

The Study of Mechanical Properties of Welded and Base Material after Exposure to Supercritical CO₂

By

Andrew Meyer Brittan

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The dissertation is approved by the following members of the Final Oral Committee:

Dr. Mark Anderson, Research Professor, ME
Dr. Kumar Sridharan, Research Professor, NEEP
Dr. Adrien Couet, Assistant Professor, NEEP
Dr. Robert Witt, Associate Professor, NEEP
Dr. Frank Pfefferkorn, Associate Professor, NEEP

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Executive Summary:

The continued growth of the developing world – especially in India and China – is increasing the demand for electrical power. In addition to examining new sources of energy, the development and implementation of more efficient power generation is important to supplying this increasing demand. The s-CO₂ Brayton cycle has provided promise in terms of dramatically increased efficiency, as well as in capitals cost savings due to smaller component sizes. However, achieving the optimal efficiency requires going to elevated temperatures, creating additional materials demands which need to be satisfied.

A large amount of research has been performed on CO₂ materials corrosion, as well as long-term, high temperature aging of candidate alloys. The research on CO₂ corrosion has focused on directly corrosion-related phenomena: mass change, oxide and carbide formation, and other phenomena involving elemental diffusion in the corrosion-affected zone. It has also focused on the corrosion of base material, with an intact, specifically engineered microstructure, leaving a gap in knowledge of welding corrosion. This work focuses on the effect of CO₂ exposure on the mechanical performance of candidate alloys and their welds.

An autoclave system at UW-Madison was used to expose samples to CO₂ in a pseudo-static system which refreshes the CO₂ volume every 2 hours to maintain a consistent gas composition. This facility can be used for exposure at conditions up to 750°C and 20MPa, with fluctuations of only $\pm 1^\circ\text{C}$ and $\pm 0.02\text{MPa}$. Calibrated tensile testing machines were also used in conjunction with a custom video extensometer to produce accurate results of stress and strain. Base material, similar welds, and select dissimilar welds were analyzed to better understand the effect of the CO₂ environment on alloy corrosion and mechanical performance.

Exposures were completed in CO₂ for 1,000 hours over a range of temperatures from 450-750°C and 20MPa, as well as in Ar at either 550°C or 750°C and 0.02MPa. Analysis of welded material was conducted which indicated no difference in corrosion performance relative to that of base material, but there were some differences related to thermal aging which were detrimental for welded mechanical performance. The primary concern in the CO₂ environment was identified as embrittlement due to carburization and carbide formation. A method involving Cu coating was investigated which could effectively eliminate carbon deposition in a structural alloy.

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1. Introduction:

1.1. Motivation:

As we enter the middle of the 21st century, the challenge of supplying energy to the people of the world continues to be increasingly important. Many countries – including China and India – are attempting to dramatically improve the quality of life of their citizens as well as grow their economies. Both of these factors are very closely related to energy usage. In fact, the US Energy Information Administration released an International Energy Outlook in 2017 that used GDP projections to estimate an increase in energy consumption by 28% worldwide from 2015 to 2040 [1]. Given that the majority of energy usage comes from fossil fuels which will become more scarce as they are used, there is a large need for innovation when it comes to efficiency of utilizing these energy sources. The majority of conventional power relies on the steam Rankine cycle or a combined gas Brayton cycle with a Rankine bottoming cycle to produce electricity, but in the search for greater efficiency, other cycles need to be explored [2]. Switching to using a Brayton cycle with CO₂ as the working fluid is an option for increasing efficiency that has become a popular research topic in recent years.

1.2. Physical Advantages of s-CO₂

There are several advantages of using CO₂ relative to other working fluids. First, CO₂ is relatively chemically inert, so corrosion and exothermic interactions with impurities is less common [3]. In addition, it has good wetting characteristics and low viscosity. These last two properties allow CO₂ to function as a very effective working fluid in power cycles. These stand-alone properties of CO₂ are aided by the accessibility of the critical point, 304.1K and 7.38MPa (see Figure 1 A), allowing for supercritical conditions to be more easily achieved for CO₂ than for water (at 647K and 22.1MPa) [4]. Around the critical point, there are dramatic fluctuations in the properties of CO₂, with properties changing nearly discretely [3]. As

can be seen in Figure 1 B, the density of CO₂ near the critical point changes with nearly the abruptness of a phase change when pressure is varied at constant pressure. These effects of varying properties near the critical point can be taken advantage of when designing power cycles. The most advantageous of these property effects is that the density changes allow for a small back work ratio. Additionally, as can be seen in Figure 2, the value for c_p increases exponentially just past the critical point. This allows for an immense amount of heat transfer by the fluid when heated or cooled through this temperature region.

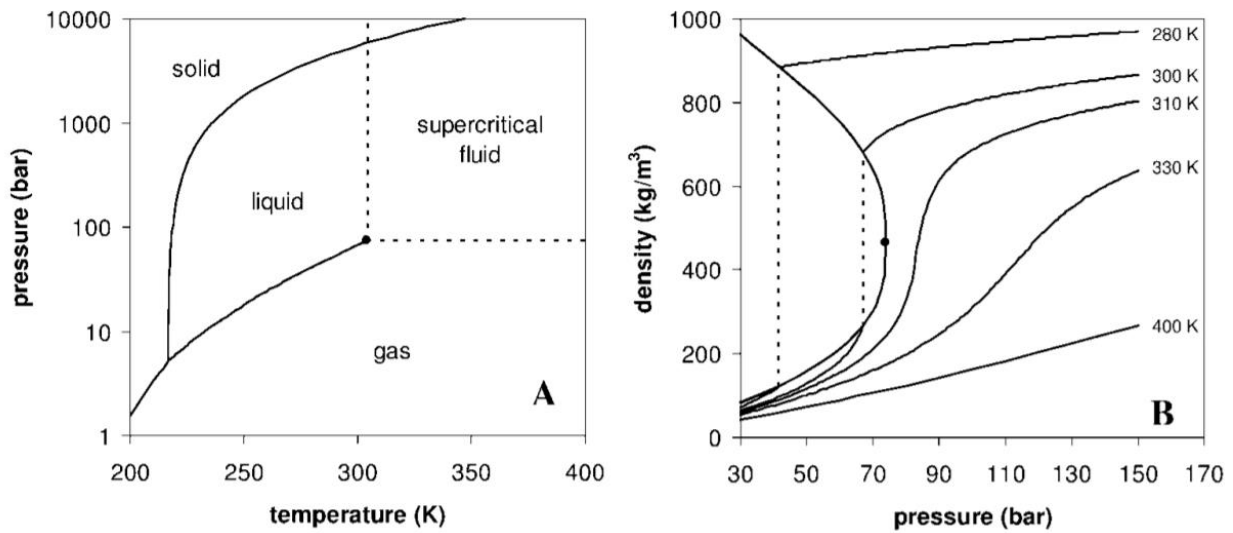


Figure 1 – A: CO₂ phase diagram (pressure on a log scale); B: CO₂ density as a function of pressure at different isotherms [3]

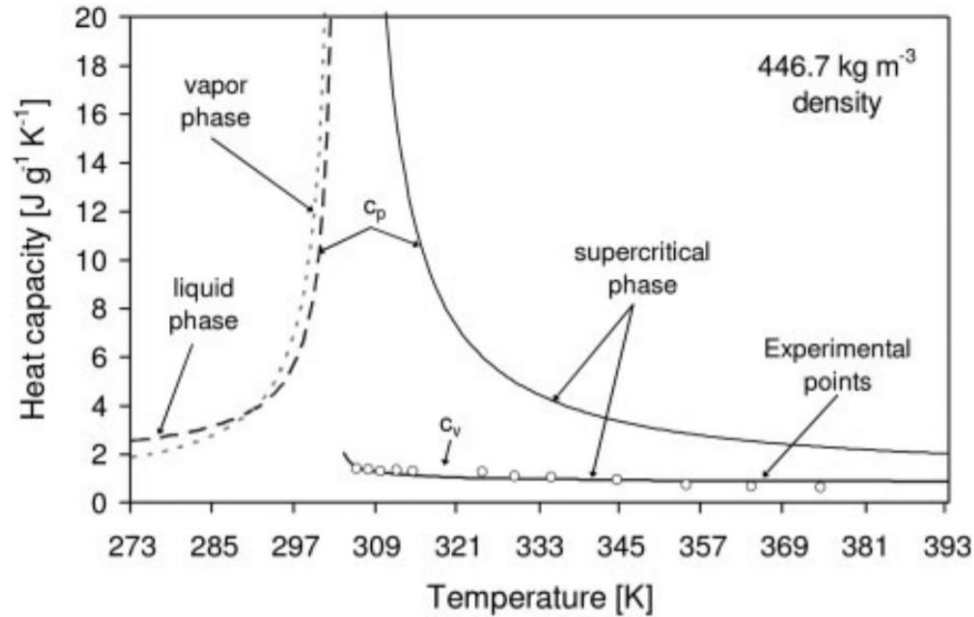


Figure 2 – Theoretical values of c_p and c_v along with experimental points of c_v [3]

1.3. S-CO₂ Brayton Cycle:

The s-CO₂ Brayton cycle has the potential to achieve much higher efficiencies than the steam Rankine cycle through operation at higher temperatures, see Figure 3 [5]. Though lower turbine-inlet temperatures (<500°C) project that superheated or supercritical water cycles should operate at higher efficiencies, there is an efficiency cross-over temperature around 500-550°C above which the s-CO₂ Brayton cycle becomes preferred [5], [6]. In addition, it is projected to reduce the overall cost of the power plant due to the simplicity and reduced size of components compared to the steam Rankine cycle [5], [7]. The s-CO₂ Brayton cycle has comparable efficiency to the He Brayton cycle at lower turbine inlet temperatures, but at higher pressures (550-650°C, 20MPa s-CO₂ compares with 850°C, 8MPa He).

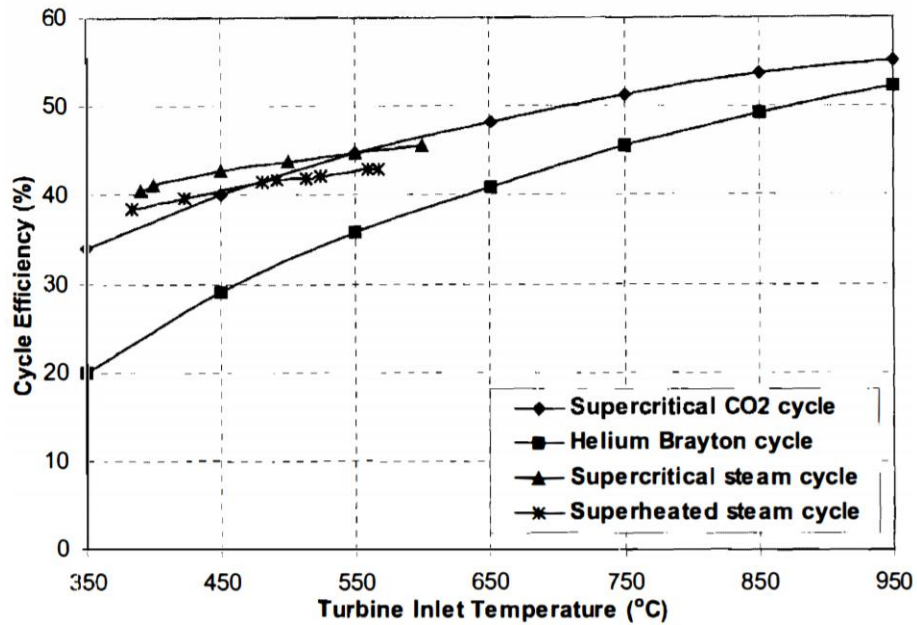


Figure 3 - Comparison of cycle efficiencies of advanced power cycles [5]

It was noted above that significant savings in capital costs can come from the use of the s-CO₂ Brayton cycle over steam Rankine cycles. This is due in large part to the large reduction in the size of the turbo machinery in s-CO₂ cycles. As an example, a steam turbine must be roughly 10 times as large as a turbine for a s-CO₂ Brayton cycle to produce the same output [5], [8], see Figure 4. Further, the use of printed circuit heat exchangers (PCHE) is projected to save nearly 90% of the mass of material when compared to a shell and tube heat exchanger, thanks to the compactness of the micro-channels to maximize heat transfer. While this number does not include any extra costs for manufacturing the PCHE, it represents a possibility to significantly cut the capital costs of constructing a new power cycle. Further research is being conducted to attempt to optimize the balance of capital costs and efficiency, with alternate-flow regenerators (acting as thermal batteries) producing an overall reduction in projected cost of electricity production [6].

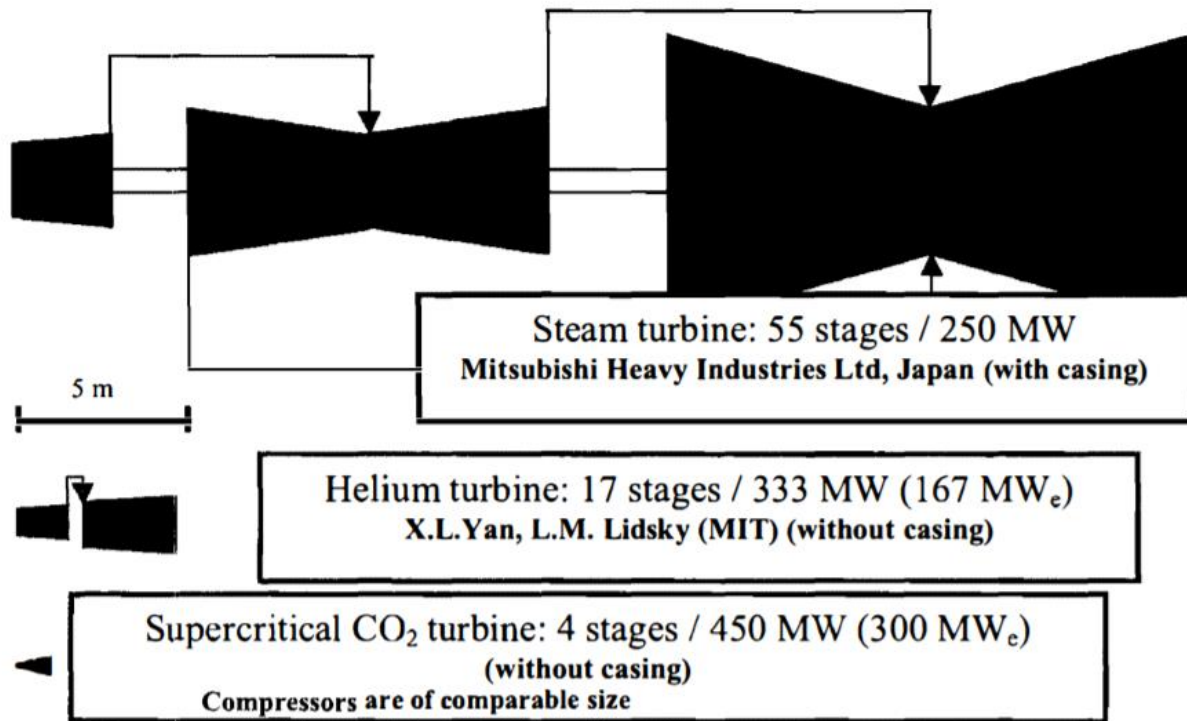


Figure 4 – Turbine size comparison for steam, He, and CO₂ [5]

1.4. Research Goals:

The goal of this work is to further the development and commercial viability of the s-CO₂ Brayton cycle. In order to do this, an increased understanding of the materials response to the s-CO₂ environment will be required. There is a gap in the current understanding of the mechanical performance of candidate alloys after prolonged exposure to the s-CO₂ environment.

1.4.1. Engineering Goals:

- Provide experimental data for the mechanical performance of candidate alloys after exposure to CO₂ under conditions applicable to each alloy.
- Understand the effects that CO₂ has on the welded region (fusion zone and HAZ) of candidate alloys relative to base material – both from a mechanical and corrosion point of view.
- Classify the impact of oxidation on reducing the effective cross-sectional area on a material.

- Determine the performance of several relevant dissimilar welds in CO₂ at temperatures applicable to the inferior alloy.

1.4.2. Scientific Goals:

- Understand the effect of the welding process – and corresponding segregation of elements – on oxidation and carburization relative to base material.
- Identify the factor in the high temperature corrosion process which becomes limiting in terms of mechanical performance.
- Develop a theoretical framework to reduce the effect of CO₂ corrosion on mechanical properties.

2. Literature Review:

There exists substantial work in the areas of both materials corrosion in CO₂ and in materials testing of base material and welds of the alloys under investigation in this research. Because this report is focused on the corrosion of materials and its effect on the properties of both base materials and welds, this literature review has been split into three main sections which deal with: 1) materials corrosion; 2) the effect of prolonged temperature exposure on these alloys, and 3) the mechanical properties associated with the respective materials and welding mechanisms.

2.1. Materials Corrosion:

The corrosion of materials is a very important factor in when choosing which alloys are used in high temperature applications. Corrosion is dependent on the environmental constituents, temperature, and pressure, along with the chemical composition of the alloy. This work focuses on the corrosion of materials in a CO₂ environment, so the effect of oxygen and carbon will be the focus of this section. The majority of the work in this section will be from one of the following texts: “High Temperature Oxidation and Corrosion of Metals” [9] and “ASM Specialty Handbook: Heat Resistant Materials” [10]. These books cover the basics of corrosion in high temperature environments.

2.1.1. Oxidation:

Oxide Formation

The stability of an oxide is determined by the Gibbs free energy of reaction (ΔG°), seen in generic terms in (1). The more negative the ΔG° , the more stable the oxide. This means that, to use an example relevant to this work, Cr₂O₃ is more stable oxide than Fe₂O₃. According to a model [10], [11], the predicted ΔG° for the oxidation of chromium to form 2/3 mole of Cr₂O₃ to be -800kJ at 750°C. Conversely, 2/3 mole of Fe₂O₃

has a $\Delta G^\circ = -270\text{kJ/mol}$. Because $|\Delta G^\circ_{Fe}| < |\Delta G^\circ_{Cr}|$ Cr_2O_3 is the more stable oxide, and in addition it will form at lower p_{O_2} . This means that if there is a point that the p_{O_2} reaches equilibrium for Fe_2O_3 , Cr_2O_3 will continue to form, possibly transforming existing Fe_2O_3 into Cr_2O_3 through the reaction detailed in (3).



Assuming that the metal in the reaction is always freely available, the equilibrium partial pressure of oxygen (p_{O_2}) for an oxide is given in (2). This value defines the p_{O_2} above which will produce additional oxide, and below which will not.

$$p_{\text{O}_2} = \exp\left(\frac{\Delta G^\circ}{RT}\right) \quad (2)$$

In oxidation of alloys, there are a few contributions to determining which elements oxidize. The first is that when oxygen is available to multiple components, there is a competing oxidation process between solute elements. This process can be described by (3), where X and Y are solutes, and a, b, c, and d are appropriate constants. The direction that reaction travels is determined by the ΔG° of the reaction and the local solid composition.



In addition to this governing process, selective oxidation results in removal of the oxidized element from the metal matrix. This creates a localized change in composition, thereby changing the oxidation preference. Therefore, diffusion of elements from the bulk to the surface through both the alloy and the oxide is important to analyze and track the oxidation process over time.

