolute 0 °K; and decreases when $T$ increases.

In contrast, in ferromagnetic materials; the magnetic moments have the tendency to align parallel to each other in the presence of a magnetic field (Figure 13b). However, contrary to paramagnetic materials, these moments will remain parallel when the magnetic field is no longer applied. Nevertheless, high temperatures provoke thermal agitation that leads to small or negative susceptibilities, $\chi < 0$. 

28
This phenomenon was described by the Curie-Weiss law [93], shown in equation 2.12.

\[ \chi = -\frac{C}{T - T_c} = \frac{M}{H} \quad (2.12) \]

Where \( C \) is called the Curie constant, \( T \) is the temperature of interest and \( T_c \) is the Curie temperature. From this equation we observe that at temperatures above \( T_c \), the susceptibility, \( \chi \), changes as the material becomes paramagnetic, and has a singularity when \( T = T_c \). At this
temperature and below; there exists a spontaneous magnetization, because if $\chi$ becomes infinite then we can have a finite $M$ for zero $H$.

As mentioned in section 2.2.1; centrifugally cast austenitic stainless steels with Cr/Ni ratios of 25/20 (Type HK) and 26/35 (Type HP) possess an austenite matrix with intergranular eutectic-like primary rich carbides such as; $M_7C_3$ or $M_23C_6$ [33–39]. The austenitic matrix is basically a Fe-Cr-Ni alloy with cubic $\gamma$-FCC structure ($Fm\overline{3}m$) that possesses paramagnetic properties at room temperature, which involves having a curie temperature below a typical room temperature of 20°C. However, as the alloys are exposed to high service temperatures and carburizing environments; fine secondary carbides are formed interdedritically while at the same time primary carbides coarsen and get enriched with alloying elements such as; Cr, W, Nb, Si, etc, leaving a Ni and Fe rich matrix and interfaces carbides/matrix [94–100]. This new austenitic matrix is still a $\gamma$-FCC structure ($Fm\overline{3}m$), nonetheless, it behaves ferromagnetically. Stevens et al [2] studied this phenomenon, looking at the Fe-Cr-Ni phase diagram and Curie temperatures of different alloys.
After gathering selected experimental data for various ternary alloys dependence of the Curie temperature; it was possible to determine a paramagnetic-ferromagnetic boundary that defines regions where the austenitic matrix behaves ferromagnetically. In Figure 14, this ferromagnetic region has been shaded in yellow; and it is apparent from this ternary phase diagram that as the Cr content decreases, or the Fe content increases in the austenitic matrix, it is likely to switch from the paramagnetic region into the ferromagnetic one (see letters A and C in Figure 13).

Figure 14. Fe-Cr-Ni phase diagram showing ferromagnetic (open symbol data) and paramagnetic (star symbol) material at 20 °C. The shaded area defines the compositions that behave ferromagnetically [2].
Not many studies took advantage of this particular phenomenon to correlate the degree of creep/carburization and magnetic properties [101–105]. However, many studies have been done in order to develop non-destructive techniques using magnetic changes in the material for the study of the sensitization of austenitic stainless steels, corrosion of low carbon steels, etc [9,91,98,99,106–113]. The objective of this study is to determine the microstructure conditions leading to this transition in magnetic behavior, which may provide key information regarding a critical stage of creep, e.g. tertiary stage that could be used as benchmark to measure remaining tube life. Furthermore, two advanced magnetic techniques are utilized to study what accounts for the magnetic behavior in the materials at the micro level. The next section gives details of these techniques.

2.5.1. **Characterization techniques to detect micrometer-sized ferromagnetic regions**

Two magnetic techniques were utilized in order to detect micrometer-sized ferromagnetic regions in crept specimens; Magnetic Force Microscopy (MFM) and Magnetic Etching with Ferrofluids (MEwF). MFM is probably the technique most commonly used to detect magnetic changes during phase transformations in stainless steel alloys [100,104,107], sensitization of austenitic stainless steels [98], or for the same purpose this work is about [3,7]. However, not many investigations have been done using the so-called MEwF technique [114], which can actually be as sensitive as MFM. The specifications of these techniques are detailed below.
2.5.1.1. Magnetic Force microscopy (MFM)

*MFM*, is a variety of Atomic Force Microscopy (AFM) where a sharp tip is coated with a magnetic film and used to scan a magnetic sample. The coated tip interacts with the magnetic domains in the sample and reconstructs the magnetic structure of the surface. This technique can be carried out at ambient temperature, in ultra high vacuum, in liquid environment, and at different temperatures. Nevertheless, the interaction with the surface contaminant layer has a stronger influence on the tip than the Van Der Waals interactions. Therefore, the solution to this problem is to keep the topography influence constant by letting the tip follow the surface at a certain height [115]. This constant distance (\(\Delta h\)) that separates the surface signal contributions is called “lift mode”. Figure 15 shows the schematics of the method where we can observe that in the first scan the topography is measured, while the second scan re-traces the first one; acquiring magnetic information.

![Figure 15. Schematic of the MFM technique in “lift mode”. The first pass measures the topography and the second one records magnetic information of the previous pass.](image)
Magnetic data can be recorded as variations of amplitude, frequency, or phase of the cantilever oscillation. However, phase detection and frequency modulation give the best results. Equation 2.13 shows the phase detection correlation ($\Delta \Phi$); where $Q$ is the quality factor of resonance, $k$ is the spring constant of the cantilever, $F$ is the external oscillating force, and $z$ is the displacement of the tip generated by the external force. It is important to notice that an attractive interaction ($\partial F/\partial z > 0$) would lead to a negative phase shift (dark contrast in the image), while a repulsive interaction ($\partial F/\partial z < 0$) gives a positive phase shift (bright contrast) [116–119].

$$\Delta \Phi \approx -\frac{Q}{k} \frac{\partial F}{\partial z}$$

(2.13)

2.5.1.2. Magnetic Etching with Ferrofluids (MEwF)

MEwF is a technique first time used by F. Bitter [120] in 1932 to reveal magnetic domain walls, and further studied by R.J. Gray et al [114] at Oak Ridge National Laboratory on the early 70’s; to detect the transformation of $\delta$-ferrite to $\sigma$-phase in stainless steels. This technique consist on placing magnetic liquid, which is colloidal suspension of small ferrimagnetic particles in a carrier liquid, on the polished surface of a magnetic sample subdivided into domains. The particles are attracted by the fringing magnetic fields and decorate the domain walls (Figure 16). These decoration patterns can be examined by means of optical microscopy.
Back in 1930s, ferromagnetic magnetite particles (Fe₃O₄) were in the order of microns or more. Moreover, they were unstable (particles sink or agglomerate) and when a magnetic field was applied they would solidify. It was until 1960s that technology to make stable ferrofluids; of 3 to 15 nm in size, was available. The stability involves; remaining liquid even when subjected to intense magnetic fields, and displaying a magnetic susceptibility sufficiently strong for them to behave like magnetic liquids [121]. Furthermore, for ferromagnetic particles not to agglomerate; they are coated with a polymer layer to isolate one from each other. These are surfacted ferrofluids, being the polymer in question the surfactant. Because of its size; the ferrofluid particles have no domain walls and consequently possess single magnetic domains. It behaves like a paramagnetic material; and is called superparamagnet due to its large magnetic moments of the entire particle which aligns in the field, while in normal paramagnetic materials; only the small moments of single ions are aligned in the field.
CHAPTER 3

EXPERIMENTAL WORK

3.1 Technical Approach

The samples for this work came from a bulged tube removed from service in a hydrogen steam reforming furnace after 44,000 hours service (5 years). During the reforming process; the tubes were exposed to temperatures in the range of 900 - 1030 °C, and under a pressure of 0.2 MPa. However, premature failure was caused by overheating at temperatures exceeding 1150 °C, which ultimately caused the bulging of the tube (Figure 17). Figure 17 also shows the overall length of reformer tubes (~ 10.0 m) and the location of the tube segment (~ 1.70 m) corresponding to the zone that underwent the highest temperatures, and where the samples were extracted from.

3.2 Characterization of Retired Reformer Tube

A considerable portion of this study was devoted to the characterization of samples extracted from the ex-service reformer tube. The understanding of phase transformations and microstructure evolution was of primary concern in order to correlate this microstructural changes with the magnetic response of the bulk material.
Figure 17. a) A top view of the steam reformer furnace, and b) its corresponding view from the inside, during shutdown inspections. c) A tube segment of ~ 1.70 m was removed from the top; where the samples for this study were extracted from.
3.2.1. **Thermal History, Selection of Samples and Composition of Samples**

The specimens for this study were selected from locations that would reflect different thermal histories and hence provide key information on the transitional changes based on gradual temperature increases. Although no details were provided about the thermal history of the tube under study, the tube segment presented a bulge located almost in the middle, which implied that this portion was exposed to the highest service temperature and stresses (> 1150 °C). Moreover, the top portion of the tube segment underwent the lowest temperatures due to insulation with fire brick around it, being the temperature in the range of 750 and 850 °C. Consequently, as Figure 18 shows; the samples were selected such that an assessment can be made of the gradual changes in the microstructure starting at the lowest service temperature (sample 1A), a low intermediate temperature (sample 4A), high intermediate temperature (sample 9A), and at the highest temperature range (sample 15A). Table 2 shows the estimated service temperatures of the selected samples. It was presumed that the microstructure in sample 1A would be closest to the as-cast condition and thus have undergone little or no change in microstructure with no creep damage. But then the microstructural changes would become more prominent as the specimens approached the bulge.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Mean exposure temperature (°C)</th>
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<tbody>
<tr>
<td>1A</td>
<td>~ 750</td>
</tr>
<tr>
<td>4A</td>
<td>850 &lt; T &lt; 950</td>
</tr>
<tr>
<td>9A</td>
<td>1000 &lt; T &lt; 1150</td>
</tr>
<tr>
<td>15A</td>
<td>≥ 1150</td>
</tr>
</tbody>
</table>

Table 2. Estimated service temperatures of selected samples.
Figure 18. Retired hydrogen reformer tube showing the location of the bulge and the procedure followed in order to extract the samples for this study.

Notes
ID: Inside diameter wall
OD: Outside diameter wall
\( \phi_{\text{Out}} \): Outside diameter in meters
Figure 18 shows the procedure followed in order to extract the samples for this study. The ~1.70 m long tube segment was sliced into 68 sections of 1” thick, where 34 of these sections along the tube were obtained however, as shown in Figure 18, only the samples 1A, 4A, 9A and 15A were selected to perform further characterization studies. After samples were extracted, they were hot mounted in bakelite to reveal the through-thickness of crept samples from the OD to ID; and the characterization techniques mentioned in the next section were carried out.

The steel composition of the crept reformer tube under study was provided by ArcelorMittal Global R&D, and Table 3 shows the chemical composition. It is worth to mention that metallurgical studies were also performed on the as-cast condition steel in order to compare the microstructure of the initial conditions with that of the crept samples.

<table>
<thead>
<tr>
<th>Fe</th>
<th>C</th>
<th>Ni</th>
<th>Cr</th>
<th>W</th>
<th>Si</th>
<th>Mn</th>
<th>S / P</th>
<th>Ti</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>0.52</td>
<td>48.4</td>
<td>28.8</td>
<td>4.16</td>
<td>0.81</td>
<td>0.87</td>
<td>&lt; 0.02</td>
<td>0.08</td>
<td>Add.</td>
</tr>
</tbody>
</table>

3.2.2. **Structural Characterization of Selected Samples**

The characterization techniques utilized in this study include: Light Optical Microscopy (LOM), Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS), Electron Probe Microanalysis with Wavelength Dispersive Spectroscopy (EPMA-WDS),

3.2.2.1. Light Optical Microscopy (LOM)

Samples were hot mounted in bakelite; rough polished with 240, 400, 600, and 1200 grit silicon carbide papers, and finished with 1.0 and 0.05 \( \mu \)m alumina paste. After polishing, the samples were etched with Glyceregia (10 ml glycerol + 15ml HCl + 5ml HNO\(_3\)) chemical reagent, and LOM observations were done using a LECO 300 Metallograph optical microscope with an attached digital camera.