Defect Structure

In order to understand diffusion-controlled oxidation better, it is necessary to understand the role the oxide plays in the diffusion process. Protective oxides are electronic semiconductors that allow for mass

transport of ions. The type of ion that they allow through defines which of two types the oxide is: p-type or n-type. P-type oxides are rich in cation vacancies and, therefore, allow the transport of positive ions (cations). In this type of oxide, cation vacancies migrate inward from the oxide-gas interface as cations migrate outward from the metal-oxide interface. This results in oxide growth at the oxide-gas interface, as well as voiding at the metal-oxide interface. P-type oxides that are applicable to this work are Cr_2O_3 , FeO , and NiO .

N-type oxides are defined by their major charge carriers being free electrons. They are further broken down into two categories: cation-excess or anion-deficient. Cation-excess oxides grow on the oxide-gas interface, just like P-type oxides, but due to interstitial cation diffusion, so no voiding at the metal-oxide interface occurs. Anion-deficient oxides occur because the cations ionize with different charges (for example, Zr forms both a Zr^{4+} ion and a Zr^{2+} ion), so there need to be anion vacancies to maintain electrical neutrality in the oxide. Anion-deficient oxides grow inward from the metal-oxide interface because the oxidation process is controlled by the inward diffusion of oxygen through these anion vacancies. Examples of n-type oxides applicable to this work are Fe_2O_3 and Al_2O_3 . It can be noted that anions are treated as larger than the cations because, while they are technically smaller, they have excess electrons and, therefore, have a larger effective volume.

Solid-State Diffusion

As described above when describing the oxide defect structure, solid-state diffusion occurs through either vacancy diffusion or interstitial diffusion. Vacancy diffusion is typically much easier and, therefore, is the more common mode of transport. The aptitude for diffusion with vacancy diffusion is defined by the number of vacancies and the jump distance in the matrix. In both metals and ionic oxides, there are usually large amounts of vacancies, so that is not a limiting factor. As far as jump distance, metals are comprised of solely cations so the jump distance is short, making for easy vacancy diffusion. However,

oxides contain both anions and cations which create a much longer jump distance. This means that the vacancy diffusion of cations is typically much quicker within the metal than within the oxide, resulting in the oxide being a limiting factor in the oxidation rate for p-type oxides. Interstitial diffusion occasionally dominates in oxides, especially if the cation is effectively small.

Because the vacancy concentration is so important in the diffusion rate – and, therefore, the oxidation rate – there can be a sizeable effect of impurities within the oxide. For example, in p-type oxides, cation impurities which ionize to a larger charge than the normal cation will increase cation vacancies. This results in faster cation diffusion outward and faster oxide growth. In n-type oxides, a cation impurity which ionizes to a smaller charge will increase the number of anion vacancies. Similarly, this results in faster diffusion inward of the anion (oxygen) and an increased oxidation rate. The processes work in reverse as well, as the addition of higher valent impurity atoms in the oxide would decrease vacancy diffusion in p-type oxides, while the addition of lower valent impurity atoms would decrease vacancy diffusion in n-type oxides. An example of this is NiO, as nickel forms both Ni^{2+} and Ni^{3+} valences. Doping with Al, which forms Al^{3+} , increases the oxidation rate because every two additional Al atoms adds one additional cation vacancy. Conversely, doping with Li, which forms Li^+ , decreases the oxidation rate because every two Li atoms removes 1 cation vacancy. This is important to understand when designing high temperature alloys, because the addition of a protective-oxide former such as Al is not always preferred.

Another result of solid-state diffusion is that the oxidation of pure metals can result in multiple scale layers when the cation can form multiple valences. Oxides are organized with the most metal-rich oxide nearest the metal. In general, the inner oxides will be p-type because the electron/electron-hole pairs form easily, and the outer oxides will be n-type because of the prevalence of anion vacancies. A perfect example of this is iron, which can form Fe^{2+} or Fe^{3+} . These valences indicate that iron is prone to form FeO (wustite) and Fe_2O_3 oxides (hematite), but it also forms a combination oxide, Fe_3O_4 (magnetite). As expected, the

p-type and metal-rich FeO forms nearest the metal, while the n-type and metal-poor Fe₂O₃ forms furthest from the metal. The combination oxide Fe₃O₄ forms in the middle, forming a somewhat discrete iron concentration gradient outward from the metal surface. With the addition of multiple oxidizing components in an alloy, this organization competes with other factors such as thermodynamics and component diffusion.

In a high temperature environment in which oxygen is constantly available at the oxide surface, the oxidation process is governed by diffusion of the oxidizing species through the alloy, and either oxygen or the oxidizing species through the oxide. Oxidation is, therefore, typically a diffusion-controlled process and the kinetics can be modelled as parabolic. The parabolic rate constant (k_p) governs the oxidation rate for an alloy in this type of environment, defined with an oxidation rate $\left(\frac{dX}{dt}\right)$ that varies with time according to (4), with oxide thickness (X) and time (t). This rate should hold if the oxide produced grows on the surface of the alloy, that is to say it should hold for p-type oxides and cation-excess n-type oxides. In analyzing parabolic oxidation, k_p varies by two main factors: the temperature (T) and the p_{O_2} . The Arrhenius relationship – see (5) – defines the relationship between k_p and T through use of the effective activation energy (Q), the temperature-independent constant (k_0 , different for each element in an alloy), and the ideal gas constant (R). This is used to extrapolate oxide growth between different temperatures at constant p_{O_2} .

$$\frac{dX}{dt} = \frac{k_p}{X} \rightarrow X^2 = 2k_p t \quad (4)$$

$$k_p = k_0 \exp\left(-\frac{Q}{RT}\right) \quad (5)$$

Conversely, at constant temperature the relationship between k_p and p_{O_2} is given by (6), where n is a temperature-independent constant. The combined effect of the variance of k_p with respect to temperature and pressure can be seen in Figure 5. This graph shows the dependence of k_p for cobalt on

p_{O_2} at two different temperatures. As can be seen, k_p scales linearly on the log-log plot with p_{O_2} until a certain point where it flattens out. This flattening is because the availability of oxygen is no longer the limiting factor, but instead it is diffusion. As the temperature is increased, diffusion occurs more quickly and the whole graph increases, as well as the “saturation” point of p_{O_2} .

$$k_p = k_0 p_{O_2}^{\frac{1}{n}} \quad (6)$$

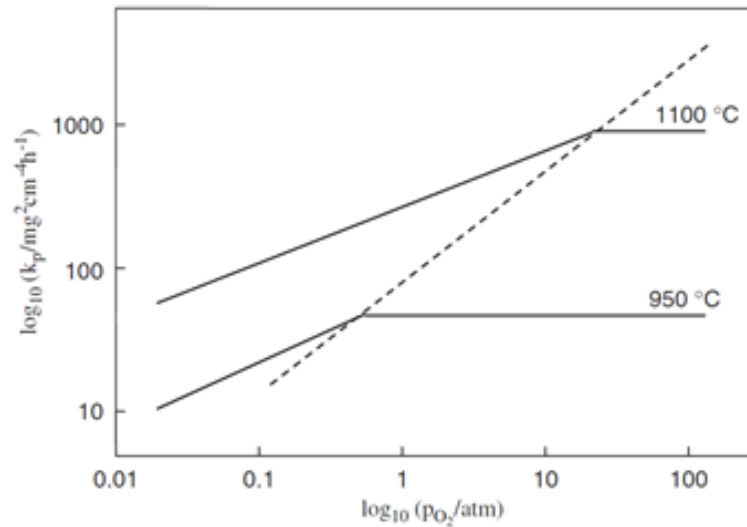


Figure 5 - Oxygen Partial Pressure Effects on k_p for cobalt [9], [12]

Pilling-Bedworth Ratio (PB)

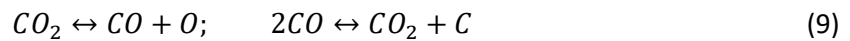
The amount to which an oxide protects the underlying surface from additional corrosive attack is very important. The Pilling-Bedworth (PB) ratio can be used to give an estimate of this behavior. The PB ratio of a given reaction is the ratio of the volume of oxide to the volume of metal. This is found by balancing the moles of metal used against the moles of oxide produced for a given reaction. For example, relative to the process described in (1), PB can be found by using (7). According to the theory, oxides are usually unprotective and porous when $PB < 1$, as they are for alkali and alkaline earth metals. When $PB > 1$ oxide scales are protective leading to oxidation proceeding through only solid-state diffusion. When $PB > 2$ the compressive stresses from oxide forming at the metal-oxide interface cause the oxide to become

susceptible to spallation. As two examples, Al_2O_3 has a PB of 1.28 while Fe_2O_3 has a PB of 2.15. Al_2O_3 is predicted to form a good, protective oxide, and this is very accurate to experimental work [13]–[15]. Fe_2O_3 is predicted to be somewhat protective but susceptible to spallation, as is also shown in experiment [16]. However, it should be noted that this theory works with the assumption that all oxides grow inward and, therefore, has many exceptions. It is most applicable to anion-deficient n-type oxides, though it can be useful in general terms in other cases.

$$PB = \frac{\text{Vol of } \frac{2}{y} \text{ mol of } M_xO_y}{\text{Vol of } \frac{2x}{y} \text{ mol of } M} \quad (7)$$

2.1.2. Carburization:

Carburization of materials is a major concern with the application of a high temperature CO_2 system. In CO_2 environments, carbon can be liberated in one of two ways. The first is given in (8) and involves the dissociation of CO_2 directly into its constituents, carbon and gaseous oxygen. The second, the Boudouard reaction detailed in (9), involves the oxidation process removing a single oxygen atom through the oxidation process and producing CO. Two CO molecules then combine to form CO_2 and an excess carbon through the Boudouard reaction. Previous work at UW-Madison [17] has shown gas analysis results which point towards the formation of CO as part of the oxidation process. This would indicate that (8) provides the steady-state partial pressure of oxygen and activity of carbon, while (9) provides the increase in the activity of carbon due to the oxidation process.



The result of this is that the majority of the free carbon in the system will be liberated during the oxidation process. This means that as you move through the oxide from the gas-oxide interface to the oxide-metal interface, the partial pressure of oxygen will go down with a subsequent increase in the activity of carbon.

The activity of carbon will, therefore, peak at the surface. Assuming that the oxide scale that is developed has a negligible amount of porosity, the penetration of oxygen or carbon through the scale must be by solid-state diffusion. This results in a parabolic profile through each scale present, shown in Figure 6 for the attack of pure chromium. It should be noted that the model used for this figure was assuming that the activities of oxygen and carbon were not interrelated, so only the activity of oxygen (approximately equal to the partial pressure of oxygen, p_{O_2} , at the temperatures and pressures investigated in this work) is representative of a CO_2 environment. Carburization is often minimized with the formation of a continuous layer of chromia scale, as the oxidation rate and, therefore, the available free carbon in the system decreases dramatically.

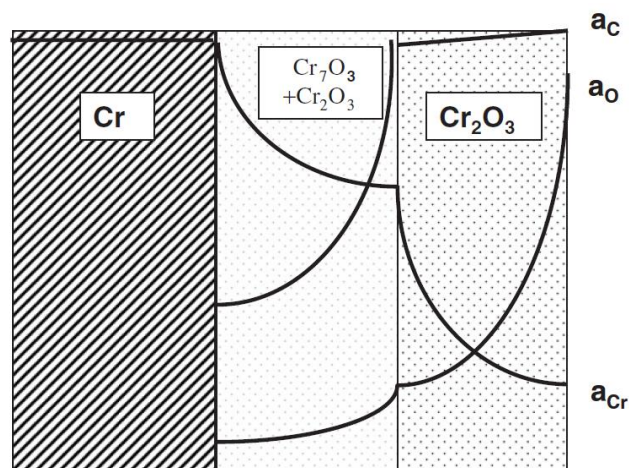


Figure 6 - Schematic of activity profiles showing the penetration of carbon and oxygen through a Cr_2O_3 scale given a fixed activity at the scale surface [9]

The location of the carbide formation is determined by the competition between the diffusion of chromium outward and the diffusion of carbon inward. This competition is more clearly defined in the case of a CO_2 environment by describing it as the concentration of chromium in the alloy versus the production rate of dissolved carbon at the oxide surface through the oxidation process. The higher the concentration of chromium in the alloy, the closer to the surface that carbides will tend to form. Conversely, the higher the surface carbon activity, the more internal carbides will form.

Understanding if carburization will occur is dependent on the a_c of both the environment and the alloy. Carburization will only occur if the a_c of the environment is greater than the a_c of the alloy. A calculation of the a_c of the local environment during oxidation can be made based off of the Boudouard reaction in (9) above, using the partial pressures of CO and CO₂, given in (11). For alloys, a_c is not very widely reported below 1,200°C. However, for carbon steels a_c can be estimated – see (11) – assuming that the equilibrium is reached with Fe₃C (cementite), assuming the activities of both Fe and Fe₃C are equivalent.

$$a_{c,environment} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)\left(\frac{p_{CO}^2}{p_{CO_2}}\right) \quad (10)$$

$$a_{c,steel} = \exp\left(\frac{\Delta G^\circ}{RT}\right) \quad (11)$$

In nickel and cobalt-base alloys as well as ferritic and austenitic stainless steels, carburization primarily results in the formation of chromium carbides. Chromium carbides come in several different phases, including Cr₂₃C₆, Cr₇C₃, and Cr₃C₂. The stability of each phase is dependent on the a_c and p_{O_2} of the surrounding environment, but a general rule is that the higher the a_c , the more stable the carbon-rich phases will be. For example, the most stable carbide at lower carbon activities, and typically the first to form internal carbides, is Cr₂₃C₆ [18]. Prolonged exposure at the appropriate temperatures and environments will precipitate more carbon-rich phases.

Internal carburization is often observed to be more prevalent than surface carbide formation. This is primarily due to oxides being much more stable than carbides. As an example, the most thermodynamically preferable carbide relevant to this work, Cr₂₃C₆, has a theoretical ΔG_f° of -450KJ/mol at 750°C, compared to -800KJ/mol for Cr₂O₃ (referenced above) [9]. This indicates that given a sufficient p_{O_2} the oxide will always form in place of the carbide. Therefore, carbides do not form until carbon has travelled further into the material than oxygen. Given that the easiest diffusion pathways are along grain

boundaries, this theory predicts the existence of a majority of carbides due to carbon ingress to occur beneath the oxide and along grain boundaries.

2.1.3. Corrosion of Industrial Alloys in this Investigation

2.1.3.1. INCONEL 740H and 282

Much work has been performed on these alloys, as they have good high temperature strength up to about 800°C [19]. Additionally, they have both shown good corrosion properties in CO₂ at 750°C, see Figure 7 [17]. 740H is shown to form a thin protective layer of chromium-rich oxide with some discontinuous, internal oxidation of Al into Al₂O₃ (alumina). The alumina formation is due to the relatively large Al concentration in the alloy to assist with formation of the strengthening precipitate phase, γ' . Similarly, 282 has exhibited a thin – though slightly thicker – protective oxide. The higher Ti-content and lower Cr-content of 282 results in this protective scale consisting of both TiO₂ and Cr₂O₃ [20]. 282 also exhibited internal oxidation of both Al and Ti, and to a larger extent than in 740H. This is likely due to the higher concentrations of these elements in 282 than in 740H (in aggregate, roughly 1 wt% greater). This internal oxidation of 282 was also seen after oxidation in air at temperatures from 871-982°C [21].

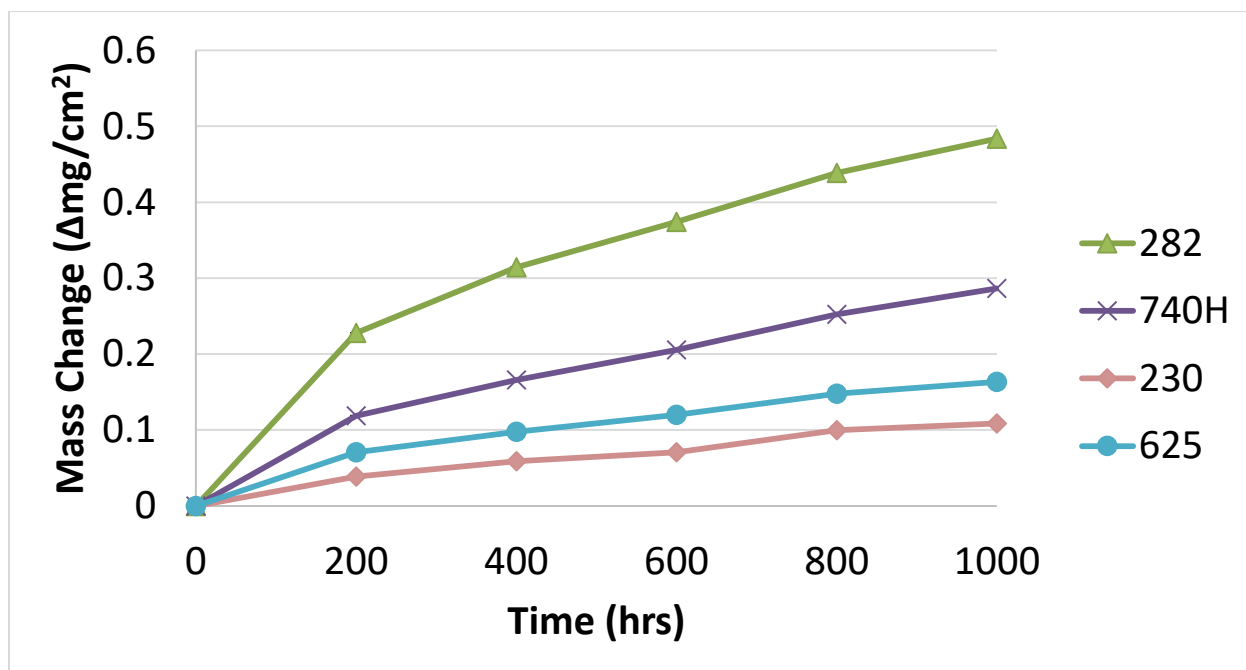


Figure 7 - Mass change for various Ni-base alloys in RG CO₂ at 750°C, 20MPa [17]. Performance of both 740H and 282 are similar to that of comparable alloys.

Exposure in supercritical water (s-H₂O) has also been investigated for both of these alloys. For 282, mass gain was observed to be roughly double that reported above for s-CO₂ exposure, as can be observed in Figure 8 [22]. These follow a pattern of s-CO₂ oxidizing Ni-base alloys less severely than H₂O under similar conditions. The protective, external oxide from the below work [22] was observed to be Cr₂O₃ and TiO₂, while internal oxidation consisted mainly of Al₂O₃. The slightly worse performance of 282 relative to other Ni-base alloys is ascribed to the higher Ti content, which appears to be harmful to the alloy's oxidation resistance. 740 (a slight variation of 740H) has similarly been shown to produce a thin Cr-rich oxide along with parabolic kinetics in s-H₂O [23].