3.2.2.2. Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS)

The SEM-EDS analysis was carried out using a Hitachi S-3000N with backscattered electron and scanning electron mode. The samples were prepared using the same procedure followed for LOM. Furthermore, SEM-EDS was also done during Electron Back-Scattered Diffraction (EBSD) studies using a SEM-JEOL JSM7000F with an HKL Technology EBSD system.
3.2.2.3. Electron Probe Microanalysis -Wavelength Dispersive Spectroscopy (EPMA-WDS)

The equipment employed for EPMA-WDS studies was the JEOL JXA-8600 microprobe equipped with three spectrometers containing the analysis crystals listed in Table 4, and an Advanced Microbeam automation system and Probe for Windows (spot analysis) and Scandium (mapping). EPMA-WDS analysis was performed at an accelerating voltage of 20 kV and a probe current of 20 nA. For identification of light elements, such as N or C; the accelerating voltage was lowered to 10 kV. Furthermore, Table 5 shows other experimental conditions used for quantitative elemental analysis.

Table 4. Crystals used in EPMA-WDS analysis.

<table>
<thead>
<tr>
<th>Crystal name</th>
<th>Type</th>
<th>(2d) (Å)(^\ast)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAP</td>
<td>Thallium acid phthalate</td>
<td>25.8</td>
</tr>
<tr>
<td>LDEC</td>
<td>Ni/C Multi-layer</td>
<td>98</td>
</tr>
<tr>
<td>LiF</td>
<td>Lithium fluoride</td>
<td>4.028</td>
</tr>
<tr>
<td>PET</td>
<td>Pentaerythritol</td>
<td>8.742</td>
</tr>
</tbody>
</table>

\(^\ast\)Where \(2d\) is the lattice d-spacing of the crystal used.
An EBSD system attached to a Scanning Electron Microscope (SEM) was used with this technique. The SEM was a JEOL-JSM7000F with a Channel 5 EBSD software from HKL Technology (see Figure 19), plus a high resolution camera for crystallographic measurements. Sample surface preparation was done with colloidal silica (0.02 μm) by polishing for 2 hours and EBSD was carried out on a specimen tilted 70° and 10 kV of accelerating voltage. While, EBSD phase mapping was carried out at 20 kV at a working distance of 10 mm and at a step-scan of 0.5 μm.

### 3.2.2.4. Electron Backscattered Diffraction (EBSD) Techniques

**Table 5. Experimental conditions used for quantitative elemental analysis.**

<table>
<thead>
<tr>
<th>Element</th>
<th>X-ray line used for microanalysis</th>
<th>Number of Spectrometer used</th>
<th>Crystal used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>$K_\alpha$</td>
<td>1</td>
<td>TAP</td>
</tr>
<tr>
<td>C</td>
<td>$K_\alpha$</td>
<td>1</td>
<td>LDEC</td>
</tr>
<tr>
<td>O</td>
<td>$K_\alpha$</td>
<td>1</td>
<td>LDEC</td>
</tr>
<tr>
<td>N</td>
<td>$K_\alpha$</td>
<td>1</td>
<td>LDEC</td>
</tr>
<tr>
<td>Cr</td>
<td>$K_\alpha$</td>
<td>2</td>
<td>LiF</td>
</tr>
<tr>
<td>Ni</td>
<td>$K_\alpha$</td>
<td>2</td>
<td>LiF</td>
</tr>
<tr>
<td>S</td>
<td>$K_\alpha$</td>
<td>2</td>
<td>PET</td>
</tr>
<tr>
<td>Ti</td>
<td>$K_\alpha$</td>
<td>2</td>
<td>LiF</td>
</tr>
<tr>
<td>W</td>
<td>$L_\alpha$</td>
<td>3</td>
<td>LiF</td>
</tr>
<tr>
<td>Fe</td>
<td>$K_\alpha$</td>
<td>3</td>
<td>LiF</td>
</tr>
<tr>
<td>Nb</td>
<td>$L_\alpha$</td>
<td>3</td>
<td>PET</td>
</tr>
<tr>
<td>Mn</td>
<td>$K_\alpha$</td>
<td>3</td>
<td>LiF</td>
</tr>
</tbody>
</table>
3.2.2.5. Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) was used to characterize fine intragranular precipitates observed in the reformer tube microstructure. Samples of the tubes were obtained by cutting slices approximately 500 μm thick using a Leco Vari/Cut VC-50 low speed diamond-impregnated saw. These slices were then mounted on a disc grinder (Gatan 623) and ground off to a thickness of about 80 μm. Slices were then mounted on a tripod polisher (South Bay 590W) and one of the faces was polished up to 1.0 μm finish with diamond lapping films (9, 5, and 1 μm).
The polished surface was bonded to a supporting copper grid, while the unpolished side was subjected to mechanical dimpling using a South Bay 515 dimpling instrument until the thinnest part of the sample is approximately 10 μm or less. The dimpled surface was then polished using colloidal silica slurry (50 nm). To obtain electron transparency, the sample was subjected to ion-milling (Fischione 1010) using argon ions with 4kV potential/4mA emission current at a gun angle of 15 degrees for less than 10 hours, followed by 3kV/3mA at a gun angle of 6 degrees for an hour.

The TEM sample was then placed in a double-tilt sample holder before being loaded into the JEOL JEM-3010 transmission electron microscope operating at 300kV with a filament current approximately 125 μA. The perforation made during the ion mill step was then located using the low magnification “SCAN” mode. Adjacent to the hole will be areas thin enough to be imaged by the TEM. Once located, the area of interest was then observed in “ZOOM” mode to obtain bright-field images. SAD patterns were obtained in “DIFF” mode. Images were collected using a Gatan digital imaging system with a Windows XP computer running Digital Micrograph software (see Figure 20). There are two cameras, an intensified TV camera for set up and a multi-scan 1K x 1K CCD camera. The microscope is also fitted with a Thermo Noran Vantage XEDS system with a light element X-ray detector.
As we can observe from Figure 21, the volume fraction of chromium carbides and voids/cracks were measured using image analysis (Image-Pro® Plus 4.5) on all selected specimens color etched with a modified Murakami’s reagent (30 g NaOH, 30 g $K_3[Fe(CN)_6]$, 100mL $H_2O$, at 100 °C, for 10 s). A minimum of 30 images were taken from different locations through the thickness of the sample. Volume fractions for each sample were then correlated with the estimated service temperatures and hardness of the austenitic matrix.

3.2.2.6. Image Analysis

Figure 20. Digital Micrograph software showing the analysis of a high resolution image obtained from a precipitate.
3.2.2.7. X-Ray Diffraction (XRD)

Mounted samples were polished up to 1.0 μm, etched with Glycergia and placed in a device especially design to hold the bakelite mounted specimen in the diffractometer. As shown in Figure 22, a portion of the cross section of the specimen was scanned. The equipment used was the Siemens D5000 with Cu Kα radiation, λ=1.5418 Å, at 40 KV and 30 mA. The scanning range was 26°–100°, in steps of 0.02° for 10 seconds to better resolve the peaks.
3.2.3. Magnetic Characterization of Selected Samples

Magnetic measurements of crept specimens were carried out in the bulk of the material and at the micro level, using the techniques mentioned in the section 2.5.1. Bulk measurements were performed at ArcelorMittal Global R&D and at the Joining Science and Advance Materials Research Laboratory (JSAMRL) -UIC. The next section will give details of the techniques utilized and developed.

Figure 22. XRD set-up used for scanning of mounted samples.
3.2.3.1. **Bulk Magnetism Measurements – UIC**

These measurements were carried out using the set up presented in Figure 23. A powerful magnet was placed first in a stand on top of the balance (Figure 23a) and the scale was set to zero. A stand for the test samples was placed over the magnet to avoid touching the magnet. The test samples were placed at a fixed short distance from the magnet (Figure 23b). As the specimen is placed on top of the stand, an attraction force will ensue if the material is magnetic and then a negative reading would result. Figure 23c shows the schematics of the technique. Samples were tested in two different conditions. First, the as crept samples with their oxide layers (close to OD and ID) were studied; and these values were compared to the values obtained when the oxide layers were removed from the samples. This procedure would permit to study the effect of the oxide layer in the magnetic behavior of crept samples.

3.2.3.2. **Bulk Magnetism Measurements – ArcelorMittal R&D**

At ArcelorMittal Global R&D, magnetic measurements of crept tubes were carried out in the actual location of the reformer plant. In addition, selected crept reformer tubes were removed from the hydrogen plant and brought to the R&D facilities, where magnetic measurements were performed for the second or third time. Since the technique developed at ArcelorMittal Global R&D is a proprietary technology; we will not address any specific detail. However, we will present the results related to the reformer tube this study is based on.
Figure 23. Set-up for the magnetic measurements of selected crept samples, showing (a) the first step in setting up the magnet and its stand, (b) setting up the sample stand and the actual sample, (c) and schematics of the technique.
Figure 24 shows the illustration of the method in which we can observe the different elements utilized. The electromagnet was constructed by coiling an aluminum spool (4 ½ in. ID, 1/8 in. wall thickness) with 800 turns of copper wire (Ø1.0 mm). As shown in Figure 25, the magnetic field was generated by connecting the electromagnet to a digital DC power supply (Shenzen-Mastech HY 3005-3) in monopolar mode. The parameters utilized were 30 V and ~4.0 A. Moreover, Table 6 lists the water-based ferrofluids with 10 nm nominal particle diameter selected from Ferrotec Corp. USA. The ferrofluid chosen was diluted in pure distilled water in a ratio of 1:3 and approximately 10 mL of this dilution was applied on the surface of the specimen to be studied using a micropipette. Observations were done after applying the magnetic field perpendicular to the surface; using an optical microscope and switching the electromagnet ON, to apply the magnetic field, and OFF to remove it. Areas as large as ~ 340 x 450 μm² were possible to study with this technique.

Table 6. Specifications and physical properties of selected ferrofluids.

<table>
<thead>
<tr>
<th>Ferrofluid Type</th>
<th>Saturation Magnetization (Ms)</th>
<th>Viscosity @27°C</th>
<th>Density @25°C</th>
<th>Magnetic Particle Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMG 308</td>
<td>6.6 mT</td>
<td>2 mPa·s</td>
<td>1.06 g/cm³</td>
<td>1.2 % vol</td>
</tr>
<tr>
<td>EMG 607</td>
<td>11 mT</td>
<td>&lt;5 mPa·s</td>
<td>1.1 g/cm³</td>
<td>2 % vol</td>
</tr>
<tr>
<td>EMG 805</td>
<td>22 mT</td>
<td>3 mPa·s</td>
<td>1.19 g/cm³</td>
<td>3.6 % vol</td>
</tr>
</tbody>
</table>
Figure 24. Illustration of the MEwF method.

Figure 25. Set up showing all the elements used in the MEwF method.
3.2.3.4. MFM

MFM studies were carried out in Tapping® mode at ambient conditions in a conventional Atomic Force Microscope (AFM); Nanoscope III SPM Multimode scanning probe from Digital Instruments (DI, Veeco Metrology Group, Santa Barbara, CA) as shown in Figure 26. The MFM probes utilized were from BudgetSensors, Bulgaria (Multi75M-G) with a resonance frequency of approximately 75 kHz, a spring constant of 3 N/m, and tip radius of <60 nm. Magnetic images were acquired in “lift-mode”, which can be explained as the tip recording the topography in Tapping® mode in the first pass; followed by the lifting of the tip at a certain height (75 – 85 nm) and recording the magnetic behavior of the previously recorded topography in the second pass. MFM probes were magnetized with a permanent magnet with a magnetic field of 3800 Gauss prior to imaging. Areas as large as 60 x 60 μm² were possible to study with this technique.

3.2.4. Vickers Microhardness Evaluation

Micro-hardness of matrix was globally measured in all selected samples using a LECO M-400 Vickers hardness tester. A load of 1000 gf, was selected to measure the hardness of the bulk material and a load of 10 gf. was selected in order to evaluate only the hardness of the austenitic matrix, isolating the effect of the carbides in the hardness measurement (Figure 27). The idea is to correlate the effect of time and temperature on the hardness of crept samples. An average of thirty to fifty measurements was taken per specimen.
Figure 26. (a) Nanoscope III SPM Multimode scanning probe from Digital Instruments and (b) the MFM holder and probe used.