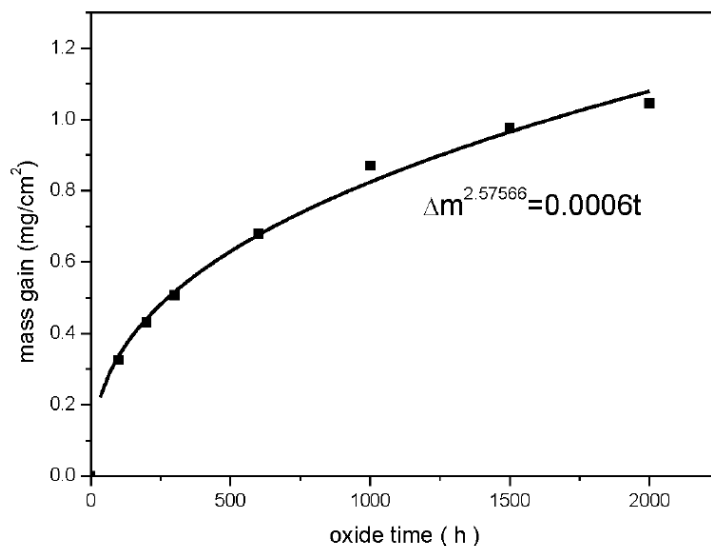


Figure 8 – Mass change of Haynes 282 versus exposure time at 750°C in H₂O [22]

2.1.3.2. 316 Austenitic Stainless Steel

Due to its popularity in industry, there has been a lot of previous work on 316 and 316L in the s-CO₂ environment. These studies all point toward 316/316L producing a protective oxide layer in conditions of 550°C and below, but exhibiting spallation and possibly breakaway oxidation above about 600°C [17], [24], [25]. An example of the effect of the protective oxide of 316 and its effect on mass uptake can be seen in the mass change plots in Figure 9 [17]. Once 316 produced an oxide layer, the oxide process was slowed to an amount which was less than the standard deviation. As could be expected, 316 outperforms the 9Cr alloy T91 and underperforms the Ni-heavy alloys listed. 316 forms a protective Cr-rich oxide, with occasional nodules consisting of a duplex oxide, with an outer, Fe-rich oxide (magnetite, Fe₃O₄) and an inner, more protective Cr-rich spinel. Exposures of 316 have also been performed in s-H₂O and found a similar oxide morphology.

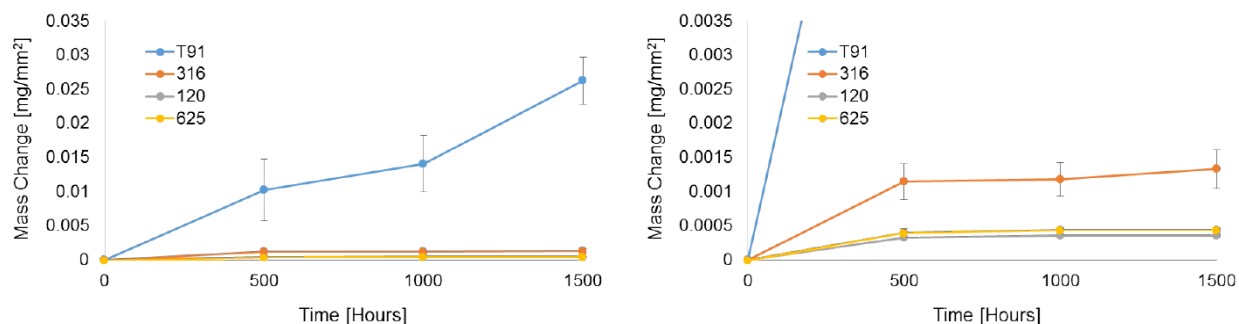


Figure 9 – Mass change for exposure to s-CO₂ at 550°C, 20MPa for up to 1,500 hours [17]

2.1.3.3. Grade 92 Ferritic-Martensitic Steel

P92 and similar 9-12% Cr steels have been shown to form a duplex oxide, with an outer magnetite and an inner Fe-Cr spinel (with an average stoichiometry of $\text{Fe}_{2.3}\text{Cr}_{0.7}\text{O}_4$) [26], [27]. Once this duplex structure has developed, the alloy exists in a pseudo steady-state, and the available space model is used to understand additional oxidation. This model describes a process by which Fe ions diffuse to the surface to oxidize into magnetite (Fe_3O_4) and hematite (Fe_2O_3) [28]. The diffused Fe then leaves vacancies in the alloy near the surface, which coalesce into voids slightly beneath the oxide-metal interface. These voids then allow “available space” for internal oxidation of Fe and Cr.

It is believed that diffusion and the internal oxidation to create the inner Fe-Cr spinel locally lower the $p\text{O}_2$ to the point that Cr oxidizes preferentially [26], [27]. Small islands of Cr-oxide have been observed underneath the inner Fe-Cr spinel, forming the Internal Oxidation Zone (IOZ) [29]. P91 (a very similar 9%Cr steel) after exposure at 600°C for 20,000 h exhibited an IOZ characterized by chromite (FeCr_2O_4) and M_{23}C_6 carbides which had left the nearby matrix nearly devoid of Cr. The oxides were preferentially situated nearer the oxide-metal interface than the carbides, reflecting the higher thermodynamic stability of the oxide. The removal of Cr from the surrounding matrix would then lead to oxidation of Fe (once the local $p\text{O}_2$ increases sufficiently) around the chromite islands to form the full Fe-Cr spinel with the above listed average stoichiometry. This process is likely to occur at lower temperatures as well.

Several experimental studies have been performed which exposed P91 or P92 to high temperature CO₂ or H₂O. Previous work at the University of Wisconsin-Madison showed that P92 exposed to CO₂ at 450°C, 20MPa for 1000 hours produced an oxide layer of roughly 8μm thickness, and carburization to a depth of up to 200μm from the surface [30]. Another study exposed P91 to CO₂ at 550°C, 25MPa for 310 hours and discovered carbon contents between 1.5-2.0 atomic percent extending from the inner Fe-Cr spinel out beyond 50μm (maximum reported depth of measurement) [26]. An additional study exposed P92 to an Ar-CO₂ 50/50 mixture at 550°C for up to 150 hours and found a carburized region of roughly 100μm [31]. In addition, P92 corrosion in supercritical water at up to 600°C for 1000 hours has also been shown to produce parabolic oxidation kinetics [32].

For 9-12Cr steels in particular, carburization and oxidation in the CO₂ environment have been linked [17], [31], [33]. This is believed to be the result of the Boudouard Reaction, given in (9). The direct oxidation of CO₂ produces CO, and the recombination of two CO molecules into CO₂ produces an excess carbon atom. Therefore, more oxidation leads to additional carbon deposition, and this leads to a greater effect of carburization on the material. In addition, as internal oxidation occurs, previously formed carbides will get oxidized (oxides are generally more thermodynamically stable [9]) and create additional free carbon. In this way, the carbon profile will get pushed inward, and build up in and near the internal Fe-Cr spinel. The IOZ, meanwhile, has been shown to be carbon-poor, with the assumption being that as carbides are oxidized, carbon is freed up and diffuses inward to find additional Cr to form carbides with [29]. In addition, the P92 microstructure consists of a dual phase of ferrite and tempered martensite which results in grains on the order of 1-10μm in diameter. This allows for good strength and ductility, but it also creates a high density of diffusion pathways of carbon, potentially enhancing the depth-dependent effects from external carburization. As discussed above, the coarsening of carbides should have a measurable effect on mechanical properties.

2.2. Effects of Long-term Aging:

The alloys analyzed in this report were exposed to CO₂ at high temperatures. Beyond absorbing carbon and oxygen via the corrosion process, the elevated temperatures cause growth and coarsening of microstructural phases which can change the macroscopic properties of the material. The range of materials examined in this research will be segregated by the type of material analyzed.

2.2.1. Nickel-Base Superalloys:

This work focuses on γ' -strengthened alloys 740H and 282. These alloys are not believed to precipitate γ'' (Ni₃Nb) either by prediction or experiment [34]. They are very similar in strength and high temperature strength, but they are different in a few ways. First, their compositions are roughly 10% different (see Table 18), and second, 740H has had much more analysis done previously. Because of the latter, the majority of the discussion in this section will be dominated by discussion of 740H. The investigation of 282 is performed with an understanding that 740H is a similar alloy which may share some characteristics of note.

Nickel-base alloys such as INCONEL 740H are developed in part for the purpose of providing high strength at elevated temperatures. They are characterized by a very high strength and hardness while maintaining good ductility. The source of these properties is the combination of a γ austenitic matrix (very ductile) interspersed with hardening γ' precipitates (Ni₃(Al,Ti,Nb)). The prescribed aging heat treatment to precipitate the γ' phase is 760-815°C, with the target temperature of 800°C, for at least 4 hours. The post-weld heat treatment (PWHT) is identical, because the fusion welding process dissolves any γ' present in the fusion zone [35]. As the potential operating conditions of these superalloys approaches this heat treatment temperature, it is important to understand the effect that further aging has on the microstructure and, therefore, mechanical properties of these superalloys. For this reason, many studies have previously been performed on this material at similar temperatures [34], [36]–[38].

One such study was performed to analyze the effect of prolonged exposures of 740H to 750°C [36]. This study analyzed samples of 740H at each stage of the heat treatment process: after solution annealing (1150°C/30min/WQ), after standard heat treatment (800°C/16h/AC), and after various time exposures at 750°C up to 10,000 hours. The differences in material microstructure and room temperature mechanical properties were then measured.

The differences in the microstructure over time were defined by an increase in carbide formation along grain boundaries and coarsening of the γ' precipitates. The carbides which formed were analyzed using Transmission Electron Microscopy (TEM) and found to be $M_{23}C_6$ carbides. The γ' precipitates – also measured using TEM – increased in size during heat treatment, following a trend that which can be observed in and Figure 10. It can also be seen from Figure 10 that the presence of γ' precipitates increases the hardness of the material immensely – by roughly 80%. This is an effect that is seen immediately with the standard heat treatment process. However, there is very little effect on hardness from the coarsening of the γ' precipitates which occurs from continued exposure. The initial hardening is likely due to maintaining the coherency between the γ' precipitate phase and the γ matrix, resulting in a coherent stress for the alloy. In addition, the precipitated $M_{23}C_6$ carbides along grain boundaries acted as barriers for dislocations as well as stabilizing dislocations. The decrease in hardness is possibly due to there being a critical diameter of the γ' precipitates for maximum hardness of the material, though this is not confirmed. If there was a critical diameter, it would likely be in the vicinity of that seen in the 300 hour treated sample, 47nm [36].

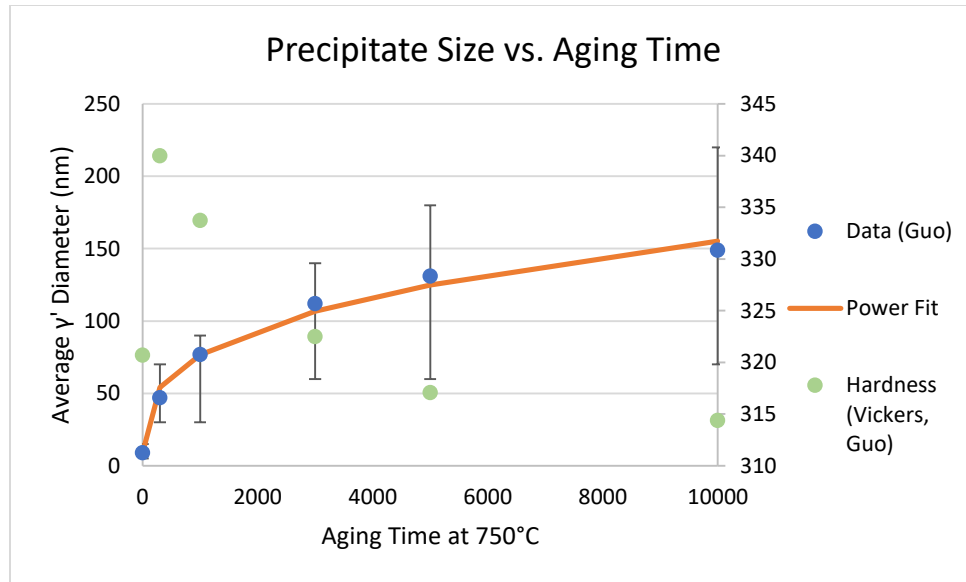


Figure 10 – Average precipitate size (and range of sizes measured) with the power fit (left axis), and room temperature hardness (right axis) plotted against aging time [36]

Figure 10 above shows the precipitate size plotted against the exposure time at 750°C after standard heat treatment. A power fit was performed on the data and found that (12) was the most accurate fit for the diameter of the precipitates as a function of exposure time:

$$\bar{r}(t) = 6.72e^{0.3344t} \quad (12)$$

According to the theory of Ostwald ripening, many small crystals form initially in a system. These crystals slowly disappear as they are consumed to produce a smaller number of larger crystals. As the larger crystals grow, the area surrounding them is, therefore, depleted of smaller crystals. This process occurs because the surface molecules of a precipitate are energetically less stable than those that are in the interior. The larger particulates are, therefore, more stable than the smaller ones because the larger the precipitate, the lower the surface area to volume ratio becomes. This results in a thermodynamically lower energy state in the larger precipitates. As the system seeks to find the lowest overall energy state, it is thermodynamically predicted that the particulates will become both larger and less numerous [39]. This trend occurs at a different rate depending on the phase precipitating, the constituents, and the temperature, but it follows a power fit, with the radius of the precipitates increasing according to (13).

$$r(t) \propto t^{1/3} \quad (13)$$

As Guo points out, this precipitate size data very closely correlates with the theory of Ostwald ripening. This indicates that the coarsening of γ' follows a diffusion-controlled growth procedure. This means that the precipitates were limited in their growth by the availability of the constituents at their boarder. As can be seen in Figure 11, there is an initial saturation of the γ' precipitates and their constituent atoms. They quickly form in a dense array, then begin diffusing together to form larger precipitates. Towards the end of the exposure in Guo's study, the precipitates have grown relatively large and have significant spacing between them that are devoid of precipitate of any size. This correlates with the speed of diffusion observed throughout the experiment.

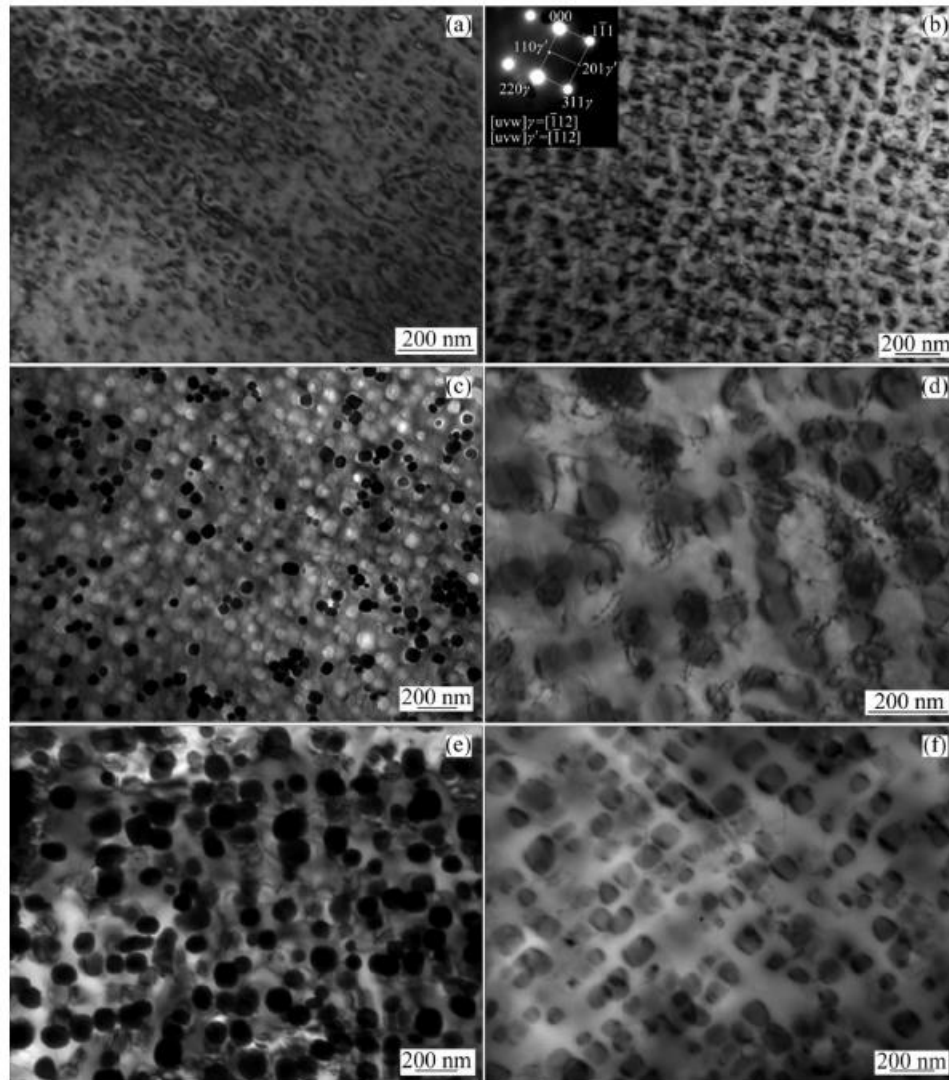


Figure 11 - TEM Images and SAED Pattern of Intragranular precipitates exposed to Heat Treatment plus exposure at 750C for a) 0h, b) 300h, c) 1,000h, d) 3,000h, e) 5,000h, f) 10,000h [36]

In addition, [37] analyzed the effects of prolonged exposures of 740H. This study analyzed the effects of aging 740H at 750°C for up to 3,000 hours after annealing (1150°C/30min/WQ) but without the standard heat treatment of 800°C for 4 or more hours. TEM was utilized to study the growth of carbides and γ' precipitates in the samples. This revealed similar results for the growth of γ' precipitates to that of [36] and can be seen in and Figure 12.