Figure 27. Image analysis of hardness indentations performed with a Vickers micro-indenter with 10gf. load. Only the austenitic matrix was studied.
4.1. **Evaluation of Bulk Creep Damage**

After long exposures to the service high temperatures, the microstructure will be expected to change. It was presumed that the microstructure in sample 1A would be closest to the as-cast condition and thus have undergone little or no change in microstructure. This is because it was exposed to the lowest temperature range. However, the microstructural changes and creep damage are expected to become more prominent as the samples approached the bulge, which is the portion of the tube exposed to the highest temperature range (1030-1150 °C). A low magnification mosaic of the dendritic structure for each of these locations was assembled as shown in Figure 28. The micrographs depict not only the changes in the dendritic microstructure, but also point to the degree of creep damage experienced in each of these locations.

Sample 15A shows the greatest microstructural changes and creep damage. Moreover, thinning of its cross section thickness is evident. Major creep damage is seen both at the OD and ID, accompanied by extensive cracking across the wall thickness. The dendritic microstructure, compared to sample 1A, has practically disappeared and carbides have coarsened and creep cavitations are quite extensive (Figure 29d). Sample 9A comes from a region above (outside) the bulge; the microstructure is mostly cellular, with OD and ID void damage, and cracking (Figure 28), but the creep damage and level of cracking is most extensive in sample 15A. Significant
carbide coarsening was observed when examining the sample at higher magnifications. Figure 29c is a high magnification LOM image of sample 9A that was etched to reveal particularly the carbides. It is seen in this figure that several carbides agglomerate by a grain boundary, and it appears that some carbide transformation is occurring based on the different shapes that can be visually identified. A better description of these carbides is described in a later section.

Figure 28. LOM images of the cross section of samples 1A, 4A, 9A, and 15A showing the microstructures and damage from OD to ID.
Sample 4A showed reduced creep damage; the dendritic structure is also maintained for most of its thickness (~ 9.6 mm from the OD), but some dendrite break-up and some cellular structure is observed in the third of the thickness closer to the ID (Figure 28). Figure 30a shows this transition from a dendritic to a more cellular structure at a higher magnification; note also the presence of creep void that already indicates some evidence of early damage (Figure 30b). Further evidence of the dendrite break up and carbide coarsening can be seen in the higher magnification micrograph in Figure 29b; where interdendritic eutectic carbides coarsen, together with notable secondary carbide precipitation.

Figure 29. Higher magnification LOM images of samples (a) 1A, (b) 4A, (C) 9A and (d) 15A shown in Figure 28.
Figure 30. LOM images of the etched sample 4A. Sample was estimated to be exposed to ~ 900 °C. Spot (a) located at ~ 9.6 mm from the OD showing the change in microstructure from dendritic to cellular, and spot (b) close to ID showing only cellular microstructure.
Sample 1A appears to have maintained its original dendritic structure throughout most of its thickness, some small coarsening or dissociation of the dendritic makeup is observed at the ID (Figure 31). Figure 32 is a higher magnification of selected locations near the OD and ID that provides evidence of the subtle carbide and dendrite differences. While Figure 32a shows a finer eutectic like morphology of carbides; it is apparent from Figure 32b that the eutectic like morphology becomes coarser.

Figure 31. LOM images of the etched sample 1A. Spot (a) close to OD and (b) close to ID.
Furthermore, we observed in sample 1A that secondary carbide precipitation has already started around the eutectic like carbides, which is also found by some other investigators [36,41,122–125]. This confirms that some degradation was experienced by this sample compared to the original as-cast condition material (Figure 33).

Figure 32. High magnification LOM images of the etched sample 1A exposed to an estimated temperature of 750°C. (a) Spot close to OD and (b) close to ID.
Figure 33. High magnification LOM images of the (a) etched as-cast sample and (b) sample 1A, exposed to an estimated temperature of 750°C.
Figure 34. LOM images of areas close to OD and ID, respectively; for samples (a-b) 1A, (c-d) 4A, (e-f) 9A and (g-h) 15A.
Another indication of creep deterioration in the material was the carbide denuded zones found close to the OD and ID walls, and characterized by a larger void density. These regions became depleted in alloying elements due to the oxidizing environment at high temperatures in the hydrogen reformer furnace (OD); and also because of the carburizing environment inside the tube (ID). Figure 34 summarizes all these areas for all samples studied. The following list provides the depth of these carbide depleted zones.

1A - ID: 0 µm, OD: 0 µm

4A - ID: ~40 µm, OD: ~0 µm

9A - ID: ~200 µm, OD: ~500 µm

15A - ID: ~200 µm, OD: ~550 µm

We can see that as the material reaches a certain deterioration level; the depleted zones close to OD and ID become almost stable.

The next section provides thorough characterization of these samples (1A, 4A, 9A and 15A), however, for comparison purposes, in some cases we will address results for other samples also extracted from the ex-service tube.
4.2. Submicroscopic Changes During Creep Damage

The metallographic analysis via LOM only revealed changes in the matrix of the steel based on modifications of the dendrite microstructure and coarsening of the primary carbides, accompanied with the precipitation of secondary carbides. The aging or creep damage of these steels, as it is known, can be correlated with changes in carbide size and composition. Due to the limited resolution of the light microscope the carbide analysis was performed with SEM-EDS, SEM-EPMA/WDS, FE-SEM, and TEM. In addition, diffraction techniques by means of XRD, EBSD, and SAD were used to determine the phase composition of precipitates in each sample studied.

4.2.1. Identification of Major Elemental Composition of Microstructural Features and Preliminary Damage Assessment via SEM-EDS

As mentioned in the literature review, section 2.2.1; the carbides encountered in alloys HP type 25Cr-35Ni + TiNb additions, are of the type M$_{23}$C$_{6}$, or M$_{7}$C$_{3}$ (where M = Cr) along with fine secondary intragranular carbides of the form; MC. Therefore, it was expected that precipitates in sample 1A were of the types MC and M$_{7}$C$_{3}$. These carbides were located within the eutectic dendrite network and contained several alloy elements. Figure 35 is a back-scattered electron (BSE) image of a region that shows basically all precipitates found in sample 1A. Some sulfides, primarily manganese sulfides (MnS), were also found and in several instances these were located next to primary carbides. Moreover, as seen in Figure 35c and Figure 36; EDS
micro-analysis was performed on selected precipitates to identify the major chemical elements present. Having the approximate chemical composition from the EDS analysis, it was possible to have a better idea of the expected precipitates, such as; MnS, NbC, (Nb,Ti)C, M$_{23}$C$_6$, and M$_7$C$_3$.

Figure 35. BSE image of a region in sample 1A showing (a) all precipitates found and (b) a zoomed detail corresponding to the squared area “1” in “(a)”, showing secondary carbides around Cr-rich precipitates, and (c) another zoomed detail corresponding to the squared area “2” in “(a)” showing an EDS line-scan across a (Nb-Ti) rich precipitate, next to Cr-rich carbides.

Sample 1A is considered the benchmark since it is expected to undergo the least damage because of its exposure to the lowest temperatures, and thus; expected to have a microstructure resembling that of to the as-cast material. However, there was evidence of considerable secondary carbide precipitation and coarsening of the eutectic carbides, as pointed in Figure 35b.
In addition, some creep voids were observed at some locations, which reflect initial creep damage. Some of these voids have been labeled in the BSE micrograph presented in Figures 36c. It was also observed that some of the voids nucleated right at the interface between (Mn-S) rich phases and the austenitic matrix, which is in good agreement with the literature [61,126,127].

Figure 36. (a) BSE image of a region in sample 1A showing (b) different precipitates with their corresponding EDS-spot analysis, 1-3 in “(d)”, and (c) another area where voids nucleated close to a (Mn-S) rich phase; studied by EDS-spot analysis, 1-5 in “(e)”.

66
Sample 4A also showed evidence of degradation, particularly close to the ID, where the number of creep voids was greater than in sample 1A. Furthermore, carbides rich in Si, Nb, Ni and W were also observed. In particular, (Ni-Nb-Si)-rich phases close to the OD and ID were identified (Figure 37). In addition, the BSE images in Figure 37 show fine (Cr-Ni-W) rich intragranular precipitates in both regions (small yellow arrows in Figure 37b) and corrosion products on the areas adjacent to the OD surface.

Figure 37. BSE images of sample 4A showing regions (a) close to the OD and (b) ID. Both regions showed (Ni-Nb-Si) rich phases along with fine W-rich intragranular precipitates (yellow arrows).
In contrast, samples 9A and 15A were the only ones that exhibited (Cr-N) rich phases, expected to be carbonitrides; and are the dark colored phases in Figure 38 (for sample 9A). It is also apparent from this image that these (Cr-N) rich phases extends over a depth of approximately 2.0 mm from the OD surface. These carbonitrides form as a result of the high temperature oxidation experienced at these particular locations.

Figure 38. BSE image of sample 9A showing a change in the microstructure from OD to the center of the sample. Dark phases are (Cr-N) rich and white precipitates are (Cr-Ni-W) rich.
in the same two samples, it was observed regions that appeared denuded of carbides at low magnifications (Figures 38 and 39), but at higher magnifications some white colored phases were observed, which were found to be rich in Cr, Ni and W (Figure 38b).

Further analyses were carried out in sample 9A, since it showed the first signs of cracking, severe cavitation, and considerable carbide morphological changes. Figure 40 presents a diverse population of carbides size and geometries, but the elemental analyses confirms the changes experienced by the carbides. It is also observed within same carbides, the nucleation of new phases or carbides.

Figure 39. BSE image of cross section of sample 19A showing dark phases rich in Cr and N, and carbide denuded zones close to OD and ID (dashed yellow circles).
Figure 40. SEM/EDS X-ray elemental mapping from sample 9A, showing the distribution of elements right where the change in microstructure takes place (~ 2.0 mm from the OD, see Figure 38a).
Figure 41 shows micrographs of sample 15A that give the most dramatic evidence of the morphological changes that carbides undergo in this region; in many cases the transformation of the carbides occurs within existing carbides. As shown in Figure 41b, a carbide transition was observed to have occurred via an in-situ mechanism that resulted in the formation of voids at the interface of the two phases involved. Moreover, redistribution of alloying elements between carbides took place; which may have affected the global chemical composition of the austenitic matrix, but also change the composition of the carbide/matrix interface.

It is important to point out that the nature of the carbide/matrix interfaces will have a metallurgical impact on the creep damage of the material. The interfaces will become mechanically weak as a result of the depletion of the alloy elements that provide the solid solution strengthening of the matrix. Hence, carbides can be readily dislodged from the matrix; inducing voids or cavities. Another aspect of the carbide/matrix interfaces is the assessment of their physical characteristics in terms of their impact on the paramagnetic to ferromagnetic behavior of the steel with service time.
Figure 41. SE images of sample 15A showing different phases and major elemental composition found through SEM-EDS. (a) Voids nucleated at the interfaces carbides/matrix or (b) at zones where in-situ transformation took place between carbides.
Other areas in sample 15A were studied in order to identify the location and morphology of cavities or unexpected precipitates that can act as nucleation points for void formation. Figure 42a-c show unanticipated (Al-O) rich phases nucleating on carbides edges. Al is expected to be an impurity in the alloy composition, however, Si is an important alloying constituent of the steel; and it can be implied from Figure 42d that these (Si-Cr-Ni-O) rich phases may be responsible for the nucleation of voids/cracks. It should be pointed out that as in Figure 41b, traces of γ-phase remaining between carbides undergoing phase transformations were also observed in Figure 42e.

Figure 42. SE images from sample 15A showing a few (a-c) unexpected precipitates nucleating adjacent to carbides, and (d and e) some cracks/voids apparently originated from these precipitates.
4.2.2. Identification of the Morphological and Crystallographic Changes of Carbides Based on Creep Damage Level.

4.2.2.1. Assessing Bulk Stoichiometry Changes of Carbides via XRD

X-ray diffraction analysis was utilized to identify the stoichiometry of primary and secondary precipitates found in each sample studied. The peaks were matched with characteristic peaks corresponding to the elements indicated in Figure 43. The phases identified corresponded to the following carbides; $M_7C_3$, $M_{23}C_6$, $(Nb,Ti)C$, $M_6C$, $M_2(C,N)$, where $M$ is Cr; and the G-phase precipitate, which is a Ni-Nb-Si compound.