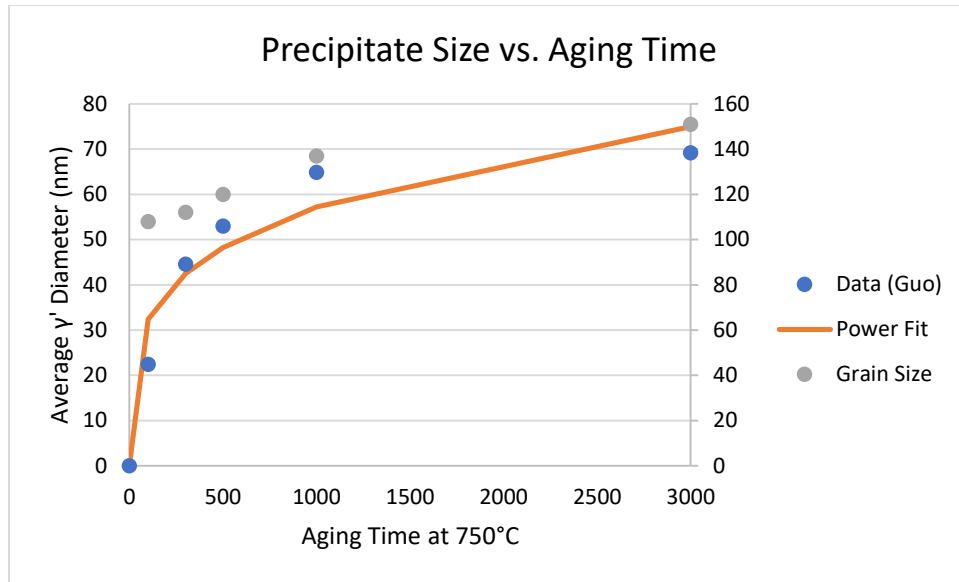


Figure 12 – γ' precipitate size (left axis) & grain size (plotted vs. right axis, μm) plotted against aging time [36]

The power function that best fits this diameter size is seen here in (14), and it is similar to (13) predicted by the theory of Ostwald ripening.

$$\bar{r}(t) = 10.40e^{0.2468t} \quad (14)$$

It can also be noted that the grain size of the 740H samples was analyzed at each aging time-step. The aging effect on grain size was described as initially “above 100 μm and evident grain growth takes place during aging.” The results of this grain growth are plotted in Figure 12 and shows a significant level of growth over the course of the total 3,000 hour heat treatment. The grain boundaries were observed to be rich in M_{23}C_6 carbides, though there was no significant coarsening of the carbides observed during aging. The carbides were found to have two distinct forms – one rectangular and more common, the other needle shaped and rarer – which were identical in composition. Grain coarsening could explain in the slight loss of hardness observed in [36] during heat treatment. It could also contribute to enhancing the effect of grain boundary carbides and the resulting precipitate free zones (PFZ).

As a result of the heat treatment, the size of the γ' precipitates increased (seen in Figure 12), but additionally the width of the interface between γ' precipitates and the γ matrix increased. The γ/γ' interface was analyzed using a proxigram – a proximity histogram of local atomic concentrations. The result of this analysis was that after 100 hours the interface was 2.0nm, increasing to 4.10nm after 3,000 hours. This was ascribed to the growth of γ' precipitates causing a misfit strain around the γ/γ' interface.

After each stage of heat treatment, tensile analysis was performed on cylindrical tensile samples at 750°C inside a temperature controlled furnace. As can be seen in Figure 13, the tensile strength gradually decreases, while elongation gradually increases. Interestingly, yield strength increases until the 500 hours of exposure, at which time it begins to decrease. Similarly to [36], this led to a conclusion that there is a critical size of the γ' precipitates which produces optimum yield strength. According to this study, that value was around 50nm (average size at 500 hours was 53.0nm), which agrees very well with the 47nm estimation that came from [36].

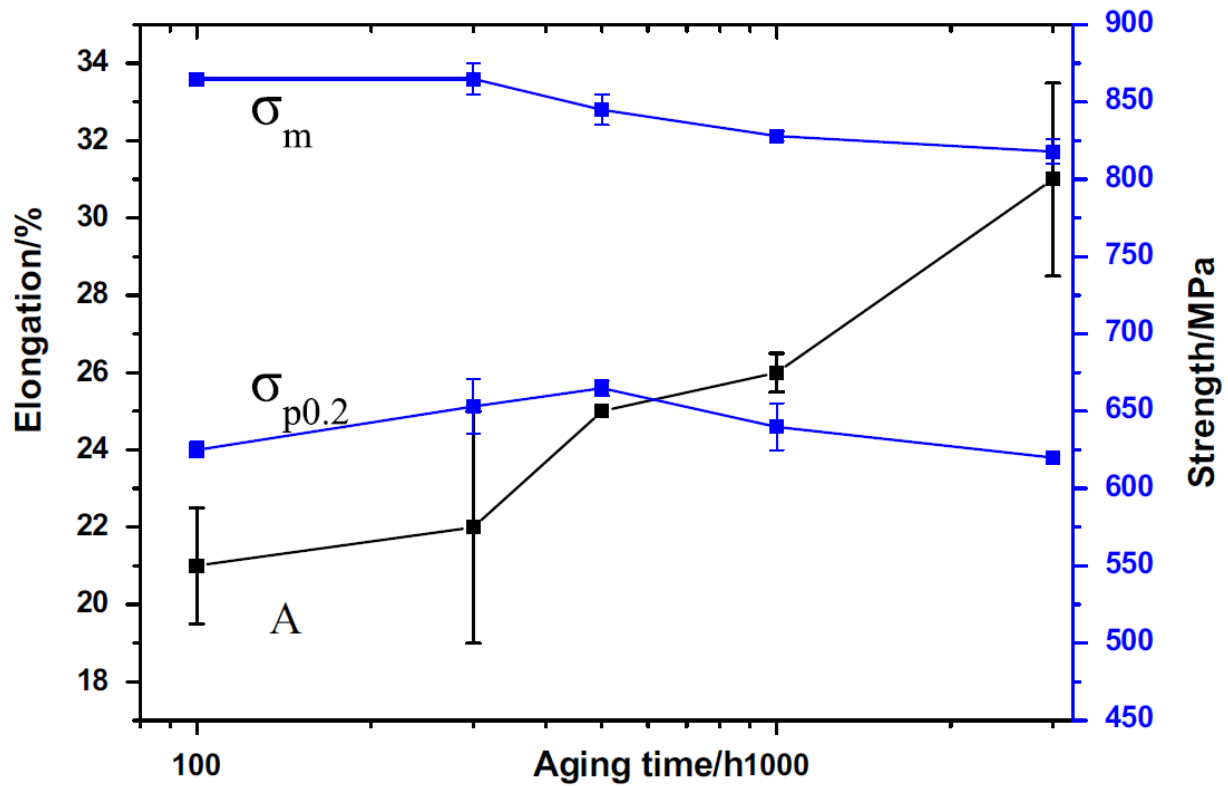


Figure 13 - Tensile Results ($\sigma_{p0.2}$ = Yield; σ_m = Tensile Strength) of Samples at 750°C (x-axis in log scale) [37]

740H has been shown to exhibit a PFZ in conjunction with Cr-carbides along grain boundaries after creep testing [38]. This has been hypothesized that it is due to chromium depletion in the region surrounding the Cr-carbides, as chromium diffuses to the grain boundaries. Because chromium is not an austenitic stabilizer, the removal of it from the matrix allows the γ' -forming elements (Ti,Al,Nb) to dissolve back into the general matrix, thereby dissolving γ' in the near-grain boundary area.

A study that aged 740H for at 750°C 2,000 hours found no evidence of a PFZ near grain boundaries, though considerable coarsening of γ' precipitates did occur [34]. A Thermocalc model predicted a γ' weight fraction of 18%, with the measured phase volume fraction growing from 14.6% (after initial heat treatment) to 17.6% after 2,000 hours at 750°C. This indicates that the nucleation of γ' is over 80% complete after the initial heat treatment, so further aging only coarsens the existing precipitates.

Consistent with this precipitate coarsening, the hardness followed a similar trend to that seen in [36], giving the appearance of a slow exponential decay out to 10,000 hours at 750°C, seen in Figure 14.

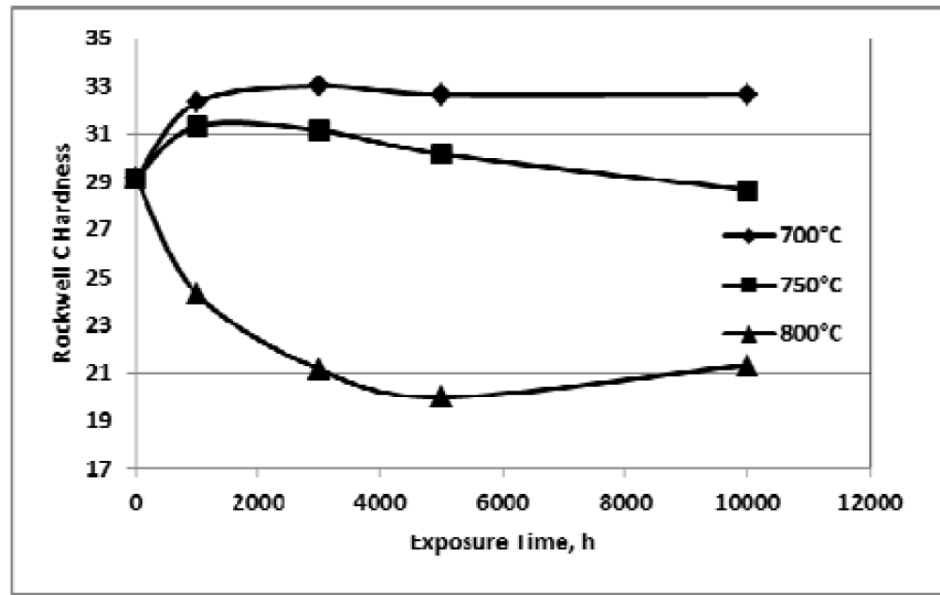


Figure 14 - Hardness of 740H after heat treatment at 700°C, 750°C, and 800°C [34]

A study of 282 has shown similar development of γ' to 740H [40]. TEM analysis has shown γ' -precipitates of roughly 60nm after 1,000 hours of aging at 760°C, equivalent to that seen in 740H after 1,000 hours of aging at 750°C [36]. In addition, the coarsening rate of precipitates was measured to be proportional to aging time according to (15), with a temporal exponent of n between 2 and 3 [40]. This corresponds to trans-interface-diffusion-controlled coarsening which typically occurs when there is a large disparity of diffusivities in the two phases, γ and γ' . This indicates slower coarsening due to the interface between the two becoming the diffusion-limiting location, and therefore slightly slower than that predicted by Ostwald ripening, seen in (13).

$$d^{2.5} \propto t \quad (15)$$

2.2.2. Austenitic Steels:

Austenitic steels are usually found in the form of stainless steels. A commonly used stainless steel is 316, which has a variation with improved welded properties due to a lower carbon content, labelled 316L.

It has been shown that intergranular precipitates and secondary phases form during aging of 316. The rate of formation and type of precipitate is highly dependent on the carbon content. [41] performed a study in which 316 (0.05wt% C) and 316L (0.021wt% C) were exposed to temperatures ranging from 600-900°C for times of up to 50 hours. 316 heat treatment resulted in intergranular precipitation in all exposures longer than 15 minutes at 750-850°C. Using TEM-EDX composition analysis, these precipitates were found to be exclusively Cr-carbides (Cr_{23}C_6), which resulted in Cr-depletion at grain boundaries due to the high concentration of Cr in Cr-carbides. 316L, however, exhibited grain boundary precipitates only after 10 hours in the temperature range of 700-800°C. These precipitates were found to be a mixture of Cr_{23}C_6 , Mo_{23}C_6 , and Laves phase, with Laves phase constituting about 90% of the intergranular precipitates at 750°C. Because of this domination by Laves phase (which had 13-17% Cr), there was no Cr-depletion observed in 316L at any temperature tested up to 50 hours of aging [41].

The growth of precipitates during the aging of 316 has been shown to be highly dependent on the carbon content of the alloy. A study by [18] similarly analyzed the comparison of 316 (0.066wt% C) and 316L (0.023wt% C) after aging at 400-900°C for up to 3,000 hours. With the higher carbon content, 316 produced M_{23}C_6 carbides (typical composition: $\text{Cr}_{16}\text{Fe}_5\text{Mo}_2\text{C}_6$) as the predominant phase at all temperatures above 500°C (below this temperature, precipitates did not form in any measurable amounts). In fact, measurable amounts of other phases were not observed until at least 100 hours of exposure. Conversely, the aging of 316L exhibited a predominance of intermetallic phases, such as chi-phase (χ , BCC α -Mn structure consisting of mostly Fe, Cr, and Mo), sigma-phase (σ , tetragonal structure, $(\text{Fe,Ni})_x(\text{Cr,Mo})_y$), and laves-phase (η , hexagonal structure, Fe_2Mo). The selection of which phase dominated was dependent on the time and temperature of the heat treatment. However, no matter which phase was most prevalent, it is noted that each phase differs from carbides in two important ways:

first, they form with the same constituents of the $M_{23}C_6$ carbide minus carbon; and second, their chromium contents are much closer to that of the base matrix [18].

Given the above information, it follows that the formation of carbides is preferred to the formation of intermetallics provided the availability of carbon. However, $M_{23}C_6$ carbides have roughly 63wt% Cr compared to 29wt% (σ), 21wt% (χ), and 11wt% (η) for the intermetallics [18]. The conclusion is that an effect of carbides, in addition to grain boundary embrittlement, is the depletion of Cr from the matrix near grain boundaries, while there should be very little to no depletion with the formation of intermetallics. This was confirmed experimentally via an oxalic acid test that showed grain boundary attack in 316 and not in 316L, and analytically via TEM EDX across a grain boundary, shown in Figure 15 [41].

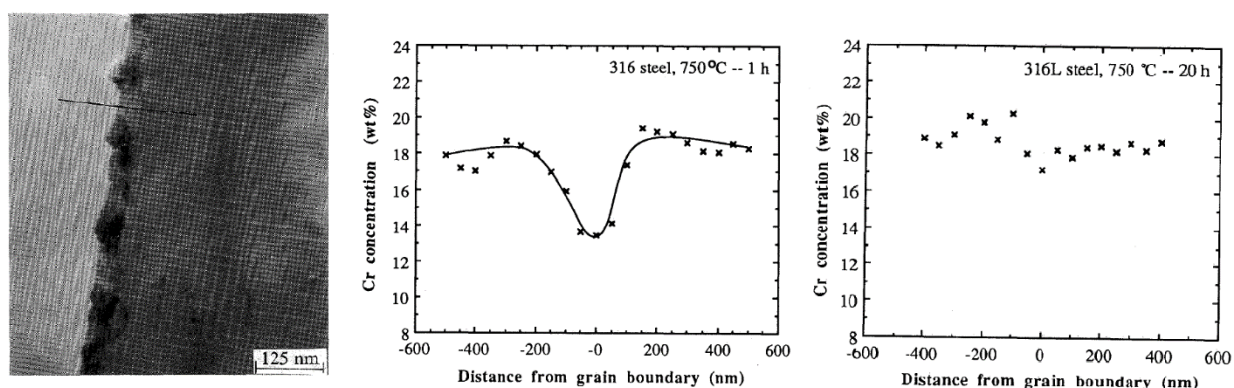


Figure 15 - Grain boundary EDX for 316 aged at 750°C for 1h showing Cr-depletion (middle) taken at the location given on the left, and the same analysis for 316L after aging at 750°C for 20h showing no Cr-depletion [41]

As it is shown that intermetallic phases commonly precipitate in stainless steels at elevated temperatures in the absence of large carbon content, their effect on materials properties should be understood. It has been shown above that they do not change the corrosion behavior of the alloy, as do Cr-rich carbides. However, they can have a significant impact on mechanical properties. χ -phase, which is the only of the intermetallics that can hold a substantial amount of dissolved carbon, is considered to be detrimental to mechanical properties in steels [42]. η -phase in austenitic stainless steels (generally stable below 815°C

[18]) is associated with precipitation hardening without a loss in ductility [42], [43]. The most thoroughly studied intermetallic for austenitic stainless steels, however, is σ -phase. This is because σ -phase is known to cause a loss of ductility and toughness because it is a very hard and brittle phase [44]–[46]. Though σ -phase is not apt to form in austenite, islands of delta-ferrite are often observed in austenitic steels above 20wt% Cr (ferrite stabilizers include Cr, Si, and Mo), and σ -phase forms very quickly in these islands [45], [46]. This process can be seen in Figure 16 which shows a schematic of the formation of various phases at different aging conditions. This shows that sigma phase tends to form in striations, with higher temperatures resulting in formation along grain boundaries, especially at the intersection of three grains (triple points).

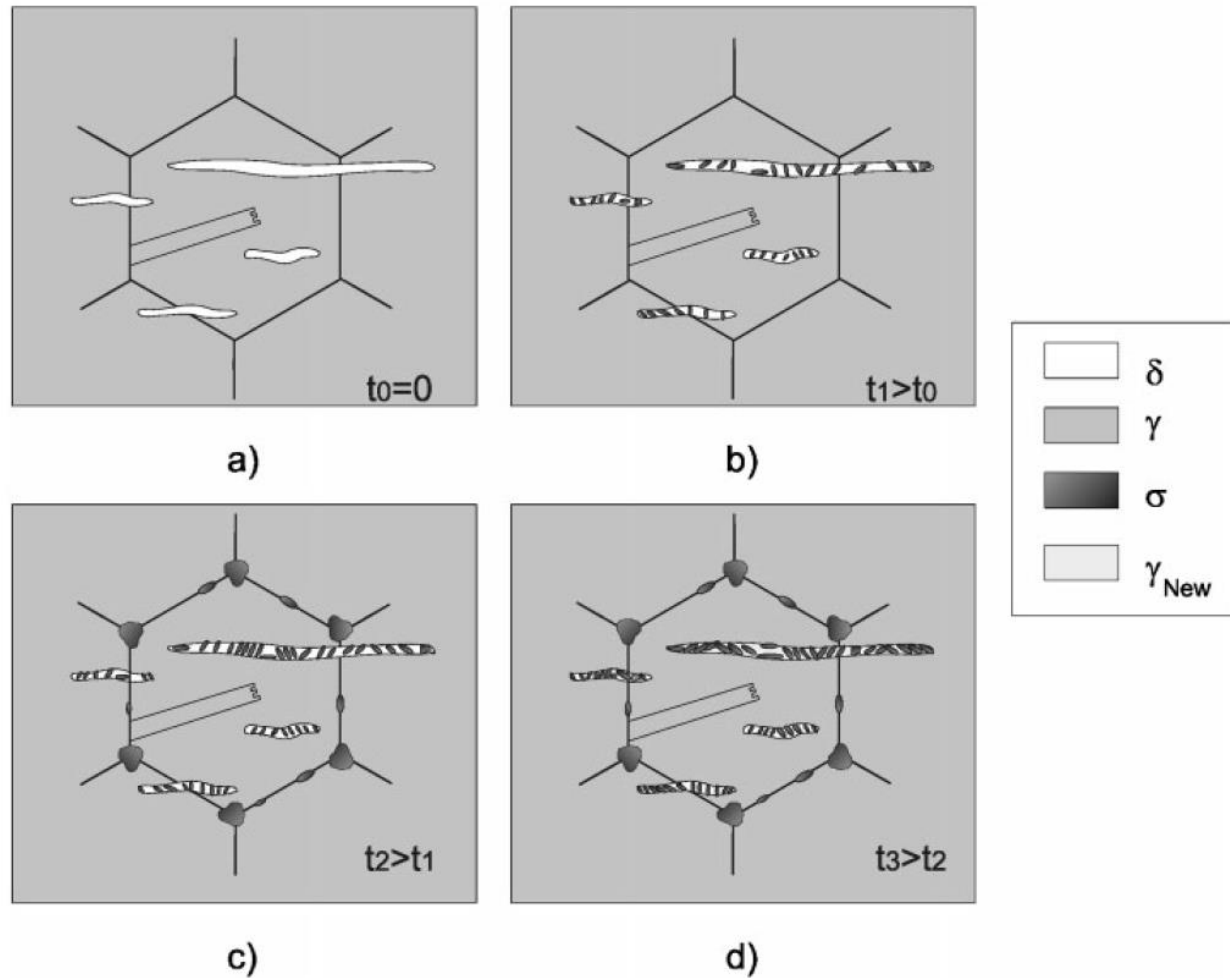


Figure 16 - Schematic representation of σ -phase precipitation in 316L at increasing aging temperature (figure (a) represents no aging) [46]

Additionally, a study conducted thermal aging of 316 (with 0.046 wt% C) at 750°C for up to 2,200 hours [47]. This study found that there was no significant grain growth from the aging process. Further, it observed a 10% increase in material hardness which occurred after 100-1,000 hours of aging, and then remained constant through 2,200 hours. This same study performed tensile testing at both room temperature and 650°C. Room temperature properties experienced a slight strengthening with a small drop in ductility. Testing at 650°C resulted in a drop in ductility similar to that of room temperature testing, but also exhibited a large increase in yield strength. The drop in ductility and slight strengthening

were likely due to the precipitation of grain boundary carbides which were observed in the fracture surfaces of samples tested after both 1,000 and 2,200 hours of 750°C aging.