Figure 43. X-ray diffraction spectra for specimens: 1A, 4A, 9A, and 15A, and identification of relevant peaks.
It is observed that as the material deteriorates; nucleation of new precipitates and secondary carbides take place. For instance, samples 1A and 4A did not show any $M_2(C,N)$ or $M_6C$ phases present, while the most deteriorated sample (15A) exhibited large amounts of $M_2(C,N)$ carbonitrides. Moreover, from the SEM-EDS results; it is confirmed that new precipitates and secondary carbides possess different chemical composition.

XRD results provided information about the stoichiometry and crystallographic nature of precipitates in the bulk of the crept sample; however, the identification of specific phases within each sample was carried out by EBSD analysis in the next section.

4.2.2.2. Identification of Local Carbides, Carbonitrides, and Sulfides via SEM-EBSD

EBSD and EDS were utilized in tandem to obtain phase identification. EBSD patterns (EBSDPs) consist of automatic detection of the Kikuchi line positions of the phase studied; and the matching of these patterns with a possible crystallographic orientation. Studies were done on samples 1A, 9A and 15A; since they were the most representative in terms of initial conditions and degrees of degradation.

Figure 44a shows the BSE image of a region where three different precipitates co-exist. These precipitates are labeled 1, 2 and 3; and their corresponding EBSDPs are shown in Figures 44b-d.
Figure 44. (a) BSE image of a specific area in sample 1A showing the locations where EBSD patterns were obtained; (b) EBSD pattern of M₇C₃ (location 1); (c) EBSD pattern of MnS (location 2); (d) EBSD pattern of NbC (location 3); and (e) BSE image identifying various phases.
Thus, precipitate 1, rich in Cr is Cr$_7$C$_3$; precipitate 2, rich in Mn and S, is MnS; and precipitate 3, rich in Nb, is NbC. These results are in good agreement with the ones found through the XRD technique. However, due to the identification of small amounts of other elements in the case of Cr$_7$C$_3$; and NbC; they should be designated as M$_7$C$_3$, with an orthorhombic structure (space group Pnma); and MC, with a cubic structure (space group Fm3m), respectively. Further EBSD studies were carried out on sample 1A in order to identify other precipitates and Figure 44e summarizes all precipitates found in sample 1A; such as MnS, TiC, (Nb,Ti)C, and NbC carbides.

It is important to mention that MnS, NbC and M$_7$C$_3$ were often found co-existing one next to each other as shown in the BSE image in Figure 45. As mentioned previously, special study was done in sample 9A; since it is the one that showed the first signs of cracking and severe cavitation.

Figure 45. BSE image of a region in sample 1A showing the precipitates MnS, NbC and M$_7$C$_3$ co-existing adjacent to each other.
In Figure 46 we superimposed a EBSD mapping image (Figure 46a) over the left half side of a SE image (Figure 46b) to summarize the precipitate morphology close to the OD.

Figure 46. (a) EBSD mapping superimposed over a (b) SE image showing the phases found close to OD in sample 9A. (c) and (d) are two individual EBSD patterns of $M_6\text{C}_6$ carbides for spots 1 and 2 in “(b)” respectively. While (e) shows the transition zone close to OD (squared area) studied in detail in (a) and (b). Note: C-DZ: Carbide depleted zone, and CNZ: Carbonitrides zone.
Compared to sample 1A, sample 9A did not show \( \text{Cr}_7\text{C}_3 \) precipitates, instead, new phases such as; \( \text{Cr}_6\text{C} \), with a FCC structure (space group \text{Fd3m}); \( \text{Cr}_2\text{N} \), with a HCP structure (space group \text{P31m}), and \( \text{M}_2\text{C}_6 \), with a FCC structure (space group \text{Fm3m}). were identified. Nevertheless, due to the high temperature oxidation environment on the OD of the tube; the material underwent significant N pick-up, causing a partial substitution of C by N. This resulted in the formation of a different carbide stoichiometry designated as \( \text{M}_6\text{(C,N)} \), and \( \text{M}_2\text{(C,N)} \), which is in good agreement with literature results [35,56,94,128–136]. Further XRD and EBSD analysis showed that \( \text{M}_7\text{C}_3 \) transformed into \( \text{M}_2\text{C}_6 \), as it released C into the austenitic matrix. Moreover, according to J. Yan et al [44], high W content in the alloy facilitates this transformation, by taking away all the carbon atoms when it dissolves in \( \text{Cr}_7\text{C}_3 \) precipitates; which increases the ratio \( \text{Cr}/\text{C} \) promoting the transformation.

As we notice in Figure 46e, other phase transformations occurred close to the OD on sample 9A. A transition zone where \( \text{M}_{23}\text{C}_6 \), \( \text{M}_6\text{(C,N)} \); and \( \text{M}_2\text{(C,N)} \) co-exist revealed that an in-situ transformation occurred. It has been addressed that \( \text{M}_{23}\text{C}_6 \) carbide is an intermediate phase [137] that leads to the formation of most stable secondary carbides such as W-rich \( \text{M}_6\text{C} \) [122,123,135,138–144]. In addition, the formation of these carbides at the expense of \( \text{M}_{23}\text{C}_6 \) close to the OD promotes the evolution of \( \text{M}_6\text{(C,N)} \) due to the diffusion of nitrogen from air [35,133,145]. In the same way, \( \text{M}_{23}\text{C}_6 \) was found to transform into \( \text{M}_2\text{(C,N)} \) close to the OD; which is also in agreement with the literature [146]. Additionally, MnS was found to precipitate more frequently at the interfaces \( \text{M}_6\text{(C,N)}/\text{matrix} \) and \( \text{M}_2\text{(C,N)}/\text{matrix} \), and it was also corroborated from Figure 46a (yellow arrows) that austenitic phase remains within \( \text{M}_2\text{(C,N)} \) carbides, what shows evidence of in-situ transformation taking place.
It was also distinguished from Figure 46e; a large carbide-depleted zone (C-DZ) of approximately 600 μm and adjacent to the OD surface; where a large number of voids were present. Moreover, a carbonitrides zone (CNZ) of approximately 1100 μm extended alongside the C-DZ.

Sample 15A was the sample that underwent the highest degree of degradation. The purpose of studying this sample was to understand what combination of precipitates led to the total failure of the material. EBSD studies were carried out in this sample; close to the OD and ID surfaces. Figure 47 shows an area close to the OD with elongated precipitates similar to the ones found in sample 9A. This image additionally shows selected locations (1-5) where EBSD-EDS analysis was performed. The phase identification of these precipitates is presented in Figures 46b-f. It is apparent from these figures that on areas close to OD, the only precipitates present are M₂(C,N), and MnS precipitating along carbonitrides’ edges. These results reveal that N pick-up greatly influenced phase transformations near the OD, by favoring the nucleation of M₂(C,N) precipitates. According to Kong et al [147], the strong affinity between N and Cr atoms induced the diffusion of Cr from the interior to the surface of the precipitate, leading to the substitution of M₂₃C₆ for Cr₂N. This process is also accompanied by the segregation of C, Fe and Ni into the matrix during the phase transformation. A detail study of this effect will be performed by EPMA-WDS in the next section.
In areas close to the ID, sample 15A presents different morphological precipitates. Figure 48 shows the same region studied by SEM-EDS in section 4.2.1 (Figure 41). Phase identification in this region allowed us to determine the phase transformation sequence taking place:
\[ \gamma_1 + M_{23}C_6 + MC \rightarrow \gamma_2 + M_6(C,N) + M_2(C,N) + MC. \]

Where \( M = Cr, Ni, W, Nb, Si \), depending on the EMPA-WDS results.

Figure 48. (a) SE image of a spot located at the center of the thickness of sample 15A showing the precipitates found by EBSD and the (b) identification of them. (c) EBSDP of \( M_6C \) (location 1); (d) EBSDP of \( M_2(C,N) \) (location 2); (e) EBSDP of TiC (location 3); and (f) EBSDP of MnS (location 4).
It should be noticed that in this region; MnS precipitates were also found attached to M_{2}(C,N) carbonitrides. Moreover, voids nucleation appears to be linked to the in-situ transformation M_{23}C_{6} \rightarrow M_{6}(C,N) + M_{2}(C,N). Although, XRD results confirmed the results found by EBSD for samples 1A, 9A and 15A, the existence of a G-phase, rich in Ni-Nb-Si; could not be corroborated by EBSD.

The transformation, nucleation and growth of secondary carbides; such as M_{23}C_{6}, G-phase, M_{6}(C,N), and M_{2}(C,N), undoubtedly influenced the chemical composition of the austenitic matrix. Furthermore, oxidation and corrosion close to the OD and ID, respectively; also play an important role in the redistribution of alloying elements in the material. Therefore, the next section investigates the changes in chemical composition on crept samples by EMPA-WDS analyses.

4.2.3. Carbide Alloy Enrichment and Matrix Element Depletion Analyses via EPMA-WDS

EBSD studies only allowed the crystallographic identification of the phases present in samples 4A, 9A and 15A, and EDS methods provided inexact chemical composition of matrix and precipitates since the overlapping of W-M_{α} with Si- K_{α}, and Mn-L_{α} with Fe- L_{α} became a problem. Therefore, EPMA-WDS mapping and spot analysis were carried out on samples 4A, 9A and 15A, in order to study the redistribution of alloying elements in the austenitic matrix.
more accurately. Furthermore, the chemical composition of phases such as; $M_{23}C_6$, G-phase, $M_6(C,N)$, and $M_2(C,N)$ was also measured.

Figure 49 and Figure 50 show the X-ray elemental mapping of a random area in samples 4A and 9A, respectively. It is corroborated the presence of phases rich in Ni-Nb-Si previously found by XRD techniques. According to these results, (Ni-Nb-Si)-rich precipitates are the so-called G-phase. As mentioned in the literature review, this phase has been found to be an intermetallic topologically close-packed (TCP) phase with different designations such as; $\text{Ni}_{16}\text{Nb}_6\text{Si}_7$ [45], $\text{Ni}_{16}\text{Ti}_6\text{Si}_7$, or $\text{Ni}_{16}(\text{Nb,Ti})_6\text{Si}_7$, which is supposed to transform from (Nb,Ti)C after long-time exposure at temperatures between 700 -1000 °C [42,46,57], and have moderate detrimental effects on the mechanical properties of high temperature alloys [148]. In samples 4A and 9A, this phase was found to precipitate close to Ti-rich phases, which is in good agreement with the literature. In contrast, sample 15A did not show evidence of G-phase precipitation, which presupposes that the exposure temperature in the bulge could have been higher that 1150 °C.

Figure 50 also shows the progress of the in-situ transformation between; $M_{23}C_6$, $M_6(C,N)$, and $M_2(C,N)$. X-ray elemental mapping images indicate that $M_{23}C_6$ phases are richer in Cr and W compared to $M_6(C,N)$ carbides, which are rich in Nb, Si and N. Moreover, since $M_{23}C_6$ has zero solubility for N [132,135], a small amount of this element causes the transformation of $M_{23}C_6$ into $M_6(C,N)$ or $M_2N$. Nevertheless, in areas away from the OD surface, where the diffusion of N from air does not play a role, the in-situ transformation $M_{23}C_6 \rightarrow M_6C$ took place only due to the Cr-enrichment of $M_{23}C_6$, and the corresponding segregation of other elements such as Si, Nb and Ni. Figure 51 shows the redistribution of elements during the in-situ transformation $M_{23}C_6$.
→ M₆C; where we clearly distinguish faceted carbides with two different chemical compositions. The main alloying elements for M₆C and M₂₃C₆ were identified and corroborated with literature results.

Figure 49. X-ray elemental mapping with EPMA-WDS on specimens 4A showing the presence of Ni-Nb-Si rich phases.
Figure 50. X-ray elemental mapping with EPMA-WDS on specimens 9A showing the presence of Ni-Nb-Si rich phases (dashed ovals) and the differences between M\textsubscript{23}C\textsubscript{6}, M\textsubscript{6}(C,N), and M\textsubscript{2}(C,N) precipitates.
Figure 51. X-ray elemental mapping with EPMA-WDS on sample 9A showing an in-situ transformation $\text{M}_{23}\text{C}_6 \rightarrow \text{M}_6\text{C}$ (arrows indicate $\text{M}_6\text{C}$ carbides).
As previously observed in sample 15A (Figure 41), the nucleation of voids has been associated with in-situ phase transformations between M\(_{23}C_6\), M\(_6(C,N)\), and M\(_2(C,N)\) precipitates. Consequently; further studies were done in sample 9A in order to study the effect of in-situ transformation M\(_{23}C_6 \rightarrow M_6C\) on the void formation.

Figure 52. EPMA-WDS X-ray elemental mapping on an area close to the ID surface in sample 9A showing void formation at the interface M\(_{23}C_6\)/M\(_6C\).
These results are presented in Figure 52; in a location close to the ID surface. We can observe that void formation occurs in regions where interfaces formed between $\text{M}_{23}\text{C}_6$ and $\text{M}_6\text{C}$ carbides. Furthermore, the precipitation of MnS phases close to the former carbides appears to play an important role in the void formation as well.

The nucleation of voids and final linking of them was also found to originate from the corrosion attack close to the ID surface. In sample 15A, this mechanism is clearly observed in Figure 53, where finger-like pits full of $\text{SiO}_2$ appear to nucleate and penetrate into the material, causing the acceleration of phase transformations of carbides and depletion of alloying elements. Moreover, the deeper growth of finger-like $\text{SiO}_2$ pits may also serve as initiation points for cracks; that lead to the failure of the material.
Figure 53. EPMA-WDS X-ray elemental mapping on an area adjacent to the ID surface in sample 15A, showing SiO$_2$ corrosion products growing into the material.
The redistribution of alloying elements was also studied by quantitative spot analysis on samples 4A, 9A and 15A. The chemical composition of secondary carbides and matrix was later correlated with the degree of deterioration and service temperatures. Figures 54, shows the compositional profile of what appears to be a $M_6(C,N)$ carbide nucleating inside a $M_2(C,N)$ carbonitride. It is also apparent from this figure that the chemical composition measurements for the $M_6(C,N)$ phase was not accurate; since the electron beam interacted with the $M_2(C,N)$ carbonitride. However, Figure 54b shows with a light-yellow dashed area, the accurate chemical composition of the carbonitride.

![Figure 54](image)

Figure 54. (a) SE image of a carbide in-situ transformation in sample 9A and its corresponding (b) EPMA-WDS spot analysis along the line shown in “(a)”, where 0.0 indicates the start point.
Various regions were analyzed in samples 4A, 9A and 15A in order to have reasonable data to come up with a proper average of the chemical composition of precipitates and matrix. For this purpose, each sample was divided in four strips parallel to the OD surface, and EPMA-WDS spot analysis was carried out in regions within these strips. Figures 55 and 56 show some of these regions in sample 9A; and Figures 57 and 58 correspond to some of the analysis done on sample 15A. The profile compositions were statistically analyzed and matched with crystallographic results from SEM/EDS-EBSD and XRD studies. Finally, the global chemical composition measurements were plotted against sample number, as presented in Figure 59.

Figure 55. (a) SE image of an area on sample 9A near OD; where various carbide in-situ transformations take place, while (b) the zoomed-area shows the line along which EPMA-WDS spot analysis was done, and the results are presented in (C).
Figure 56. (a) SE image of carbide in-situ transformations in sample 9A near OD and its corresponding (b) EPMA-WDS spot analysis along the line shown in “(a)”. 0.0 indicates the start point.
Figure 57. (a) SE image of carbonitrides in sample 15A near OD and its corresponding (b) EPMA-WDS spot analysis along the line shown in “(a)”. 0.0 indicates the start point.
Figure 58. (a) BSE image of carbide in-situ transformations in sample 15A near ID and its corresponding (b) EPMA-WDS spot analysis along the line shown in “(a)”. 0.0 indicates the start point.
These results clearly demonstrate that the changes in the chemical composition of alloy are directly associated with the degree of creep damage. The ratio (wt. % / wt. %) of the main alloying elements; Cr / Ni, was found to change from about 21.3 / 51 for sample 4A, to 14.6 / 58 for sample 15A. These changes were related to the phase transformations and the redistribution of alloying elements. In the case of sample 4A, M_{23}C_6 carbides were confirmed to be rich in Cr (~69 wt. %), Ni (~8.8 wt. %) and W (~8.5 wt. %). However, the nucleation of new precipitates such as; M_2(C,N) and M_6(C,N) provoked changes in the composition of M_{23}C_6 carbides in samples 9A and 15A. Cr-content decreased down to ~66.4 wt. % (sample 9A) and ~61 wt. % (sample 15A). Moreover, a substantial increment in the W-content in M_{23}C_6 carbides (from ~8.5 to ~14 wt. %) was observed on samples 9A and 15A. This is probably because the W solubility decreases as the C gets depleted from the austenitic matrix, therefore the segregation of W in M_{23}C_6 carbides took place.
Figure 59. Major chemical composition of precipitates and matrix in samples 4A, 9A and 15A. The dashed lines in the MATRIX plot represent the nominal values for Cr (28.8 wt. %) and Ni (48.4 wt. %) in the alloy composition.
Additionally, in sample 9A, M$_{23}$C$_6$ transformed into M$_2$(C,N), by getting enriched with Cr (~83.6 wt. %) and N (~11.4 wt. %). While M$_6$(C,N) becomes rich in Ni (~32.5 wt. %), Si (~6.7 wt. %) and N (~2.8 wt. %) but; lowering its Cr content (~38.5 wt. %).

In the same way, from sample 9A to 15A (Figure 59 - M$_2$(C,N) graph); carbonitrides underwent significantly N loss, presumably because the degree of degradation increased. This can be explained by the fact that the solubility of N depends on the Cr, C and Ni contents [149,150]. Cr and C increase the solubility of N in austenite, while high Ni contents lower it down. In consequence; as the alloy deteriorates, the matrix gets depleted of Cr and C, but enriched in Ni, which ended up decreasing N solubility, thus; lowering the N-content in carbonitrides.

EPMA-WDS spot analysis was also done specifically on the carbide depleted zones, close to the OD and ID surfaces in samples 4A, 9A and 15A. Figure 34 showed in detail the morphology of these regions, and it was found that samples 9A and 15A exhibited carbide-depleted zones close to both surfaces, sample 4A only on the inner surface, and sample 1A did not show any depletion. In chapter 4.1 the depth of these areas was measured and we present them next; herewith the values of Fe/Cr/Ni in weight percentage:

4A - **ID:** ~ 40 μm. (18.5/20.8/50.7), **OD:** ~ 0 μm. (18.3/21.7/51.2)

9A - **ID:** ~ 200 μm. (17.7/21/53.3), **OD:** ~ 500 μm. (20/13.3/60)

15A - **ID:** ~ 200 μm. (19/15.2/59), **OD:** ~ 550 μm. (19.3/14.1/59)
These results clearly demonstrate that oxidation on the OD and ID surfaces, along with the nucleation of new precipitates and secondary carbides during creep, has a great impact on the chemical composition of the austenitic matrix. Furthermore, it is also expected that interfaces carbides/matrix underwent similar changes. Hence, changes in their physical properties are supposed to take place. Nonetheless, the effect of changes in chemical composition was also visible when measuring mechanical properties of the matrix by means of micro-hardness testing. These studies will be addressed in section 4.2.6.1; however, it was found that the hardness of the austenitic matrix in sample 1A; was intimately related to the precipitation of nanoscale primary carbides. Therefore, the next section is aimed at identifying these fine and ultra-fine precipitates.

4.2.4. Identification of Nanoscale Primary Carbides via TEM

As mentioned above; fine intragranularly precipitates were also present in the alloy under study. Sample 1A was the alloy close to the as-cast condition; and TEM studies were only performed in this sample in order to characterize the fine primary carbides present in the initial (close to as-cast) condition.

Figure 60a shows a bright-field TEM image, where profusely distributed carbides were found to nucleate at dislocations. Ultra-fine carbide sizes were between 10-18 nm; while fine carbides size ranged from 85 to 120 nm. Interestingly, as shown in Figure 60b; bright-field imaging mode did not allow the observation of these precipitates. Furthermore, it has been addressed that the nucleation of carbides at dislocation structures provides “Orowan pinning” of
dislocations, which decreases the amount of strain accumulated during primary creep and prolong the secondary creep regime [28], which increase creep resistance. Additionally, other fine intragranular (Nb,Ti)C carbides were observed as shown in Figure 61.

High resolution TEM (HRTEM) images and fast Fourier transform (FFT) analysis were carried out on the carbides found in Figure 60. It is anticipated that these carbides are; M7C3 and M23C6. However, further characterization was done to study their morphology and carbide/matrix interfaces. Figure 62a shows the TEM image of a carbide embedded in the austenitic matrix. HRTEM image of the interface carbide/matrix allowed the measurement of the lattice spacing (d-space) of the planes (040). This value, 3.011 Å, confirmed the anticipated assumption that this carbide was M7C3.

Figure 60. TEM images of fine intragranular carbides nucleating at dislocations. These precipitates are visible in (a) dark field imaging mode, but were not noticeable in (b) bright field mode.
Similarly, in Figure 62b, TEM studies were carried out on carbides that showed different morphology, compared to the previous precipitates (M₇C₃). HRTEM was also performed as shown in the inset in Figure 62b. Again, HRTEM image allowed the measurement of the lattice spacing (d-space) of the planes (220). This value, 3.75 Å, confirmed that the carbide was M₂₃C₆, even though XRD or EBSD studies did not detect this phase, probably because of the size of these precipitates.
Figure 62. TEM images of (a) M₇C₃ and (b) M₂₃C₆ carbides showing also HRTEM images of these precipitates where the d-spacing was measured.
Further analysis was carried out by analyzing the FFT spectra of the HRTEM images for M7C3 and M23C6 carbides. This study consists on comparing the SAD patterns of carbides with their corresponding FFT spectra, and evaluating the similarities between them. Figure 63 shows that SAD patterns of M23C6 (Figure 63a) and M7C3 (Figure 63c) carbides are consistent with FFT spectra (Figure 63b and 63d) respectively, which corroborates our previous results.

Figure 63. TEM-SAD patterns of (a) M23C6 and (c) M7C3 carbides and (c and d) their corresponding FFT spectra, respectively. Note: Zone axis of M23C6 is [110]
4.2.5. Mechanical Assessment of Selected Samples Exposed to Different Creep Damage.

4.2.5.1. Vickers hardness Evaluation of Bulk Samples

Previous sections allowed the identification of precipitates present in all samples studied, and their chemical composition, as well as the matrix. It was determined that there is indeed a direct relationship between compositional changes in the alloy and creep degradation. Matrix and carbides undergo redistribution of alloying elements that is expected to change the mechanical properties of the material. Initially, Vickers hardness using a load of 1.0 kg. was used to measure the bulk hardness of the material. The results are presented in Figure 64, where it is apparent that there is almost a difference of 70 HV1.0 kg. between the hardness of samples near the bulge (9A and 15A) and samples away from it (1A and 4A). However, this graph also shows that the hardness of sample 4A is greater than 1A, even though sample 4A should be softer, since it was exposed to higher heat conditions (1000 < T < 1150 °C). This is because; secondary carbides precipitated inside austenitic grains (Figure 29b and Figure 65 - 4A), therefore the hardness increased. Furthermore, from Figure 65, we observe that the coarsening of carbides on samples close to the bulge; caused the growth of the austenitic grains; to the point that Vickers hardness sometimes was only measured on austenitic phases (Figure 65 - 15A). Nonetheless, since the test load chosen was 1.0 kg., the values obtained were still representative of the bulk hardness.

Another detail observed from Figure 64 is that the hardness values close to the OD surface on samples 9A and 15A; appeared to be the lowest among the values obtained through the wall thickness. This is because they were the most alloying depleted regions, with Cr-contents as low
as ~14 wt. %. Moreover, the amount of carbides in these regions is significantly less than for samples 1A and 4A.

Figure 64. Bulk Vickers hardness profile across the wall thickness of the samples studied. Note: The load used was 1.0 kg.
Bulk hardness test results demonstrated that morphology, type, and volume fraction of carbides greatly influence the mechanical properties of crept samples. Therefore, the best way to compare these properties between each crept-sample was by measuring the hardness of austenitic matrix only. In order to do this, the influence of carbides was excluded; making the hardness indentations smaller, thus; more sensitive to outermost austenite surface. The next section presents the results of this study.