2.2.3. Ferritic-Martensitic Steels:

Grade 92 F-M steel, under investigation in this work, has been used in the components of power plants within the temperature range of 580-625°C [48]. 9-12% Cr steels are highly dependent on the density, morphology, distribution and size of $M_{23}C_6$ carbides (comprised of Fe, Cr, W, and Mo) and MX carbo-nitrides. The addition of W to this alloy suppresses the tendency to form delta phase (δ) [49], as well as increases high-temperature strength. High temperature strength is believed to increase for two reasons: first, because it decreases the self-diffusivity of iron within the matrix [50]. Second, because it stabilizes the growth of both $M_{23}C_6$ carbides (assisted by the presence of boron [51]) and MX carbo-nitrides which allows them to remain small enough that they can contribute a pinning effect on the glide of dislocations without becoming large enough to cause embrittlement of the material. The design of these precipitates was to remain relatively small and have a somewhat homogeneous distribution near grain boundaries [52]. A homogeneous distribution (continuous along grain boundaries) will occur as long as the carbon content is sufficiently high [53]. This effect is very important to the application of this material, so any change in this microstructure should be understood.

The formation of χ -phase in ferritic steels has been shown to help precipitate a microstructure which produces excellent high temperature stress-rupture properties [54]. However, χ -phase is not a major contributor to the understanding of the P92 morphology. This is observed through several studies which have not seen any evidence of χ -phase after standard heat treatments [48], [51], [55], [56]. The only time that χ -phase has been observed in P92 is during creep rupture tests at elevated temperatures [57].

η -phase precipitation has been shown to decrease fracture toughness of ferritic-martensitic duplex steels. In addition, it increases the ductile-to-brittle transition temperature and lowers the upper shelf energy

[58]. The aging of 9Cr-2W at 600°C has been shown to decrease fracture toughness, but only after the formation of η -phase precipitates [56], which appear to form out of $M_{23}C_6$ carbides [59]. There appears to be little-to-no negative effect from the coarsening of $M_{23}C_6$ carbides on fracture toughness, while η -phase appears to promote crack propagation. The weld appears to age very similarly, as a study which aged P92 at 625°C exhibited similar morphology, with η -phase – of composition $(Fe,Cr)_2(W,Mo)$ – coarsening to 0.6 μm after 1,000 hours and 1.5 μm after both 3,000 and 9,000 hours of aging [55]. As a reference, η -phase is considered mechanically detrimental when the precipitates coarsen to 0.5 μm or larger. This was confirmed in the same study through a fracture toughness analysis which showed a large drop in toughness after 1,000 hours, with only a small effect with additional aging. Similarly, hardness decreases after 1,000 hours but does not appear to change with subsequent aging.

2.3. Mechanical Properties of Alloys and their Welds:

The welding process causes a complete breakdown of the base microstructure of the alloy within the fusion zone. The weld pool is then quenched from the outside towards the center, creating a new grain structure usually biased along the welding path. Depending on the composition of the base material and filler metal, the resulting weld will have various properties and segregation (micro and macro) of constituents. In addition, there is often a post-weld heat treatment (PWHT) that is performed on the weld. The PWHT can grow grains, precipitate phases, and relieve residual stresses from the welding process. It is used to develop the optimal properties of a weld without the option of a re-homogenizing anneal. It is important to understand the contribution that each impacting variable has on the resultant weld, and how that might affect material strength or corrosion properties. The different materials analyzed in this research are each welded differently, and their welds must, therefore, be evaluated separately.

2.3.1. Nickel-Base Superalloys:

The welding process in nickel-base superalloys such as 740H is a non-trivial procedure in the fabrication of load-bearing structures and pressure vessels. There is a segregation of elements into and out of the fusion zone which can have large effects on the materials properties. Further, the melting of material causes dissolution of any phases present, and those that regrow are subject to the cooling rate characteristic of the end of the welding process. Any microstructure for the base material that was carefully engineered through the manufacturing process is destroyed. It is important to generate an understanding of how to achieve the optimal properties of the weld through the least post-weld work performed.

In analyzing the weld, [60] analyzed the weld of 740H in terms of segregation and how solution heat treatments affected the microstructure. A plate of 740H was welded using gas tungsten arc welding (GTAW) and segregation was seen on a macro level. In microanalysis, it was revealed that the dendritic core – made up of a material composition which solidifies at higher temperature – contained enrichments in Cr and Co, and depletions in Nb and Ti (0.5 and 1.0wt%, respectively). The interdendritic regions, however, were enriched in Nb and Ti (5.4 and 3.3wt%, respectively) while depleted in Cr and Co. Ni and Al remained constant throughout these regions.

This micro-segregation effect of the welding process was observed to be effectively removed due to the solution annealing post-welding heat treatment of 1100°C/4h. As can be observed in Figure 17, this temperature (1373K) either results in a thermodynamic steady state of a nearly complete γ matrix (a,b) or a largely γ matrix (c, d), so it makes sense as a good homogenizing temperature. It can be assumed from the results in desegregation that 4 hours was a long enough anneal to allow the kinetics of the phase transformation to γ to occur.

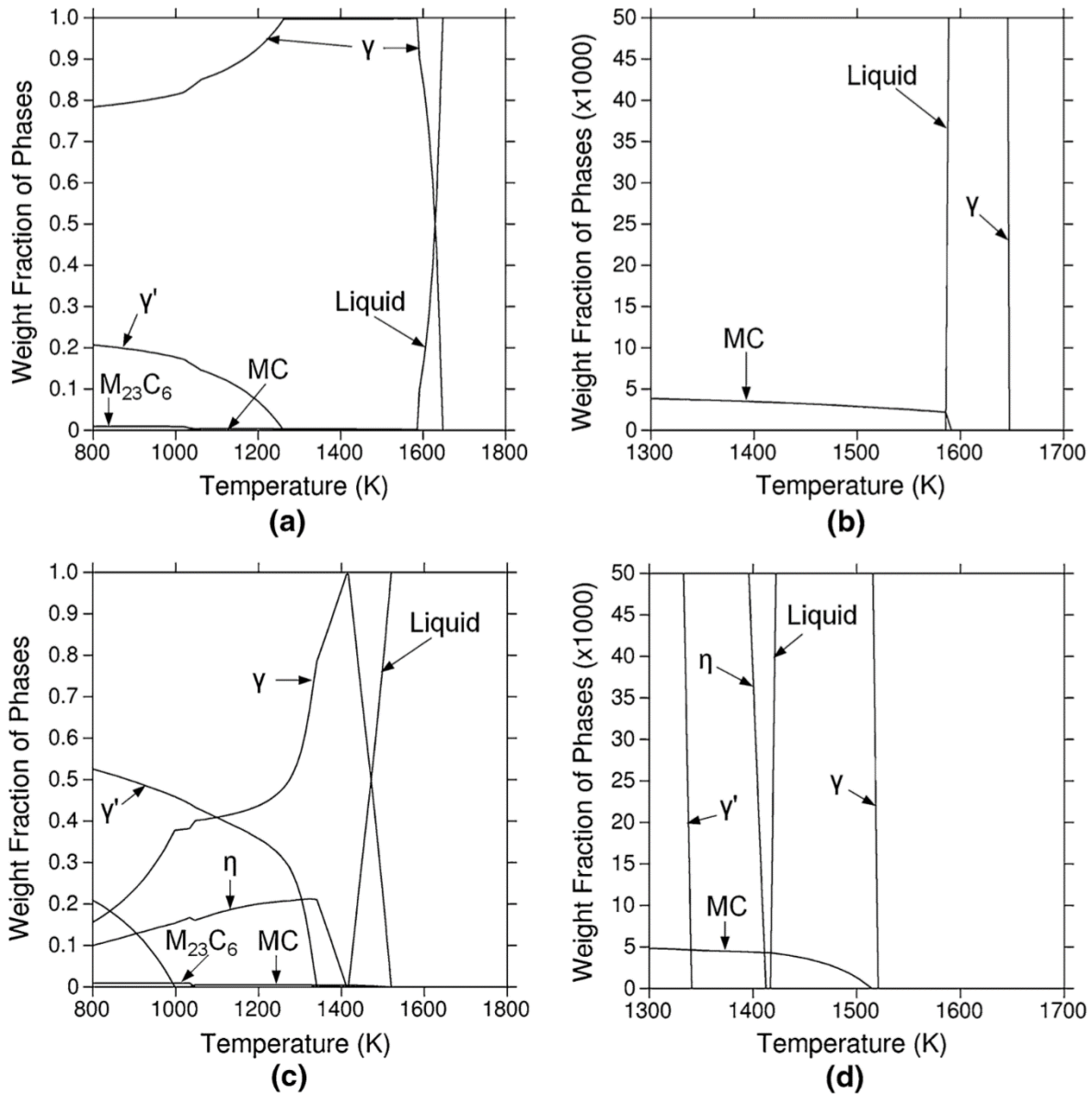


Figure 17 - Phase Stabilities Calculated for 740H Alloy Compositions a) Nominal, b) Nominal (magnified), c) Scheil-predicted interdendritic region (0.99 fraction solid), d) same as (c) but magnified [60]

However, without homogenization, the welding process with standard PWHT (800°C/4hr/AC) has been shown to produce regions in 740H which, while not being PFZs, are precipitate-poor [61]. These regions occur inside the dendritic cores, which are depleted in Ti and Nb [60], [61]. This is most likely due to the micro-segregation discussed above, and it follows that a majority of the precipitates inside the dendritic cores may be with Al as the precipitate-forming element.

As covered above, superalloys such as 740H are strengthened by the presence and prevalence of γ' precipitates throughout the γ matrix. This is altered slightly inside the fusion zone, even after PWHT. As described above with heat treatment, the welding process creates PFZs along grain boundaries inside the fusion zone [62]. It has not been investigated if these zones are eliminated or expanded during static aging near the heat treatment temperature.

Haynes alloy 282 has been shown to be a Ni-base alloy with relatively good weldability [63]. Recommended PWHT for high temperature application is a three step process. First, a solution annealing step of 1,135°C for 30min to achieve a partial recrystallization. Second, the first age-hardening step at 1,010°C in order to precipitate $M_{23}C_6$ carbides at grain boundaries. Third, the second age-hardening step at 788°C to precipitate the high strength phase γ' . After these stages, it has been shown that 282, unlike 740H, does not exhibit a PFZ near grain boundaries within the weld metal. This is an important feature for creep strength, and as a result 282 is considered as a potential filler metal for similar joints of 740H. In addition, 282 has shown good resistance to solidification cracking and liquation cracking, the latter in the age-hardened condition.

Further, the fusion joining of 282 has been shown to result in micro-segregation, but in a different fashion from that of 740H. Laser welding has been shown to result in a dendritic microstructure with dendrite arm spacing of roughly 3 μ m [64]. However, since this should vary depending on cooling rate. The expected dendrite arm spacing for GTAW should be in the range of 7-10 μ m [65]. The dendritic structure of 282 was shown to result in the formation of γ dendrites and interdendritic precipitation of Ti and Mo-rich MC-type carbides [64]. These carbides are predicted to form based on the availability of carbon during welding, and have been shown to reduce the formation of the γ - γ' eutectic. This γ - γ' eutectic induces additional micro-segregation, which in turn increases the solidification temperature range. This increase causes an increase in the susceptibility of an alloy to solidification cracking. For this reason, the

carbon content is kept above a minimum threshold and the Ti and Mo-rich carbides are precipitated throughout the fusion zone.

2.3.2. Austenitic Steels:

Austenitic steels are designed to have very good corrosion resistance while maintaining good mechanical properties at elevated temperatures. 316L strength, as is shown in Figure 18, maintains strength at elevated temperatures up to around 550°C, at which point the ultimate tensile strength (UTS) drops off severely with increasing temperature [19]. This makes austenitic stainless steels like 316L very useful at medium temperatures for the Brayton cycle.

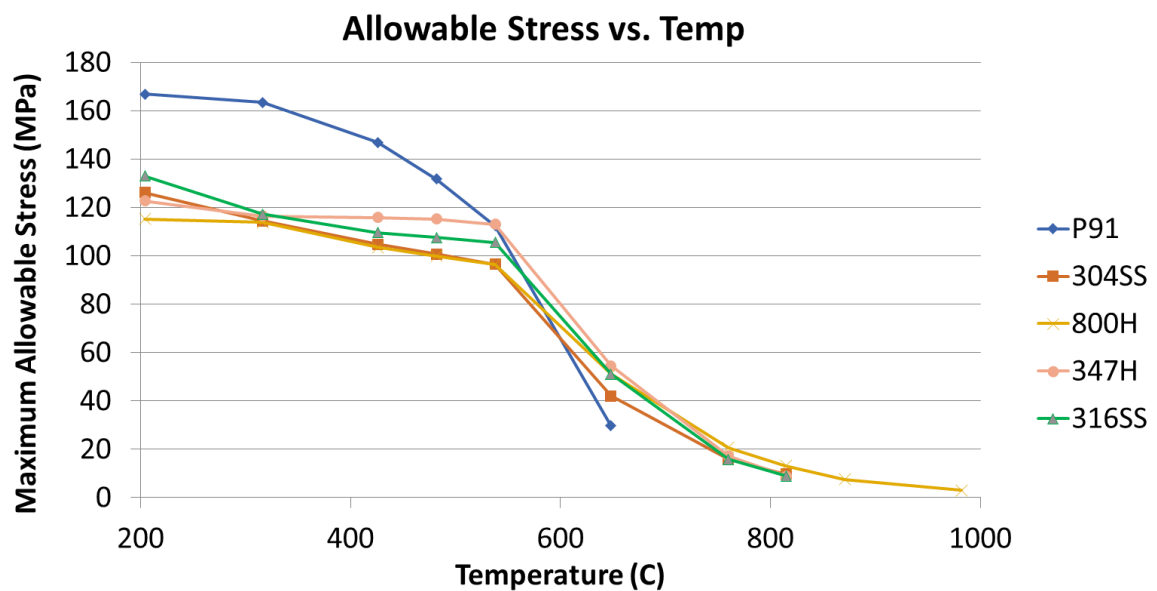


Figure 18 – Allowable stress of 316L and other comparable steels at elevated temperatures [19]

It is important that the baseline properties are maintained throughout the welding process as well as possible. One concern is a process of weld decay called sensitization. This is a phenomenon during which chrome carbides (Cr_{23}C_6) are formed along grain boundaries. The formation of these chrome carbides is highly dependent on the availability of carbon, as well as the time that the material is kept at the formation temperature. The Time Temperature Transformation (TTT) diagram for 304 stainless steel is shown in

Figure 19. Depending on the thickness of the weld and the welding procedure, an austenitic steel with greater than roughly 0.05%C will form Cr_{23}C_6 along grain boundaries both in the heat affected zone (HAZ) and the fusion zone during cooling after solidification [66].

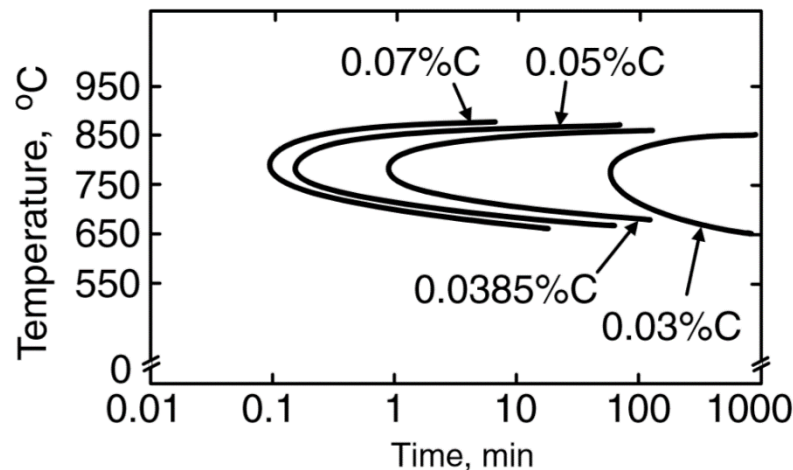


Figure 19 – Time Temperature Transformation Curve for Cr_{23}C_6 in 304 Stainless Steel [66]

The effect of forming Cr-carbides along grain boundaries is that a Cr-depleted region is created in the matrix along the grain boundaries (observed in the middle of Figure 15). When the resulting steel is exposed to a corrosive environment there is preferential corrosive attack at these Cr-depleted regions. Depending on the conditions and design, the attack can be detrimental enough to compromise the integrity of the steel. The formation of Cr-carbides must, therefore, be avoided if possible [66].

Several remedies for this formation are possible. The steel can undergo a PWHT above the solvus temperature of Cr_{23}C_6 – about 1,000-1,100°C – followed by a quench which prohibits the reformation of the carbides. This treatment is not always possible, however, as the heating and subsequent quench can cause distortions in the weldment. Another solution involves adding small amounts of strong carbide-forming elements such as niobium or titanium – used in 347 and 321, respectively – to tie up the excess carbon and allow the chromium to remain in the base matrix. These are called “stabilized” alloys. These

alloys, however, are susceptible to knife-line attack, a phenomenon in which the stabilizing carbide is dissolved in the near fusion zone part of the HAZ. Any reheating of this region (multi-pass welding or PWHT) causes the chromium present to bond with the liberated carbon. This region is then depleted of chromium in the base matrix and so is preferentially attacked in the subsequent corrosive environment [66].

As can be seen in Figure 20, Cr-carbides form in the temperature range of 600-850°C for austenitic steels with 0.05% wt% carbon, but dissolve above about 850°C. Ti and Nb-carbides can survive at temperatures up to 1,100-1,200°C, so they form and absorb the free carbon before chromium can react. These alloys are able to enjoy the high strength from carbon addition, while avoiding the negative corrosion effects that carbon can cause after welding (as long as knife-line attack is avoided) [66].