Figure 65. Bulk Vickers hardness indentations performed with a load of 1.0 kg. on all samples studied.
4.2.5.2. Effect of Alloying Elements on the Variation of Microhardness in the Austenitic Matrix

Figure 66 shows the micro-hardness indentations on samples 1A, 9A and 15A; performed with a load of 10 grams. It is apparent from the images that the indentations are small enough to only pick up the hardness of austenitic phases. Moreover, the low load used; prevented the indenter from penetrating deep into the subsurface and hitting precipitates located underneath the surface. The microhardness values of the austenitic matrix of all samples studied are summarized in Figure 67; where the average values for each sample were calculated from indentations performed on spots located along the wall thickness (from OD to ID surface), including the carbide depleted areas; in the case of samples 9A and 15A. These values were found to follow a good linear relationship with exposure temperature.

Figure 66. Vickers micro-hardness indentations on austenitic matrix of samples 1A, 9A and 15A. Note: Load used was 10 grams.
Furthermore, among all samples; 1A showed the largest standard deviation, probably because of the fine and ultra-fine intragranular precipitates found through TEM studies; that acted as reinforcing elements in the matrix. Similarly, samples 4A and 9A also exhibited large microhardness standard deviations, but lower than in sample 1A. In contrast, sample 15A revealed to have the lowest standard deviation. This is because, as the material deteriorates; the coarsening of carbides occurs at the expense of others’ carbides dissolution. This leads to the disintegration of fine/ultra-fine intragranular carbides; and to the final loss in mechanical properties of the matrix. Therefore, the hardness in every spot tends to be almost uniform.

In addition, compositional changes also played an important role in the softening of the austenitic matrix. This is clearly observed in Figure 67, where the depletion of Cr and enrichment of Ni and Fe; appear to lower the mechanical properties of the matrix. As mentioned before, redistribution of alloying elements occurs because of different factors; such as phase transformations and oxidation. Therefore, it is important to study the effect of carbides morphology and density, and how they affected the bulk hardness of crept samples. These studies were done in the next sections, by measuring the hardness of selected precipitates and the volume fraction of carbides in each crept sample.
4.2.5.3. Microhardness of Selected Precipitates

The hardness of the austenitic matrix (Figure 67) on each sample was found to be considerably lower than its corresponding bulk hardness, as presented in Figure 64. This is because we eliminated the hardness contribution of carbides; by reducing the indentation size. However, in this section, this contribution is evaluated by measuring the hardness of selected carbides; such as M\textsubscript{23}C\textsubscript{6}, M\textsubscript{6}C/M\textsubscript{6}(C,N), and M\textsubscript{2}(C,N). It should be mentioned that; because of the size of indentations, hardness of M\textsubscript{7}C\textsubscript{3}, and MC carbides was not possible to measure.
Proper identification was previously done by EBSD studies such that the hardness values obtained represented the right type of carbide under study. Microhardness indentations were done using a load of 10 grams, as explained in the experimental procedure. According to the XRD results, samples 4A, 9A and 15A exhibited some carbides that were common in all samples; however, the chemical composition was different from one sample to the other, depending on the level of deterioration of the selected sample. Therefore, it is expected that the hardness of similar carbide-types in each sample differ from each other. Consequently, various carbides were hardness tested and an average value was calculated. Figure 68 shows some of the different regions where only M$_{23}$C$_6$ carbides were present. Hardness indentations were performed in the center of precipitates such that the values obtained were as accurate as possible.

The hardness of M$_{23}$C$_6$ carbides was in average approximately 1516 HV$_{0,01}$ (14.87 GPa), which is in good agreement with the values found by Liao et al [151] and Yefei et al [152] and his references. Conversely, M$_6$C/M$_6$(C,N) carbides were found next to M$_2$(C,N) or M$_{23}$C$_6$ precipitates as shown in Figure 69. In some cases, islands of M$_6$(C,N) carbides were found inside M$_2$(C,N) carbonitrides (Figure 69b and 69c) and sometimes M$_6$C carbides were next to M$_{23}$C$_6$, because of the phase transformation; M$_{23}$C$_6$ → M$_6$C, they underwent. The average value obtained for both M$_6$C type carbides was approximately 1990 HV$_{0,01}$ (19.51 GPa). L. Zheng et al [153] found that for a M$_6$C phase composition of 71.4W-14.3Ni-4.1Co-6.5Mo-1.4Nb-1.7Al-1.0Cr-0.6Ti (wt. %); the hardness was ~ 14 GPa., which is lower than the value found in this work. However, according to S.A. Shiryaef et al [154], the hardness values of Cr$_3$C + Cr, which is close to Cr$_6$C phase, are in the range of 17 – 27 GPa, which agrees with the value found here.
As mentioned above, $M_2(C,N)$ carbonitrides were found surrounding $M_6(C,N)$ carbides (Figure 69b and 69C; and Figure 70a) or as isolated phases close to the OD surface (Figure 70b). The average hardness was approximately 1777 $HV_{0.01}$ (17.43 GPa), which is close to the values found by C. Nouveau et al [155], N. X. Randall et al [156] and M.A. Djouadi et al [157].

Figure 68. Microhardness indentations on $M_{23}C_6$ carbides randomly picked up from samples 9A and 15A. Note: White arrows point out indentations; otherwise difficult to distinguish.
Figure 69. Microhardness indentations on (a and d) $M_6C$, (b and c) $M_6(C,N)$ (location 2), and $M_2(C,N)$ carbides (location 1); randomly picked up from samples 9A and 15A.
Figure 70. Microhardness indentations on $M_2$(C,N) and $M_6$(C,N) carbides (a) coexisting next to each other and (b) close to the OD surface in sample 15A.
It is worth to mention that in some cases, indentations on $\text{M}_2(\text{C}, \text{N})$ carbonitrides provoked cracks formation due to their brittleness. According to L. Yajiang et al [158]; precipitation of carbonitrides may promote crack initiation points and the propagation of cleavage cracks in ferritic alloys. In addition, other minor precipitates; such as MnS (Figure 71) was found to have a hardness value of $333 \text{ HV}_{0.01}$ (3.26 GPa), which is in excellent agreement with the values found by N.X. Randall et al [159]; (3.34 GPa).

Finally, Figure 72 summarizes all hardness values for the most representative precipitates found in samples 9A and 15A. The standard deviation of these values is rather large; because of the changes in chemical composition of the actual precipitates; which clearly have an impact in the hardness results.

![Figure 71. Hardness indentation on a MnS precipitate in sample 15A.](image)
Figure 72. Average microhardness values for major carbides present in samples 9A and 15A.
4.3.  **Relationship Between Reformer tube Metallurgy and Mechanical Properties of Austenitic Matrix**

So far it has been observed that the chemical composition and morphology of precipitates played an important role in the mechanical properties of the bulk material. Moreover, as the number of precipitates increased; the possible sites for voids to nucleate also increase. The growing of voids, linking, and formation of cracks suggest that the material reached the third stage of creep; and final failure of the material is imminent. Therefore, the effect of the volume fraction of precipitates and voids/cracks was correlated with the mechanical properties of the austenitic matrix.

Figure 73 shows the volume fraction of precipitates and voids/cracks, and the insets corresponding to some of the image analysis done in all samples studied. It is apparent from this image that the density of both increased with the exposure temperature, thus, the degree of damage. These results were further correlated with the mechanical properties of the austenitic matrix, evaluated by microhardness testing.
Clearly, Figure 74 demonstrates that the softening of the matrix can be closely correlated with the increment of the volume fraction of precipitates; which went from about 12.6 % to almost 24.6 % for samples 1A and 15A, respectively. Moreover, it is also observed that the degree of degradation (voids/crack fraction) has a great impact on the hardness obtained. In addition, Figure 73b shows again the location where the samples studied were extracted; to have an idea of the level of degradation expected from samples 9A and 15A.
Previous sections allowed the identification of precipitates and the determination of changes in chemical composition that caused variations in the mechanical properties of crept samples. Moreover, a good linear relationship was found between the exposure temperature and the...
softening of the austenitic matrix in all samples studied. However, the other main goal of this work is the determination of how these changes in the matrix composition, new phase formation or carbide transformation are linked to the changes in the magnetic response in the crept material. For this purpose; advanced magnetic techniques were utilized to qualitatively detect magnetic changes in the crept samples, and how these changes can be correlated with their degree of degradation.

4.4. Assessing the Paramagnetic to Ferromagnetic Behavior

In section 2.5; the magnetic properties of cast austenitic alloys was addressed by studying the ternary phase diagram Fe-Cr-Ni; and the curie temperature of different alloys. According to Stevens et al [2], it is possible to determine a paramagnetic-ferromagnetic boundary that defines regions where these alloys behave ferromagnetically (Figure 75). This is because of the changes that occur during high service temperatures and oxidizing/carburizing environments that end up leaving a Ni and Fe rich matrix and interfaces carbides/matrix [94–100].

The average major-elemental composition of the austenitic phase in crept samples was plotted in Figure 75. It is clearly observed that samples 9A and 15A fall within the ferromagnetic region, while samples 1A and 4A would behave paramagnetically. In order to roughly detect these differences in magnetic behavior between crept samples; the procedure explained in section 3.2.3.1 was carried out (scale-magnet technique). For this purpose; samples 1A and 15A were selected, since they should show a fairly marked difference.
Studies were done in pieces with an average weight of 16 g. and oxide layers attached to the OD and ID surfaces; as shown in the inset in Figure 76. The attraction force exerted on each sample (1A and 15A) was obtained and divided by their corresponding mass; so the values are normalized. Table 7 shows the weight of each sample; and Figure 75 presents the normalized magnetic-response (magnetic susceptibility) values for each sample.

Figure 75. Fe-Cr-Ni phase diagram showing ferromagnetic (open symbol data) and paramagnetic (star symbol) material at 20 °C. The shaded area defines the compositions that behave ferromagnetically [2]. Note: Major elemental composition of austenitic matrix in crept samples has been approximately plotted in red.
It is evident from these results that sample 15A, extracted from the tube bulge, shows the largest magnetic susceptibility. Sample 1A, on the other hand, showed much lower susceptibility, but still presented some degree of ferromagnetic behavior.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (g)</th>
<th>Magnetic Force (g)</th>
<th>Magnetic susceptibility (g/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>12.407</td>
<td>1.126</td>
<td>0.091</td>
</tr>
<tr>
<td>15A</td>
<td>18.272</td>
<td>27.522</td>
<td>1.506</td>
</tr>
</tbody>
</table>

Table 7. Magnetic susceptibilities of samples 1A and 15A.

Figure 76. Magnetic susceptibility of samples 1A and 15A with oxidation scales on the OD and ID surfaces.

It is evident from these results that sample 15A, extracted from the tube bulge, shows the largest magnetic susceptibility. Sample 1A; on the other hand, showed much lower susceptibility, but still presented some degree of ferromagnetic behavior.

It is obvious that the degree of creep damage could be associated with the magnetic property of the location. In the case of sample 15A, the metallographic analysis showed greater creep.
deterioration; therefore the magnetic response is larger than sample 1A, which had the least amount of damage. It is worth to mention that, besides the temperature effect on the microstructure the immediate atmosphere at these locations would also impact on the level of oxidation that may be experienced at a given spot.

An evaluation was also done on the oxide layers of areas on the bulge; close to sample 15A, where it was found that a thicker oxide layer was present. An X-ray diffraction analysis of this layer showed the presence of magnetite, Fe₃O₄ (Figure 77). This implies that probably the most significant contribution to the magnetic susceptibility must come from the oxide layer.

![X-ray diffraction results of the oxidation scale of the OD surface wall of a spot near sample 15A.](image)

Figure 77. X-ray diffraction results of the oxidation scale of the OD surface wall of a spot near sample 15A.
However, in order to isolate this effect; the oxide layers on the OD and ID surfaces were removed mechanically, and samples were again submitted to magnetic measurements. It turned out that the magnetic susceptibility of sample 1A remained almost constant, what basically demonstrates that the oxide scales did not have a great impact on the magnetic behavior of the bulk material. Nevertheless, the magnetic susceptibility of sample 15A decreased by ~21.5%, which gives insight into the impact of the oxide scale in magnetic response. Figure 78 presents this data, along with the isolated contribution of the removed scales. These results did raise some questions about what accounted for the magnetic behavior of the material. Hence, additional studies were carried out to elucidate the role of creep deterioration on the magnetic response of the material at the micro-level.

Figure 78. Magnetic susceptibility of samples 1A and 15A, with and without oxide scales on the OD and ID surfaces. Magnetic response of just the scale was also measured.
4.4.1. Detection of Ferromagnetic Regions in Matrix and Interfaces Carbide/Matrix via MEwF

MEwF was performed following the procedure explained in the section 3.2.3.3. However, it should be mentioned that in this section, the images will be labeled as OFF or ON; depending on the activation or deactivation of the magnetic field, respectively. These studies were done on selected samples, taking into account their magnetic susceptibility. Samples as-cast, 9A and 15A were chosen because of the following reasons:

- Sample 1A magnetically behaved the same as sample as-cast.
- Sample 9A was the first sample that showed the presence of cracks and carbonitrides at the OD surface.
- and sample 15A, since it exhibited the highest degree of degradation and because it underwent full transformation of precipitates.

As mention previously, sample 1A and the as-cast condition of the material is expected to be fully paramagnetic. However, as found from the magnet-scale technique, a slight magnetic behavior was detected on the oxide layer-free bulk of the material. Initially, it was thought that this magnetic response originated from $\delta$-ferrite phases (BCC structure), although this phase was not likely to precipitate in this alloy. Attempts to identify this phase by optical microscopy, SEM-EDS and EBSD were not successful, since this phase looks morphologically similar to $M_7C_3$ carbides, as J. P. Shingledecker et al [28] found. Figure 79 shows $\delta$-ferrite phases nucleating next to $M_{23}C_6$ carbides; in a cast austenitic alloy (mainly 19Cr-10Ni wt.%).
Since $\delta$-ferrite behaves ferromagnetically, it is expected to confer certain magnetic properties to the alloy; but more importantly; it can rapidly transform into sigma ($\sigma$) phase during prolonged high-temperature exposure, which end up embrittling the alloy. Therefore, MEwF was utilized to detect this phase.

Figure 80 shows the application of the technique where two different areas were studied BEFORE (Figure 80a and 80c) and AFTER (Figure 80b and 80d) the application of the magnetic field. It is clearly observed that agglomeration of ferrofluid takes place around phases that look similar to the ones shown in Figure 78, thus; it is confirmed the presence of $\delta$-ferrite phase. Various random areas were studied and the same pattern was found.
As shown in previous sections, long time exposure to higher temperatures caused the nucleation, transformation and redistribution of alloying elements in the material. In sample 9A, the nucleation of M$_2$(C,N) carbonitrides (Cr: ~ 83.6 wt. %), close to the OD surface, highly depleted the neighboring austenitic regions, to the point that they started to behave ferromagnetically (Figure 81).

Figure 80. MEwF on (a and c) two different random spots in sample as-cast; showing more likely δ-ferrite phases nucleating adjacent to M$_7$C$_3$ carbides, detected by (b and d) the agglomeration of ferrofluid around them, after a magnetic field was applied (ON).
Figure 81. MEwF on areas (a) close to OD and (c) ID, showing (b) ferrofluid rich areas on carbonitrides rich zones close to the OD surface, and (d) agglomeration of ferrofluid near voids. Note: ON and OFF define the activation and deactivation of the magnetic field, respectively.
In this set of images, two different areas were analyzed. An area close to the OD surface (Figure 81a); where carbonitrides precipitated; and another area near the ID surface (Figure 81c). It is worth to mention that before MEwF studies; the oxide scale on the OD surface was mechanically removed in order to avoid distortions caused by the strong ferromagnetic scale. After applying the magnetic field (Figures 81b and 81d), it is distinguishable that the ferrofluid concentrates on the area where carbonitrides are present. In contrast, the carbide depleted zone (CD-Z) appears not to have changed its magnetic properties, and looks denuded of ferrofluid. However, this is not totally true; as we will explain later.

Figure 82. MEwF on a region adjacent to the OD surface on sample 9A. Magnetic domains were detected on the CD-Z, near the OD corrosion scale.
The MEwF study on the area close to the ID in sample 9A is presented on Figures 81c and 81d. Before applying the magnetic field (Figure 80c), the ferrofluid appears to be well distributed over the surface. It is after the magnetic field is applied (Figure 81d), that the agglomeration takes place in regions close to creep voids. This is congruent with the fact that Cr-depletion takes place during phase transformations and void formation, thus; matrix, grain boundaries, and regions surroundings carbides become weak; and behave ferromagnetically.

Figure 82 shows the MEwF studies done on an area next to the OD surface; where an interesting magnetic behavior was observed on the CD-Z. When the ferrofluid was applied, the corrosion scale in this case was still attached to the sample. Apparently, most of the ferrofluid is being dragged out from the surface due to the strong ferromagnetic behavior of the oxide scale (see Figure 82, zone 1). However, the ferromagnetic behavior of the CD-Z, adjacent to the oxide scale; is made visible by the maze-like magnetic domains shown on the half portion of the CD-Z. Moreover, the poor concentration of ferrofluid in the zone 2 is due to the leakage of ferrofluid through the voids in the CD-Z. When the electromagnet is OFF, ferrofluid comes out of the voids and forms a layer on top of the specimen again. This behavior was not observed in the previous study (Figure 80b) because in that case the oxide scale was mechanically removed. Therefore, the CD-Z looks denuded of ferrofluid; only because of the leakage through the voids.

MEwF was also done in sample 9A at higher magnifications. However, there was no a marked ferromagnetic behavior of interfaces carbides/matrix. Figure 83 shows the weak ferromagnetic behavior of an interface M₆(C,N)/matrix and the zoomed-in images in Figures 83b and 82d provide a better detail of this region.
Sample 15A was also studied by MEwF and the results are presented in Figures 84, 85 and 86. Again, areas close to the OD (Figure 84a) and ID (Figure 84c) surfaces were analyzed in order to observe the effects of oxidation in air, and carburizing environment, respectively. Figures 84b and 84d are the corresponding MEwF images that clearly show the effectiveness of this technique.
Figure 84. MEwF on areas (a) close to OD and (c) ID, showing (b) ferrofluid rich areas on interfaces $M_2(C,N)$/matrix and matrix; and (d) agglomeration of ferrofluid on the grain boundaries and interfaces $M_2(C,N)$/matrix. Note: The ferrofluid-free optical micrograph in “(c)” corresponds to the polished and glyceregia-etched region in “(d)”. 
Detection of ferromagnetic interfaces $M_2(C,N)/\text{matrix}$ and the actual matrix was achieved close to the OD surface in sample 15A. Moreover, island-like ferrofluid agglomerations were observed inside the austenitic grains; what denotes that ferromagnetic regions are also located underneath the surface (magenta, white, and yellow dashed ovals in Figure 84b).

In the case of the area close to the ID surface in sample 15A; this was polished and etched with glyceregia, such that the grain boundaries and carbides are more noticeable (Figure 84c). Its corresponding MEwF image is presented in Figure 83d, where it is evident that not only the interfaces $M_2(C,N)/\text{matrix}$ are becoming ferromagnetic, but also the grain boundaries (see colored arrows in Figure 84d). This is in good agreement with the fact that, as the material degrades; nucleation of secondary carbides ($M_{23}C_6$) takes place on the grain boundaries, what ends up Cr-depleting these regions, thus; becoming ferromagnetic.

A closer look at the CD-Z in sample 15A was found to coincide with the results from sample 9A, where maze-like magnetic domain structures decorate these regions (Figure 85). Further analysis was carried out on a different area but at higher magnifications; in order to see whether is feasible or not the measurement of these depleted (ferromagnetic) regions.
Figure 85. MEwF on the CD-Z in sample 15A, (a) before and (b) after the magnetic field is applied. (c) The zoomed-in area shows make-like magnetic domain structures; what denotes the ferromagnetic character of this region.

Figure 86 shows the selected area; that shows the same pattern as previously noted in Figure 84d. However, at higher magnifications, the detection and measurement of depleted (ferromagnetic) regions becomes possible.
It is important to mention that in the case of dealing with cracks, shallow gaps or grooves with some ferromagnetic behavior, MEwF was not sensitive due to the accumulation of ferrofluid inside these flaws and the difficulty in observing the pattern of the accumulation. Therefore; a more accurate method will be used. This method is Magnetic Force microscopy (MFM) and the procedure we will follow was explained in section 3.2.3.4.

Figure 86. MEwF on an area in sample 15A (a) close to OD, before applying magnetic field, showing (b) ferrofluid rich areas on interfaces $M_2(C,N)$/matrix and matrix; and (c) the optical micrograph and (d) MEwF magnification of a selected region where ferromagnetic interfaces are delineated by the ferrofluid (brownish color).
4.4.2. Detection of Ferromagnetic Regions in Matrix and Interfaces

Carbide/Matrix via MFM

MEwF on samples as-cast, 1A or 4A did not show a representative change in their magnetic behavior; since they did not undergo severe creep deterioration. Instead, samples 9A and 15A were selected because of this reason. As mentioned in the experimental procedure, the topography was also obtained during MFM studies. This information provided better details of flaws and carbide morphology. It is also worth to mention that in the MFM images shown in this section; the magnetic behavior properties are presented as dark or bright colors depending on the scale used (phase (°) or frequency (Hz)). In every case the magnetic property will be indicated.

Figures 87 and 88 show the MFM studies close to the OD surface on sample 9A. In both cases a 3D AFM image is presented in order to give a better detail of the carbides morphology. Figures 87 shows an area in samples 9A where voids nucleate on interfaces $M_6(C,N)/$matrix. 3D AFM image (Figure 87a) clearly shows these voids, and MFM image give information of the magnetic behavior of these microstructures. From Figure 87c, MFM phase (°) scale; it is obvious that no magnetic behavior was acquired from the actual void, since the tip was not in contact with any physical structure, thus; the MFM image shows in dark color these regions. Moreover, slightly brighter colored structures next to the voids; represent the magnetic behavior of $M_6(C,N)$ carbides, which demonstrates their paramagnetic behavior. Finally, it is also observed that the austenitic matrix is colored with the brightest color, which provides information about its slight ferromagnetic behavior.
Figure 88 shows an area in sample 9A where crack/grooves appear to nucleate on the actual carbides. In this case; the MFM frequency (Hz) scale was acquired in order to show the difference with the phase (°) scale. Interestingly, the length of the magnetic MFM probe was able to acquire magnetic information inside the cracks/grooves, since they appeared to be shallow. Figure 88c shows some of these cracks/grooves as darker colors, which in this case indicate that they behave ferromagnetically.
Additionally, the paramagnetic behavior of carbides was confirmed (bright colored), as well as the slight ferromagnetic behavior of the austenitic matrix (slight dark colored). It is important to mention that it was not possible to detect any ferromagnetic interface carbide/matrix, possibly because, as shown in Figure 82, they were weak. However, as found from MEwF studies, sample 15A showed abundant depleted (ferromagnetic) regions.

Figure 88. An area in sample 9A showing (a) 3D and (b) 2D MFM images of the topography and its corresponding (c) MFM image.
Extensive studies were done in sample 15A since they represented the highest degree of degradation and somehow, the culmination of phase transformations, which becomes important to understand the creep mechanism of the material. Figure 89 focuses on the ferromagnetic behavior of interfaces \(M_2(C,N)/\text{matrix}\); which clearly showed to coincide with MEwF carried out previously. The optical micrograph (Figure 89b) shows austenitic phases inside \(M_2(C,N)\) carbonitrides and cracks/grooves, just as observed in previous studies in sample 9A (Figure 89b). From the MFM image; it is obvious that interfaces become ferromagnetic, even the interfaces inside the carbonitrides (yellow arrows in Figure 89a). A 3D MFM image of the interface \(M_2(C,N)/\text{matrix}\) (Figure 89c) show strong evidence that interfaces undergo severe Cr-depletion, therefore they become ferromagnetic.

It is worth mentioning that because of the topography (carbides height) of crept sample 15A, the MFM probe (magnetic tip), sometimes could not acquire data or even worse, the tip broke. Figure 90 shows the defective data acquired on a region where a \((\text{Nb,Ti})C\) carbide rises on top of a carbonitride, which causes the disruption of the tip vibration, and final defective data. However, we can still observe the ferromagnetic regions around carbonitrides, and inside crack/grooves.
Figure 89. An area in sample 15A showing the (a) 2D MFM image, (b) its corresponding optical micrograph and the (c) 3D MFM representation of the ferromagnetic behavior at the interface $M_2(C,N)/$matrix.
MFM technique allowed the detection of ferromagnetic regions more accurately; otherwise impossible to do with MEwF methods. Figure 91 gives evidence of these differences, where the optical micrograph and corresponding MFM image show ferromagnetic regions around carbonitrides, just as shown before. However, when looking at the MEwF image, we observe a ferromagnetic region that appears totally different on the MFM image (dashed lines in Figures 91b and 91c). This region corresponds to a ferromagnetic region surrounding a carbonitride that barely sticks out of the surface. Moreover, in this case, cracks appear to disturb the tip vibration, consequently; the MFM image exhibits some line defects.