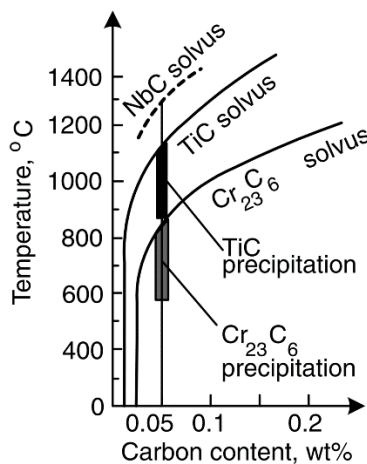


Figure 20 - Solvus Curves of Carbides in 304 Stainless Steel [66]

An additional concern in the welding of austenitic stainless steels is stress corrosion cracking (SCC). Although the base material of 316 does not have a large risk of this phenomena, it has been shown to initiate in the HAZ. These cracks are transgranular and can propagate into the base material and cause failure. Crack initiation is assisted by the presence of residual stresses in the HAZ due to the welding process. Therefore, SCC can usually be avoided by performing a stress-relieving heat treatment after the

weld. However, when performing this heat treatment, it is important to avoid sensitizing the material through the formation of Cr-carbides during cooling. As stated above, this is avoided by using low carbon content or grades which are stabilized with a carbon absorber such as niobium or titanium [66].

The simplest solution to this issue is to use a low carbon stainless steel such as 316L. The material would then avoid both sensitization and knife-line attack because there is not enough carbon in the material to form a substantial Cr-carbide. This can be observed in the right of Figure 15, which shows very little drop in chromium content at the grain boundary, which is in stark contrast to the dramatic dip observed in the middle of Figure 15.

The Cr-equivalent ($\%Cr + \%Mo + 1.5\%Si + 0.5\%Nb$) and Ni-equivalent ($\%Ni + 30\%C + 0.5\%Mn$) of the 316 grades used in this work were calculated [66]. For 316L, the Cr-equivalent is 19.4%, while the Ni-equivalent is 11.2%. For 316H, they are 18.9% and 12.1%, respectively. These qualify for a Cr-equivalent to Ni-equivalent ratio of 1.72 for 316L and 1.57 for 316H. These ratios indicate these alloys have a high resistance against solidification cracking during cooling after welding [67]. It further indicates that there will be roughly 5% ferrite in the re-solidified weld pool, based on the Schaeffler diagram [66]. This δ -ferrite will form primarily on the axes of the dendrites (with a vermicular or lathy shape), and in interdendritic regions (roundish shape). These ferritic regions are Cr and Mo-rich along with being Ni-poor, since Cr and Mo are ferrite stabilizers, and Ni an austenite stabilizer [68].

2.3.3. Ferritic-Martensitic Steels:

Ferritic stainless steels are considered less weldable than austenitics. However, one advantage is that though sensitization occurs, it occurs above 925°C and an easy remedy is an anneal at 650-815°C for 10 minutes to an hour [66]. This is fortunate as lowering the carbon content is not an easy fix to sensitization, as it is in austenitics, due to the rapid diffusion of Cr and carbon in the BCC matrix. It does, however, mean

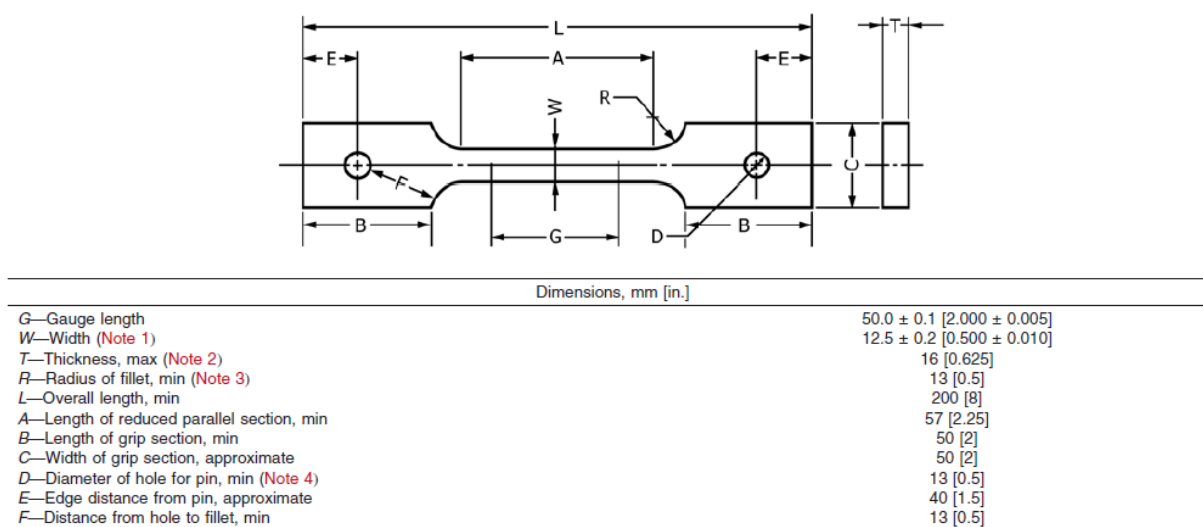
that welding processes of ferritics demands a PWHT for weld performance to meet standard mechanical properties.

In ferritics, type IV cracking (creep cracking in the HAZ) is commonly observed [55]. Type IV cracking is a form of cracking in which the rate of creep void formation is enhanced in the fine grained and intercritically annealed HAZ of the weld [69]. This leads to significantly earlier creep failure when compared with that of base material. Boron addition, without the formation of boron nitride from a post-weld normalizing heat treatment, suppresses grain refinement in the HAZ and, therefore, limits type IV cracking [52]. This occurs because boron suppresses the preferential recovery of the martensitic microstructure as well as limiting localized creep deformation near grain boundaries. Use of the alloy much higher than 500°C becomes difficult, as the strength of the material decreases drastically above 400°C and becomes relatively small above 500°C [70].

3. Experimental Facility:

3.1. Sample Design:

The dimensions of the tensile samples were designed in compliance with the ASTM standard E8/E8M section 6.3 (sheet-type specimens), seen in Figure 21, with slight elongation of the gauge to incorporate a maximum amount of the weld [71].



NOTE 1—The ends of the reduced parallel section shall differ in width by not more than 0.1 mm [0.002 in.]. There may be a gradual taper in width from the ends to the center, but the width at each end shall be not more than 1 % greater than the width at the center.

NOTE 2—The dimension T is the thickness of the test specimen as stated in the applicable product specifications.

NOTE 3—For some materials, a fillet radius R larger than 13 mm [0.500 in.] may be needed.

NOTE 4—Holes must be on center line of reduced parallel section within ± 0.05 mm [0.002 in.].

NOTE 5—Variations of dimensions C , D , E , F , and L may be used that will permit failure within the gauge length.

Figure 21 - ASTM Standard Tensile Specimen [71]

The final tensile specimen design is given in Figure 22. One side has a 0.125 inch diameter hole to suspend the sample from a supporting alumina rod inside the autoclave during exposure. The tab with the hole is

also elongated slightly to maintain constant surface area on each tab to ensure no slippage during tensile testing.

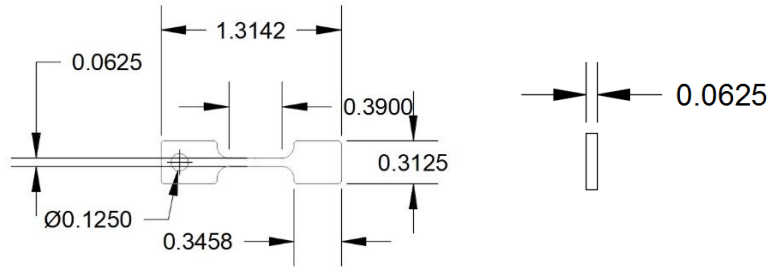


Figure 22 - Tensile Specimen Design for this Study

3.2. Sample Production:

Samples of Special Metals Alloy 740H and Haynes 282 were acquired from the respective manufacturers, 316L and 316H was received from a vendor, and grade 92 (P92) was obtained from a section of a pressure vessel. Samples were electrical discharge machined (EDM) or acquired in 1/8" and 1/16" thick plates. Base material tensile and corrosion samples were then produced through EDM from 1/16" plates or thicker bar. The 1/8" plates were welded – 740H and 282 by the manufacturers – according to materials specifications, then machined to 1/16" thickness using a mill.

Tensile samples were cut transverse relative to the weld, with a center-of-sample separation of 0.38 inches. Corrosion samples were taken from the gap of weld between each tensile sample, an example of which can be seen in Figure 23. Samples were offset along the weld for the purpose of incorporating a section of all the potential regions of failure: ¹⁾ the fusion zone, ²⁾ the partially melted zone (PMZ), ³⁾ the HAZ, and ⁴⁾ the base material. The fusion zone was found by etching the machined plate (see Table 1).

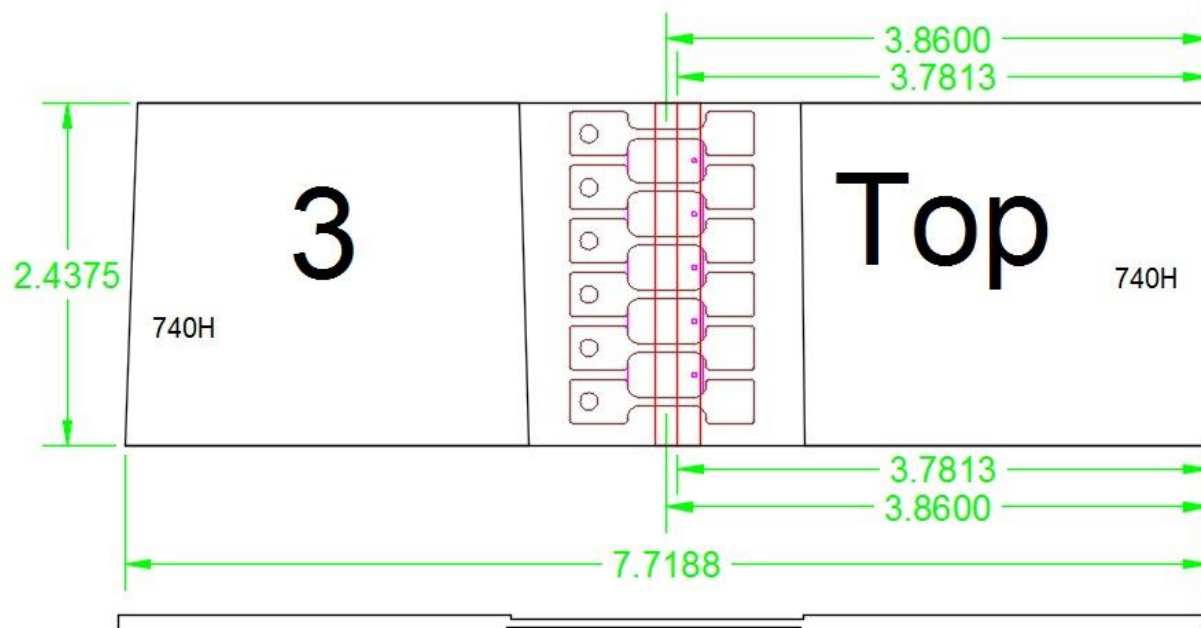


Figure 23 - Samples cut out of 740H welded plate with tensile samples (brown) and corrosion samples (pink) cut out to incorporate fusion zone (red) and any adjoining HAZ

Samples were then polished to 800-grit using silicon carbide polishing paper. Following this step, samples were separated into those which would be exposed and those which would not. Welded tensile samples which were tested in the unexposed condition were etched prior to testing, using an etchant designed to reveal the location of the fusion zone (given in Table 1). This allowed for knowledge of failure location without affecting bulk properties of the sample.

Table 1 – Etchants and etching procedures used to observe fusion zone of each weld

Weld	316-316	282-316	740H-316	P92-P92	282-P92	740H-P92	740H-740H	282-282
Etchant Used	Kalling's Waterless #2			5% Nital			Glyceregia	
Etchant Formula	100mL Ethanol 100mL HCl 5g CuCl ₂			100 mL Ethanol 5mL HNO ₃			15mL HCl 10mL glycerol 5mL HNO ₃	
Etching Time	15 sec			2 min	30 sec – 1 min		30-60 sec	1-3 min

Samples planned for exposure were cleaned with ethanol and DI water. They were then weighed using a high precision Sartorius scale with an accuracy of $\pm 2\mu\text{g}$. They were dimensioned using a Starrett No. 795M digital micrometer with an accuracy of $\pm 1\mu\text{m}$ for thickness and a digital camera in tandem with image

processing for cross-sectional area, resulting in a total surface area measurement with an accuracy within 1%.

3.3. Welding Procedure:

The welds performed in this experiment were performed either by the manufacturer of the materials (all 740H and 282 welds) or by a professional welder using a standard procedure for the material(s) involved (316 and P92 similar). Similarly, the PWHT was performed in accordance with standard procedures for each alloy, with 740H and 282 welds begin PWHT by the manufacturers. The full procedures for the welds are given in the appendix in Table 20, while the alloy compositions for both the welded alloys and filler metals are also in the appendix in Table 18 and Table 19. Plates were initially lined up and tack welded on either side (or at intervals of 1-2 inches if a long weld) prior to full welding in order to assure constant spacing during the welding process (cut down on pinching).

The welding of P92 is somewhat difficult, because the martensitic microstructure must be maintained as well as the hardening phases regrown. First, the base material must be pre-heated into the martensitic range (200-350°C) before beginning the welding process [72]. A thermal imaging camera was used to ensure the temperature was in this range prior to welding, and an image is shown in Figure 24. Second, a slightly dissimilar filler rod is used (9CrWV-TIG, see Table 19) with a composition designed for maximum fracture toughness after welding (including a higher Ni content). Following the completion of the weld, the weldment must be cooled to below the martensitic finish temperature, 120-150°C, in order to ensure a full martensite structure. A PWHT of 760°C for a minimum of 2 hours is then performed to regrow the hardening precipitates ($M_{23}C_6$ carbides and MX carbo-nitrides) for correct hardness and strength. The longer the PWHT, the higher the resulting fracture toughness. In the case of dissimilar welds, this procedure was replicated to similarly regrow the hardening precipitates in the P92, anticipated to be the weaker of the materials in any heat-treated condition.



Figure 24 - Thermal image of P92 plates prior to similar welding ($>200^{\circ}\text{C}$), clamped on a copper backing plate

740H and 282 similar welds were also given a PWHT in order to re-grow the strengthening phase γ' . In both cases, the PWHT of $800^{\circ}\text{C}/4\text{h}/\text{AC}$ was used because of the recommendation of the manufacturer for use at the temperatures examined in this work (maximum of 750°C).

3.4. Facility Overview:

3.4.1. Exposure Facility:

Samples were exposed to s-CO_2 in a high temperature, high pressure autoclave system. The system has been described in several previous works [17], [73], [74]. There are currently four autoclaves in service (two of which are pictured in Figure 25), all of which are capable of containing s-CO_2 at conditions up to 750°C and 20MPa. Temperature can be specified to within $\pm 1^{\circ}\text{C}$ and pressure within $\pm 2.5\text{psi}$ (0.017MPa). Two thermocouples are located at each of the inlet, outlet, and middle of each autoclave, one welded onto the surface and one located at the radial center of the autoclave. The external thermocouples regulate the temperature seen by the autoclave wall, while the center thermocouples show the

temperature which is directly on the samples being exposed. Each autoclave contains an Omega pressure transducer to monitor and log pressure during testing, as well as a visual pressure gauge and a pressure relief valve as backup.

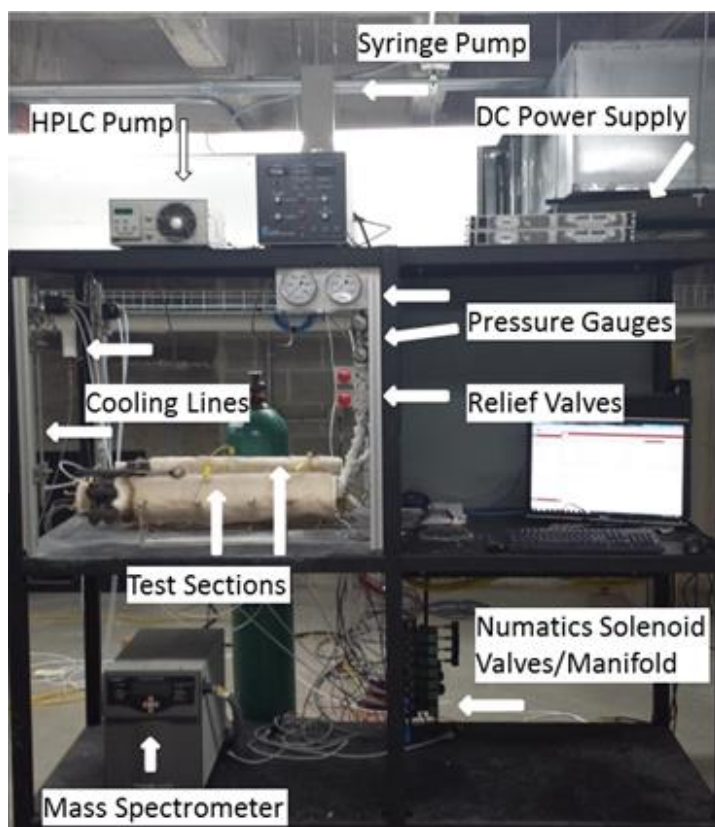


Figure 25 – Autoclave system setup at UW-Madison, used for sample exposure in s-CO₂

By convention, the test was started at room temperature when the heaters were turned on, and ended at the testing temperature when the heaters were turned off. However, the heating and cooling rates are important to understand during corrosion testing, especially when testing at elevated temperatures. Thermal mismatch between the oxide and the alloy can cause cracking or spallation of the oxide, with increased effects with increasing heating/cooling rates. As can be seen in Figure 26, heating from room temperature to 750°C typically took 4-6 hours, while cooling from 750°C to room temperature typically took at least 8 hours (rate different depending on when insulation was removed (in the cooling from Figure 26 the insulation was removed after around 10 hours). While the experiments performed for this

work were all planned as single exposures – so there should be no thermal cycling – there were occasional losses of pressure which required full cooling in order to re-seal the system. This caused some thermal cycling which will be discussed in subsequent sections.

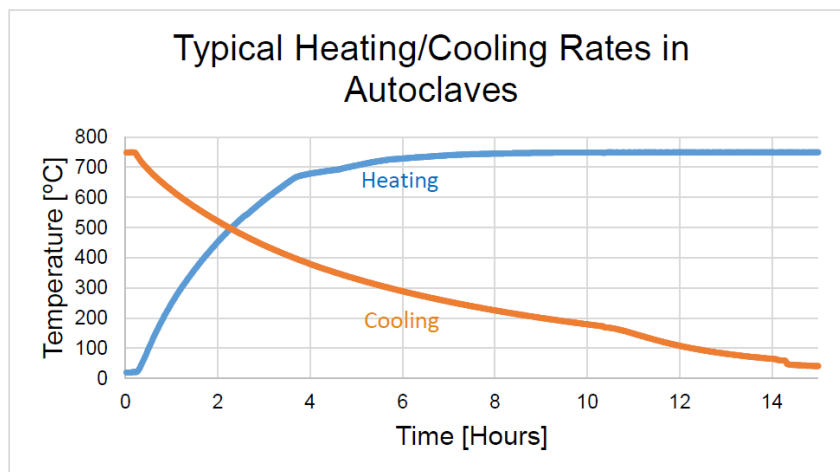


Figure 26 – Typical heating and cooling rate for a test at 750°C [17]

In addition to CO₂ exposures, prolonged aging experiments were performed in these autoclaves. In this case, ultra high purity Ar (99.999% pure) gas was fed in with a regulator set to 0.02±0.01MPa (gauge) in order to maintain low concentrations of oxygen and other impurities while keeping positive pressure to avoid sucking in atmosphere. In addition, a titanium oxygen-scavenger was used to eat up the oxygen impurities, and the system was sealed (except for inherent leaks) for the entirety of the test. Two exposures were performed, and the mass of Ar used was measured and found to be roughly 8kg (750°C) and 3kg (550°C). Using the molar volume for Cr₂O₃ (the primary oxide likely to form at such low pO₂) of 29.20cm³/mol [75], the total oxide volume which could have been produced (assuming a passivated autoclave) was calculated and found to correlate to <100nm of growth on each sample. Even this amount of oxidation was not observed thanks to the oxygen scavenger, so the aging exposures will be considered neutral aging for the analysis which follows.

3.4.2. Tensile Testing Settings:

Tensile testing was performed with observance of the ASTM E8/E8M – 16a standard [71]. The strain rate is very important because relaxation occurs inside the material as it is being tested. This relaxation occurs at a set rate and allows the material to remain elongated at a lower stress than it would otherwise be under. The result of this is that a faster strain rate causes a larger measured stress value. This is especially impactful when measuring yield strength, and as such it is defined within the ASTM standard: when measuring yield strength, the cross-head speed is defined by the strain rate 0.015 ± 0.003 mm/mm-min. Given the effective gauge length of the physical tensile samples after the EDM process (10mm), the advised elongation rate is 0.15 ± 0.03 mm/min. Therefore, the crosshead speed was set to 0.15mm/min during every test performed on the standard samples in this work.

The strain rate of 0.015mm/mm-min is, however, too slow to measure tensile strength in a material with any amount of ductility. As an example, a sample which ruptures at 50% elongation would take over 30 minutes to rupture. As a result, the strain rate defined in the ASTM standard for ultimate tensile strength analysis during plastic deformation is higher than that for yield strength: 0.055-0.55mm/mm-min. The strain rate of 0.25mm/mm-min (or a crosshead speed of 2.5mm/min) was used for the entirety of this work, roughly in the middle of the advised range. A strain switchover point (at which the strain rate switched from slow to fast) was defined sufficiently after the anticipated yield strain so as to ensure accurate measurement of the yield stress (typically after a crosshead movement of 1.20mm). This led to the tensile tests typically lasting between 4-12 minutes.

3.4.3. Tensile Testing Facility:

3.4.3.1. Stress Data Acquisition

The tensile testing for this work was performed on tensile machines and load cells which were calibrated within 18 months of the testing. Work has been or is planned to be performed on three different machines. However, in an effort to eliminate as much possible error as possible, every material pre-

exposure and post-exposure has or will be tested on the same machine. The load cells were used to get force data (transferred to stress via the cross-sectional measurements of the sample gauges pre-testing). All force data obtained above 1% of the load cell rating is defined as accurate to within 1% of the measured load. This is a calibration standard for MTS, and most measurements are well within that 1% upper limit.

An MTS QTest 5 with a 5kN load cell, see Figure 27, was used for the of the 740H and 282 base material as well as their similar welds (that were removed from plates). An MTS Sintech 10/GL with a 50kN load cell was used for 316 and its similar weld (as well as copper coated) exposed to 750°C. The rest of the analyses will be performed with an MTS Criterion 43 with a 5kN load cell. While it is not necessary, one goal of testing was to attempt to have yield and fracture occur within the range of 10-90% of the maximum capacity of the load cell. As most ruptures were designed to occur from 1-3.5kN this was only possible with the 5kN load cell, so that size cell was used when possible.



Figure 27 – MTS QTest/5 tensile machine

3.4.3.2. Strain Data Acquisition

Strain data was acquired from a custom video extensometer setup. Given the very small size of the tensile sample design, neither classic extensometers nor strain gauges would be able to fit onto the gauge. This was due to the small length (extensometer) and small cross-sectional dimensions of the gauge (strain gauge). The video extensometer was created through the use of a tripod-mounted Nikon D7000 digital camera and a Fiber-Lite High Intensity Illuminator series 180 light source. The digital camera takes one picture per second throughout the test. One picture per second was deemed sufficient to provide semi-continual data given the duration of each test (see 0). The images were analyzed based off of contrast between important elements which are described below.

Samples were prepped for the video extensometer by covering the appropriate sample edge with black marker. Overall strain – applicable to the strain at rupture was measured through analysis of markings on the sample tabs. Samples were levelled in a vice on a mill and marked at precise points along the tab by creating a horizontal line using a very small centering bit (three points on the short tab, four points on the long tab), see Figure 28. These seven markings were then used to measure all 12 distances between the markings on opposite tabs. Each of these distances were then compared with the initial measurement and then averaged into a measurement of the total displacement, and therefore elongation, of the sample during the test. While this technique was incredibly accurate, it inherently incorporated a small amount of error due to strain in the sample outside of the gauge – in the fillet between the gauge and the tabs. This error was very small at large strains, but very large at small strains (often incorrect by a factor of two for yield strain). An additional technique was, therefore, necessary in order to get an accurate measure of the Young's modulus and yield strength.



Figure 28 – Tensile sample clamped in the mill, with the edge-finder in the mill chuck

This additional technique to measure the strain during small amounts of displacement (on the order of 10s of microns) involved making 4 marks along the gauge using a shiny silver marker. These marks resulting in two measurements; one between the outer marks and one between the inner marks. The silver markings exhibited strain without any slippage or hidden elongation because they were applied directly on the gauge, similar to a strain gauge or classic extensometer. These markings are more prone to errors, however, as there are both fewer measurements to average and the gauge is often deformed during plastic deformation. These effects make these markings necessary for measuring small strain values (<0.03 strain) but impossible to use to measure the strain at rupture. Therefore, both the gauge and tab markings were used to measure the strain in these tensile tests.

Image processing was performed using a MATLAB script utilizing a filter to create a binary image and then the centroid function to find the location of all the bodies of interest. Separate filters were used for the tab and gauge markings due to differences in reflected brightness. An example of a correctly analyzed image is shown in Figure 29. Before each test, a series of at least 15 photos were taken to establish an

accurate initial position of each of the markings. This method was verified to an accuracy of 1.2% for the Young's Modulus and median difference per tensile measurement of 3% using an off-the-self extensometer to compare with on larger samples.

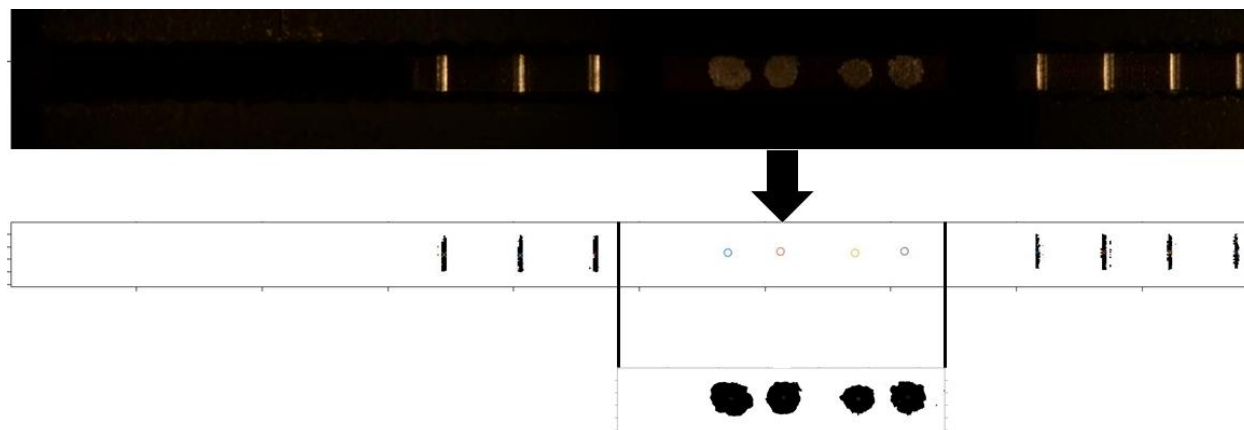


Figure 29 – Image processing on a calibration photo for a completed tensile test, with the centroid of each marking marked (circle for gauge, x for tabs)

3.5. Materials Characterization/Analysis:

Samples were analyzed using a field emission scanning electron microscope (SEM) equipped with the capability for energy dispersive spectroscopy (EDS) and electron backscatter diffraction (EBSD). Raman spectroscopy and X-Ray Diffraction (XRD) were used to obtain chemical bonding information of the base material and oxide. Mass measurements were made both before and after exposure using a high precision Sartorius scale with an accuracy of $\pm 2\mu\text{g}$. Elemental depth profiles were acquired using a Horiba GD Profiler 2 – a glow dispersion optical emission spectrometer (GD-OES) – and the sputtering depth was calibrated using a Zygo NewView 6K profilometer. Microhardness measurements were performed on cross-sectioned samples which had been polished to a final step of $0.02\mu\text{m}$ colloidal silica, using a Buehler Micromet II microhardness tester. Testing was performed using settings defined by ASTM standard E92: load of 25 or 50 gf; dwell time of 15 s; and spacing of at least 2.5 diagonal lengths between impact centers. Hardness values for each bulk region were taken from an average of 25 measurements.

4. 740H – Precipitation-Hardened Ni-Based Alloy:

4.1. Sample Fabrication

Samples of Special Metals alloy 740H were acquired from the manufacturer in two forms: ½” thick bar and 1/8” thick plate, both of which had been annealed and heat treated by the manufacturer per their specifications (anneal: 1,120°C/water quenched; heat treatment: 800°C/4hrs/air cooled) [35]. To acquire the base material samples, the ½” bar was sliced by waterjet cutting and then any surface roughness and oxide (from heat treatment) removed by use of a mill. The appropriately sized bar was then sent offsite to be EDM sliced into tensile samples.

1/8” thick plates of 740H were welded together by the manufacturer, Special Metals, on an automated welding machine (with specifications viewable in Table 20). The resulting 1/8” plates were then milled down to 1/16” thickness to remove any surface effects and extra thickness or strength due to the weld bead. The plates were then etched with glyceresia (see Table 1) to identify the location of the fusion zone on the now flat plates. Each plate was dimensioned and entered into AutoCAD to ensure that samples would be located correctly on the plate to get the different regions (base material, HAZ, fusion zone) present in the gauge (see Figure 23). The plates were then sent offsite to get samples EDM cut (transverse relative to the weld), along with the corrosion samples mentioned in section 3.2.

4.2. Pre-Exposure Tensile Results

Samples of both base material and weld were tensile tested in the unexposed condition. Samples were polished to the same standard as corrosion samples (800-grit) so no additional error would be incorporated from differences in initial surface roughness. In order to identify the location of failure of the welded samples, they were again etched with glyceresia until the fusion zone was visibly identifiable, then images were taken of every sample. An example of this is shown in Figure 30.



Figure 30 – 740H welded tensile sample etched with glyceric acid showing the weld in the center of the gauge

Sample gauge cross-sections were measured using a micrometer (mentioned in section 3.2) using five measurements for each thickness and the width. Samples were marked according to the procedure given in section 3.4.3.2 and then pulled in a calibrated tensile machine with the video extensometer noted in section 3.4.3.2 to account for strain measurements. Initial data, given in Table 2, show that base material samples exhibited good repeatability with strength values slightly below that of the reference provided by Special Metals for material taken from the same heat. This is a difference which was most likely caused by surface roughness and the measurement of the cross-sectional width (the sides of the gauge were not polished, so the surface finish was equivalent to that of EDM quality) and is assumed to be present with all samples. In addition, elongation was very consistent with the provided result from Special Metals.

Table 2 – 740H pre-exposure tensile results, compared to those provided by Special Metals, * = [76]

	Sample #	UTS (MPa)		0.2% YS (MPa)		Elongation %	
		Measured	Difference	Measured	Difference	Measured	Difference
Special Metals – Base		1,150.70		736.68		35.57%	
Base Material	1	1,109	-3.6%	679	-7.9%	38.4%	2.8%
	2	1,101	-4.3%	680	-7.7%	40.2%	4.7%
	3	1,118	-2.8%	680	-7.6%	36.8%	1.2%
	4	1,118	-2.8%	674	-8.5%	38.6%	3.0%
	5	1,110	-3.6%	681	-7.6%	36.6%	1.0%
	Average	1,111 +/- 6.4	-3.4%	679 +/- 2.4	-7.9%	38.1% +/- 1.3%	2.5%
Special Metals – Welded*		1,102.2		774.1		22.3%	
Welded	1	807	-26.8%	702	-9.3%	2.7%	-19.5%
	2	872	-20.9%	725	-6.3%	6.2%	-16.1%
	3	788	-28.5%	778	0.5%	2.9%	-19.4%
	4	856	-22.4%	775	0.2%	4.0%	-18.3%
	5	796	-27.8%	754	-2.6%	2.1%	-20.1%
	Average	863 ± 48.9	-26.3%	739 ± 26.1	-4.5%	6.3% ± 3.5%	-16.9%

Analysis of the pre-exposure results of welded samples, however, were not as positive. Table 2 shows that the both the strength and elongation values recorded were much lower than the corresponding

Special Metals results [76]. The yield strength was not significantly different, indicating the PWHT was most likely performed correctly. However, the loss in elongation indicates premature failure, likely due to an issue with the welding process. This performance of the weld was not acceptable if a comparison of macroscopic mechanical properties before and after exposure is desired.

4.2.1. Investigation of Weld Quality

The poor tensile results inspired more detailed analysis of the quality of the weld. To do this, a cross-section of the weld was produced, which was then polished to a mirror finish using several polishing steps and finally etched by glyceresia to reveal the grain structure. The resulting light images, displayed in Figure 31, reveal that the weld was not fully penetrating. There was a thin, persistent strip of base material that was comprised of base material grains that had obviously not been melted. There is no obvious crack from the separation of the two plates, so it appears that there may have been some inconsistent or weak solid-state bonding that took place. The end result, however, is that the weld was of too poor a quality to use for the purposes of this work.

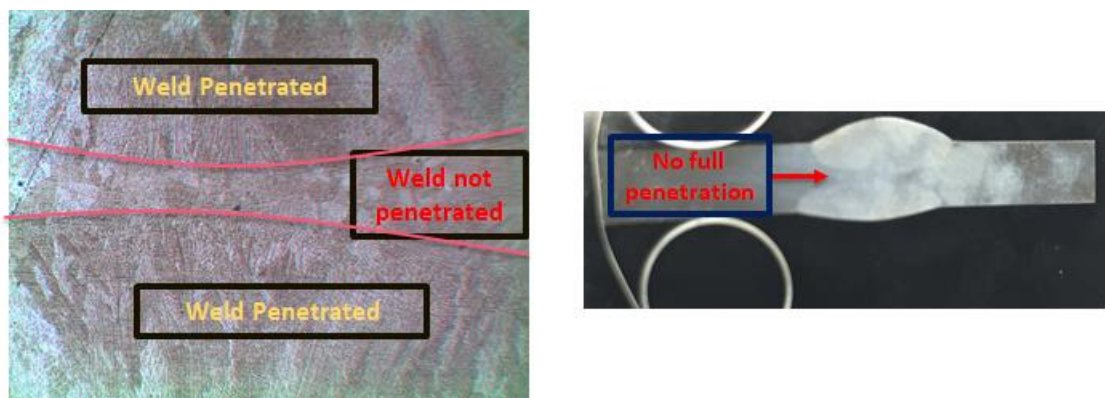


Figure 31 – Light images of the initial 740H weld that has been etched with glyceresia; shows that the weld was not fully penetrating

4.2.2. New Welding Procedure

The above results were relayed to Special Metals, who had previously not had the experience of welding thin plates such as this – their work had focused on the welding of pipes, and mostly thick-walled pipes due to the inherent difficulty of such a weld. They changed their procedure to ensure a fully penetrating weld between the two plates. The original and new welding procedures are given in Table 3, with the final procedure given in the appendix (Table 20). The new welding procedure introduced a root gap of 3/32” between the plates as well as increased the heat input by about 40%. This resulted in a fully penetrating weld, with confirmation in the form of SEM of etched 740H shown in Figure 32.

Table 3 – Comparison of new and old welding procedures for 740H similar welding of 1/8” thick plate

	Original Weld	New Weld
Type	Flat, butt weld	Single V, butt-weld
Root Gap	None	0.093”
Arc Voltage	10.5V	14.5V
Travel Speed	9.5 in/min	9.5 in/min
Wire Speed (average)	20 in/min	15 in/min
Amperage	150A	
Shielding Gas	75/25	
Passes	2 (one from each side)	
Filler Metal	Same Heat	
Base Material	Same Heat	



Figure 32 – SEM image of etched 740H weld interface after new weld procedure

4.2.3. Pre-Exposure Results of 740H Weld after New Procedure

As can be seen in Table 4, the fully-penetrating weld made by the new welding procedure produced very similar results to those reported by Special Metals for welded 740H samples [76]. Similar to the base material results (Table 2), the strength values were slightly lower than previous work, while the elongation was slightly higher. This is a trend that should be expected to continue throughout this work, as it is ascribed to the sample dimensions and method of measurement. These results indicate that the weld was of sufficiently high quality to judge the effect that exposure will have on the mechanical properties of a typical weld.

Table 4 – Pre-exposure tensile results of 740H welded samples which were welded with the new procedure, * = [76]

	Sample #	UTS (MPa)		0.2% YS (MPa)		Elongation %	
		Measured	Difference	Measured	Difference	Measured	Difference
Special Metals – Welded*		1,102.2		774.1		22.3%	
Welded	1	1,068	-3.1%	763	-1.5%	26.6%	4.3%
	2	1,042	-5.5%	737	-4.7%	23.0%	0.7%
	3	1,095	-0.7%	775	0.2%	29.3%	7.0%
	Average	1,068 ± 21.8	-3.1%	759 ± 15.9	-2.0%	26.3% ± 2.6%	4.0%

4.3. Exposure Results

Once the weld was confirmed to be of sufficient quality, exposure to CO₂ was begun. Samples of 740H and its weld were exposed at 750°C in either CO₂ at 20MPa or Ar at 0.02MPa, each for 1,000 hours continuously. Samples were then analyzed using mass change, RAMAN, XRD, and SEM analysis to understand the effects that the environment had on the material. Tensile samples were pulled in a tensile test, and the fracture surfaces were subsequently analyzed with SEM to identify failure modes. The combination of these data provides a thorough understanding of the base material and the weld performance after exposure in the above environment.

4.3.1. Corrosion Analysis

4.3.1.1. Mass Change

Mass change (normalized by surface area) was measured for all samples and compared with previous work, revealing consistency with previous work within 20% in the same conditions and time for base material [17]. There was no apparent spallation for either base material or welded, so mass change can be understood (cautiously) to be representative of the amount of carbon and oxygen uptake. Base material gained $0.2542 \pm 0.0075 \text{ mg/cm}^2$ while welded samples gained $0.3122 \pm 0.0017 \text{ mg/cm}^2$, an increase over base material by 23%. This indicates that welded material performed slightly worse from a corrosion standpoint than base material. It should be noted, however, that the fraction of base material to fusion zone present on each sample varied (and was not near 100%), so no quantitative analysis is possible from these numbers. As a quality assurance check, mass change was taken for the neutral aging exposure and found to be negligible: $0.0297 \pm 0.0075 \text{ mg/cm}^2$ for base material and $-0.0360 \pm 0.0148 \text{ mg/cm}^2$ for welded samples.