Figure 90. (a) MFM image of an area in sample 15A and (b) its corresponding optical micrograph showing the precipitates present.
Figure 91. An area in sample 15A showing the (a) optical micrograph and corresponding (b) MFM image (c) MEwF image is also presented as comparison between magnetic techniques.
From Figure 91 it was demonstrated that MFM and MEwF were able to detect ferromagnetic regions effectively. However, was also observed the higher sensitivity of MFM techniques. Furthermore, from Figures 86d and 89a a good matching on the ferromagnetic depleted interfaces carbide/matrix was found. Additionally, a quantitative comparison on the ferromagnetic depleted interfaces carbide/matrix was carried out and it was found a very good agreement between these two measurements (~ 1.0 μm). This value is not that different from the values found by Takahashi et al [99] (~0.6 μm) for Cr-depleted zone near grain boundaries.

These results validate the hypothesis that the switching from paramagnetic to ferromagnetic behavior is related to even slight changes in chemical composition. Interfaces carbide/matrix showed the strongest ferromagnetic behavior, although the matrix becomes more ferromagnetic from sample 9A to 15A as well. Moreover, carbide depleted zones (CD-Z) close to the OD surfaces, exhibited maze-like magnetic domains patterns, which denotes its strong ferromagnetic character that greatly contributed to the magnetic behavior of the bulk material. Consequently, we can affirm that, since creep degradation is accompanied by the formation of voids and increase in the volume fraction of carbides; the interfaces carbides/matrix will also increase. Thus; the ferromagnetic regions proliferate, making the magnetic response of the material much stronger. In addition, the depth of CD-Zs also increased with creep degradation, which provided additional magnetic response to the crept material.
4.5. Relationship Between Reformer Tube Metallurgy, Magnetic Response and Creep Degradation

So far we have been able to identify what accounts for the magnetic behavior on the selected crept samples. Moreover, the detection and measurement, in some cases, of these ferromagnetic regions was successfully achieved by advanced magnetic techniques. However, the analysis done in previous sections was basically qualitative; and it was intended to understand the microstructural and magnetic changes with temperature and time.

Quantitative studies were done by calculating the degree of damage in each crept sample; using the Larson-Miller parameter (LMP) and correlating this number with the hardness of the austenitic matrix and magnetic measurements (MU) acquired with the proprietary equipment at ArcelorMittal R&D. Taking in consideration that the entire tube was in service for about 5 years (43800 hours), and having the approximate service temperatures of the selected samples; the LMP was calculated for each of them.

Following the theory addressed in section 2.4, the hardness of the austenitic matrix corresponding to each crept sample; was correlated with the degree of degradation parameter (LMP). These results are presented in Figure 92, where we can corroborate the linear relationship expected. Moreover, as a comparison, the hardness of the as-cast material is included. Even though the hardness between samples 1A and as-cast are different, the degree of deterioration in sample 1A was not dramatic.
According to the section 2.4, hardness measurements can also indicate the resistance of the material to deformation thus; it can provide an estimate of the degree of damage by measuring the loss of mechanical properties.

Figure 92. Vickers microhardness on austenitic matrix against LMP for each selected crept sample.
However, as a non-destructive technique; magnetic measurements allow the estimation of the creep damage in-situ and in a simpler manner. Magnetic measurements were carried out on the total length of the tube after being removed from the hydrogen reformer plant. From this tube, the selected samples were extracted; each one with its corresponding magnetic measurement value. The correlations between magnetic measurement values (MU), hardness of austenitic matrix (HV₀₀₁), degree of deterioration (LMP), and volume fraction evolution (VF%) are presented in Figure 93. This set of data summarizes the different ways to estimate the degree of deterioration in the material, but more importantly; it shows the magnetic values (MU) associated to each degree of damage.

From Figure 92, it is also corroborated that volume fraction of carbides and carbonitrides greatly influenced the magnetic behavior of crept samples, by increasing the depleted (ferromagnetic) regions carbides/matrix. In addition, the softening of the austenitic matrix in crept samples is perfectly correlated with their magnetic behavior. This correlation was fitted to the polynomial equation: \( \text{HV}_{0.01} = 262.82 + 3.55 \text{ MU} + 0.038 \text{ MU}^2 \). Similarly, the degree of degradation of each crept sample (LMP) was correlated with its corresponding magnetic measurement (MU), fitting the equation: \( \text{LMP} = 29094.46 - 470.7 \text{ MU} - 6.28 \text{ MU}^2 \).
These two equations provide a quantitative technique to estimate the degree of degradation of crept samples, by only having the magnetic response value (MU). Moreover, since the degree of deterioration of crept samples was studied metallurgically; they were approximately plotted on the creep-rupture curve, as shown in Figure 94. Hence, this technique also provides information about the stage of the material creep life.

Additionally, it is possible to detect the critical MU value corresponding to the point before the start of the final creep stage, so that proper maintenance schedules can be arranged in the
hydrogen reformer plant. This confirms the adequacy of this technique as a non destructive method.

Figure 94. Creep-rupture curve and approximate location of crept samples selected from the ex-service tube. MU axe is also included since these values were found for every samples studied. Note: * indicates the rupture of the material.

However, this magnetic technique will also detect creep conditions such as the ones labeled as X and Y in Figure 94. Obviously, these samples are not yet in the last stage of their creep life, and possess some residual life. Therefore, further studies intended to calculate this remaining life were needed. The initial findings of this study are presented in the next section.
4.6. Remaining Life Calculation Approach

Although this part of the study is in progress and preliminary results have been obtained, it will not be fully included in this document. However, the approach to calculate the remaining life will be explained.

Calculation of the remaining life of service-exposed sections of the tube; was carried out by submitting selected specimens to accelerated creep-rupture tests at the conditions that closely replicated the ones found in service. The criteria for selecting these specimens was taking in consideration the degree of degradation based on the volume fraction of voids/cracks and the approximate service temperatures at which the selected specimens were exposed. Figure 95 shows the approximate location of samples that possessed degrees of deterioration corresponding to 20, 30 and 40% (8 specimens per condition). Moreover, Figure 95b shows the geometry and appearance of specimens submitted to creep-rupture tests, before and after testing. The temperature was kept constant (980 °C) and the stresses were selected such that the tests lasted a reasonable time. The stresses chosen were: 44.5, 40, 30 and 20 MPa, and at least 2 specimens were tested per condition. It is worth to mention that, before creep tests, the magnetic response of each service-exposed specimen was measured (MU_{20\%}, MU_{30\%} and MU_{40\%}).
From the creep tests, the time to rupture ($t_r$) was obtained, and having that the test temperature was 980 °C (1253 K); the LMP was calculated. Figure 96 shows the curve stress vs. LMP for the as-cast material provided by the manufacturer (Schmidt + Clemens), and the preliminary results for specimens with 30% degradation. These values were fitted with the following equation: $\sigma = 311.9 - 34.53\ln(LMP-25438.6)$, and the residual life of the service-exposed specimen was calculated at the hoop stress of the reformer tube ($\sigma = PD/2t = 4.4$ MPa). The remaining life for this degree of deterioration was 43829 hours (~5 years). The same
procedure will be repeated with specimens with 20% and 40% creep degradation, and the curves illustrated in Figure 96 (MU\textsubscript{20\%} and MU\textsubscript{40\%}) are approximately expected.

Finally, having the magnetic measurements for all service-exposed specimens (MU\textsubscript{20\%}, MU\textsubscript{30\%} and MU\textsubscript{40\%}); and their corresponding calculated residual life, it is feasible to predict the remaining life of any service-exposed reformer tube; based only on the measurement of magnetic response (MU).

Figure 96. Life prediction models for ex-service reformer tubes with different degrees of deterioration. Note: In MU\textsubscript{X}, MU is the magnetic measurement of service-exposed material, and X is the degree of deterioration in percentage.
Furthermore, since the inspection of these tubes occurs during the shut-down of the hydrogen reformer furnace (approximately every four years), it is important to determine the soundness of reformer tubes such that they do not fail unexpectedly and cause unplanned shut-downs. Having that the MUs are correlated with the remaining life of service-exposed tubes at different degrees of deterioration; this technique is of great value in determining the time when tubes need to be replaced based on the calculated residual life (If residual life is < 4 years; the tube is removed from the furnace).
CHAPTER 5

CONCLUSIONS

• It was found that the high Ni-Cr alloy steel changes from a paramagnetic to ferromagnetic behavior as a result of the degree of creep damage that it experiences. The microstructural and compositional changes of the carbides and matrix were the factors that promoted this change. These results were based on the analyses of four samples exposed to different estimated temperatures (750, 900, 1075, and 1150 °C) for the same service time (5 years).

• It was observed that the alloy carbides underwent changes in stoichiometry, but none of them (M7C3, M23C6, (Nb,Ti)C, MnS, M6(C,N), M2(C, N), and G-phase) were found to be ferromagnetic. However it was determined that the increase of alloy elements (Cr, Nb, W, and Si) in the final carbides, and the formation of the G-phase (Ni-Nb-Si rich phase) affected the composition of the precipitate/matrix interface and bulk matrix that showed paramagnetic-to-ferromagnetic changes.

• Quantitative chemical analysis of the austenitic matrix in service-exposed samples showed that the Cr-content decreased with the degree of degradation. Moreover, a marked increment of Ni and slight increase in Fe was also observed. These changes in chemical composition did not change the crystallographic properties of the matrix (γ-FCC), but it certainly affected its magnetic behavior.
Magnetic etching with ferrofluids and magnetic force microscopy confirmed the ferromagnetic properties of the matrix, as well as the interfaces carbides/matrix and carbonitrides/matrix. In addition, ferromagnetic carbide-denuded regions close to the OD surfaces, highly contributed to the ferromagnetic behavior of the bulk material. From these results, a good qualitative correlation was found between the degree of degradation and magnetic behavior of service-exposed samples.

As expected the austenitic matrix softened as the material underwent creep. The Larson-Miller Parameter for each of the four samples was estimated; and it was found a good linear relationship between these values and their corresponding microhardness. This provided a simple way to estimate the degree of deterioration by only measuring the hardness of the austenitic matrix.

Quantitative magnetic measurements were also carried out with proprietary equipment provided by ArcelorMittal R&D. It was found a good correlation between magnetic measurements (MU) and degree of degradation (LMP), and MU and hardness of austenitic matrix (HV$_{0.01}$). These results were fitted to polynomial equations of second degree, what allowed the determination of creep deterioration by only having the MU values.

A graph Stress vs. LMP was built up for samples that underwent different degrees of deterioration, and correlated with its corresponding magnetic response (MU). Preliminary results allowed the calculation of the remaining life of a sample with 30% of deterioration (~
4 years). These results provide an excellent non-destructive technique that permits to detect
the degree of degradation and determine the time when tubes need to be replaced.

ONGOING WORK

Current studies are focused on the accelerated creep-rupture tests of service-exposed section
of the tube, so we can calculate the remaining life of samples with different levels of
deterioration. These values will allow the construction of a master curve that will correlate;
magnetic response (MU), remaining life (years), and degree of degradation for any service-
exposed sample. Therefore, having the MU values obtained during the shut-down of the reformer
plant, and the master curve. The determination of tube removal, depending on its remaining life,
can be done in a simple fashion.

Regarding the advanced magnetic techniques utilized (MEwF and MFM) in this study; they
can actually be used for other applications. In this work we detected ferromagnetic regions on
Cr-depleted zones, such as carbide/matrix interfaces and carbide-denuded zones However,
MEwF was also used to study the effect of aging of Duplex Stainless Steels (DSS 2304 and DSS
2205) and the determination of ferromagnetic regions around sigma (σ) phases. In the same way
other materials that undergo paramagnetic-to-ferromagnetic transitions can also be studied, e.g.
MEMS, 304 Stainless steels that undergo phase transformation; austenite-martensite, etc.
REFERENCES


**VITA**

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PUBLICATIONS


PRESENTATIONS