4.3.1.2. Surface Characterization

RAMAN spectroscopy and XRD were performed to characterize the oxide through acquiring bonding information. RAMAN was acquired using a 532nm laser and compared using the online database rruff.info (Cr_2O_3 is eskolaite). Figure 33 shows that a comparison between base material and the fusion zone are very similar, indicating that the oxide composition is very similar. It also shows that they are both very similar to the reference value for pure Cr_2O_3 , indicating that it is the dominant surface phase of oxide. This is expected, as RAMAN is a surface analysis technique that does not penetrate more than a few nanometers.

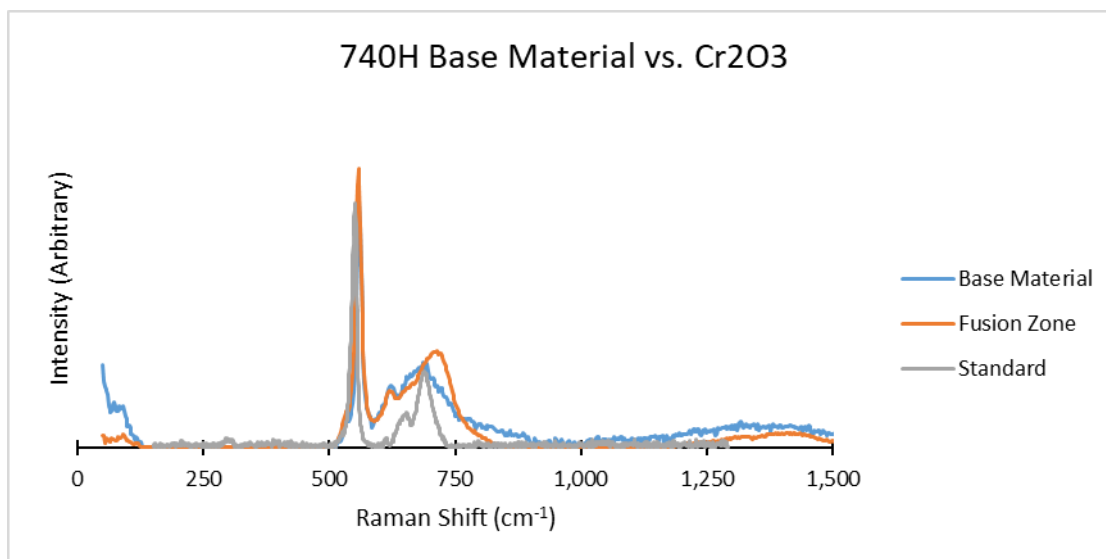


Figure 33 – Comparison of the surface of CO₂ exposed 740H base material and fusion zone to the reference for Cr₂O₃ (Eskolaite)

XRD analysis on the surface of 740H samples that were exposed to CO₂ revealed a similar oxide composition. The results, given in Figure 34, showed that the majority of peaks correspond to locations and relative intensities of characteristic peaks for Cr₂O₃. In addition to these peaks, XRD has a much deeper penetration depth than RAMAN so the intensities were dominated by bulk diffraction from the underlying nickel matrix (labeled on the figure). The unlabeled peaks observed in the fusion zone measurement could be attributed to Al₂O₃, but the intensity was not high enough for enough characteristic peaks to be identified to confirm this. These results confirm the RAMAN information that indicated the majority of the oxide was composed of Cr₂O₃.

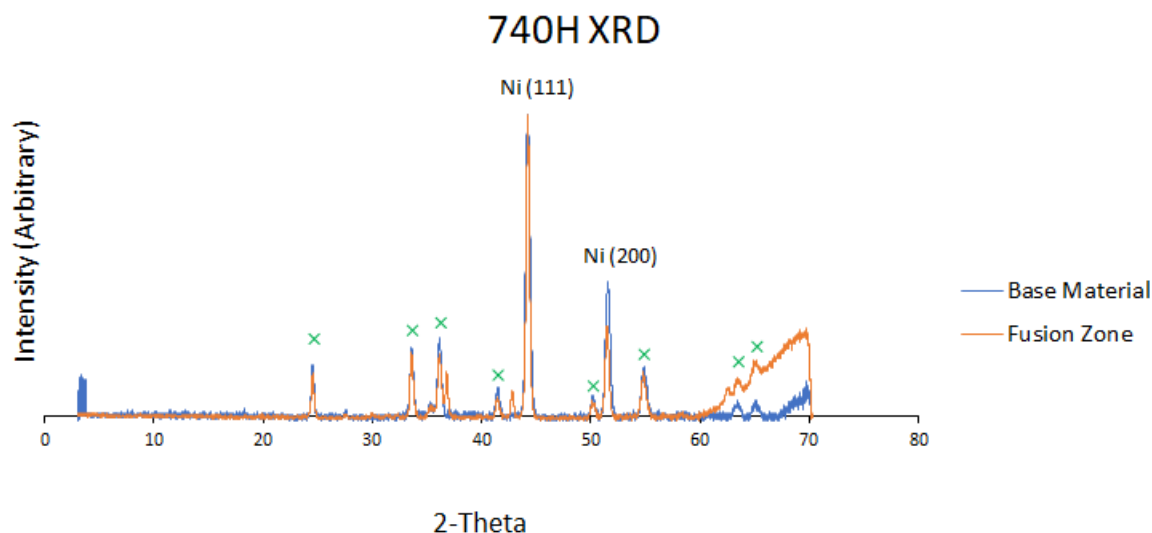


Figure 34 – Comparison of XRD performed on the surface of CO₂ exposed 740H base material and fusion zone with Ni peaks dominating and Cr₂O₃ characteristic peaks marked with a cross

4.3.1.3. Cross-Section Analysis - Surface

Corrosion samples, described earlier in section 3.2, were formed into cross-sections and analyzed to observe the depth-dependent effects of corrosion as well as the bulk effects of heat treatment. As described above in section 2.2.1, the heat treatment of 740H at 750°C has been shown to coarsen grains and high-strength γ' precipitates, both of which impact mechanical properties. In addition, the depletion of the γ' precipitates from any region – mainly near the oxide or grain boundaries – is important to the understanding of tensile strength and the projection of creep and fatigue strength. For that purpose, samples were polished to a mirror finish (last step of 0.02 μ m colloidal silica) and analyzed with SEM.

Analysis of the surface region revealed very similar oxides in both base material and the fusion zone. Mean oxide thickness measurements were taken from three images at different locations of each of base material and fusion zone located on the same sample. These results revealed no measurable difference between the two locations: $1.33 \pm 0.11\mu$ m in base material and $1.40 \pm 0.09\mu$ m in the fusion zone, with a range of 1-3 μ m for both zones. Further, there is no obvious increase in internal oxidation or near-surface

carbide formation observed in the 2-D SEM images. Given the small scale of the corrosion-affected region in 740H in these conditions, the source of the additional mass change could not be determined. The near-surface of both regions is imaged in Figure 35.

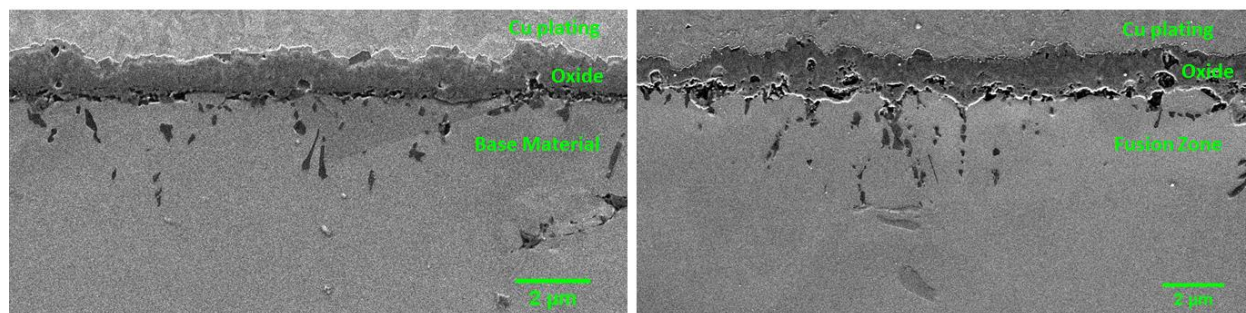


Figure 35 – Surface of 740H base material (left) and fusion zone (right) after exposure to CO₂ at 750°C for 1,000 hours. Oxide thickness not measurably different.

EDS analysis of the surface region of both base material and fusion zone, shown in Figure 36 and Figure 37 respectively, revealed similar compositions of a Cr-rich oxide with Ti-enrichment. These were accompanied by an adjacent Cr and Ti-depleted region which extended 1-4μm directly below the oxide (marked on the figures). The depletion region indicates that the oxide formation may be limited by the diffusion of Cr and Ti through the matrix to the surface. This depletion region is characterized further by an enrichment of Al which is likely oxidized into Al₂O₃. This internal oxidation was observed to extend as much as 10μm into the material – typically along grain boundaries. This Al oxidation is much more inconsistent, however, and the Al-depletion zone correspondingly extends around the enriched areas wherever they are. This results in regions which are depleted in Al at distances of up to 10-15μm into the material, depending on the depth of the internal oxidation. 740H base material has randomly dispersed TiC particles and occasionally these are located on the surface [17]. This is shown in Figure 36, and appeared to encourage internal oxidation of Al.

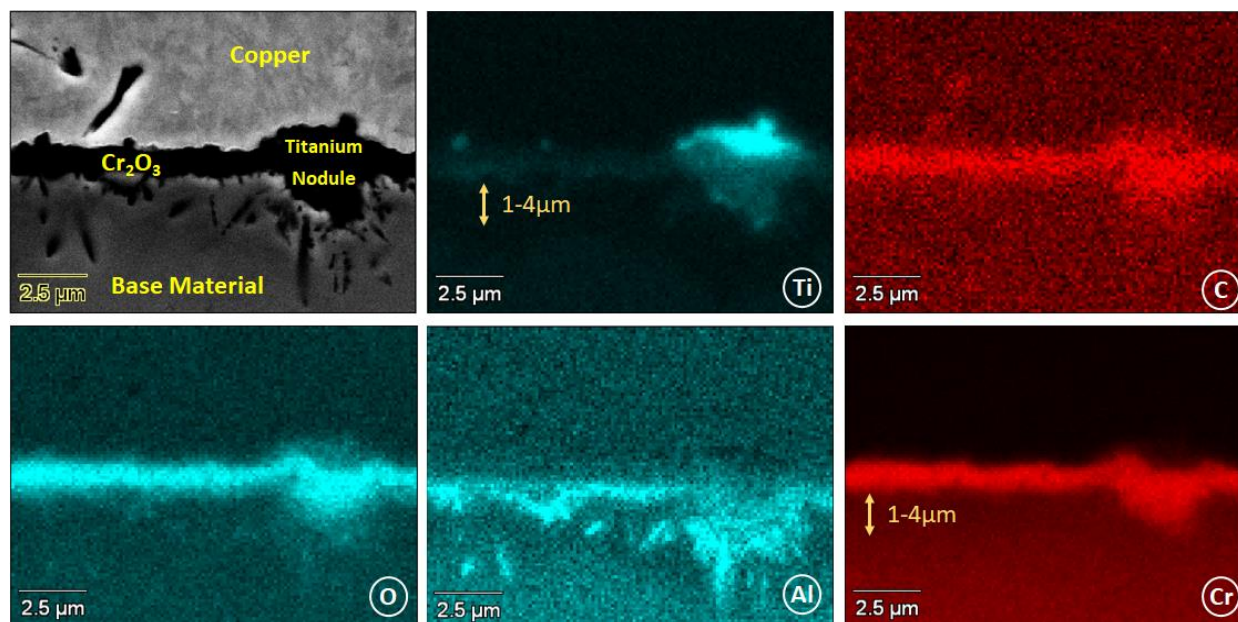


Figure 36 - 740H CO₂ Exposed Sample in Base Material. Shows Ti precipitate on surface of sample leading to internal oxidation beneath it. Ti and Cr maps have the depletion zones marked.

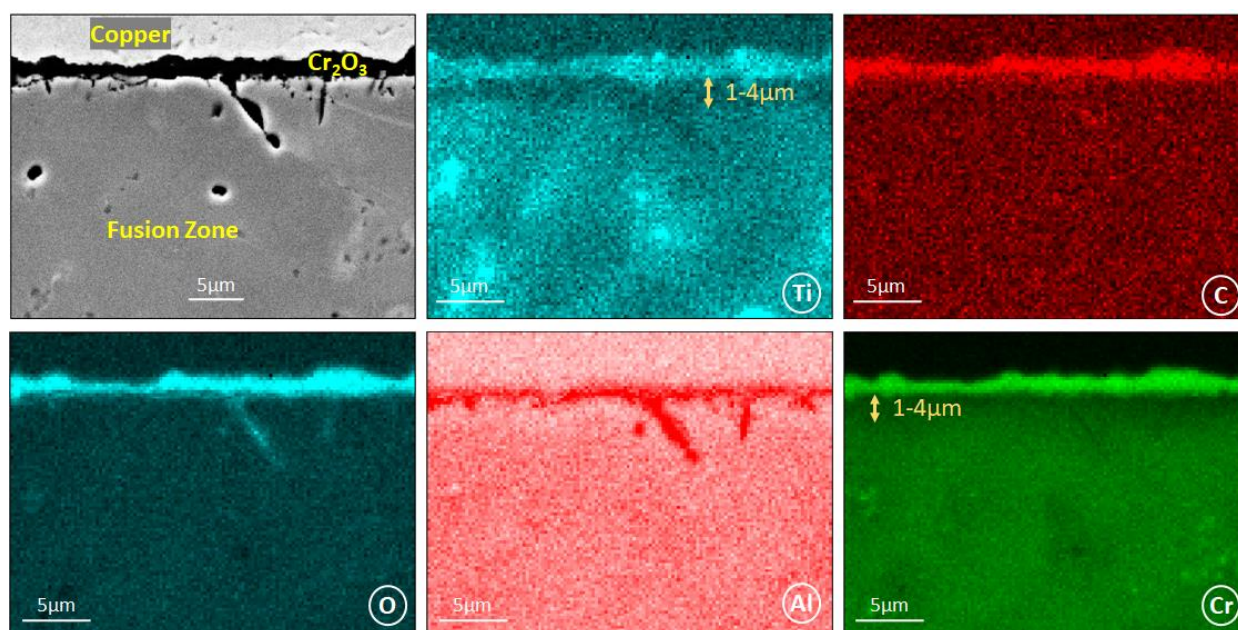


Figure 37 - 740H CO₂ Exposed Sample Inside Fusion Zone. Shows Cr and Ti depletion zone underneath oxide, as well as internal oxidation via Al along grain boundary. Ti and Cr maps have the depletion zones marked.

Additionally, samples were etched with HCl + 1% H₂O₂ for 3 seconds (by submersion) to reveal the presence of γ' precipitates near the surface. Images of both the base material and fusion zone in this

etched condition are shown in Figure 38. These show a γ' -denuded region of 1-4 μm in thickness – corresponding to the Cr and Ti-depleted regions – directly beneath the oxide. Further imaging showed that this γ' -denuded region was also present surrounding internal oxide formation, corresponding to the Al-depleted regions, at depths of up to 10-15 μm . The lack of γ' in these regions could be attributed to one or a combination of the following: the depletion of Cr can cause γ' to be unstable in the γ matrix; and the depletion of primary γ' -forming elements reduces the total amount of γ' which can form [38], [60]. Given that the PFZ extends into 740H around both Cr/Ti and Al-oxides, it appears that the larger of these effects is the depletion of primary γ' -forming elements. The determination for 740H, regardless of base material or fusion zone, is that the formation of an oxide creates the conditions for a typically 1-4 μm thick γ' -denuded region after 1,000 hours of exposure to CO_2 at 750°C, 20MPa, with the occasional extension of up to 10-15 μm from the oxide.

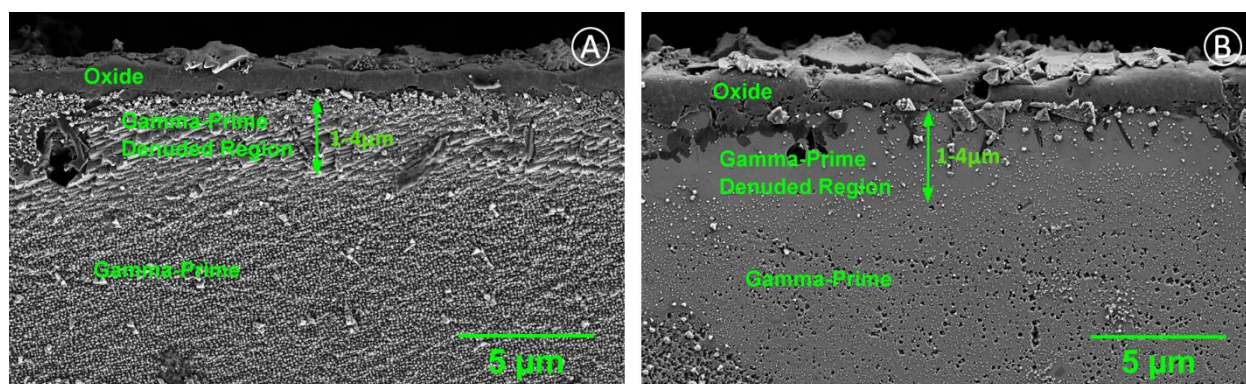


Figure 38 – 740H sample etched with HCl-1%H₂O₂ solution showing γ' density in the near-surface region for base material (A) and inside the fusion zone (B). γ' -denuded region is of similar thickness for both regions, and correspond to Cr-depleted region.

The above provides some projections of mechanical performance of 740H after exposure in s- CO_2 . The removal of γ' leaves a relatively soft, weak γ matrix behind. Its strength is such that it will not contribute much to the measured macroscopic strength of the material. The γ' -denuded region, therefore, effectively represents a 1-4 μm deep removal of material on all sides of the gauge, equivalent to a 1% loss in strength given tensile sample cross-sectional dimensions. This is an effect which must be recognized

when evaluating these results, but will also diminish over time due to the protective nature of the oxide, as well as during application with increasing pipe wall thickness. Of additional concern is the effect of the γ' -denuded regions corresponding to internal oxidation. These regions are likely as or more impactful as the near-surface γ' -denuded regions in terms of tensile strength. They could also function as crack initiation sites while under creep or fatigue, as PFZs are known to have poor creep strength [62], especially adjacent to the brittle Al_2O_3 . Surface analysis, therefore, provides a potential explanation for a small loss in strength and ductility. However, as the corrosion-affected region is less than 5% of the total gauge cross-section, bulk effects from prolonged aging at high temperature must be incorporated into the analysis of s-CO_2 exposure.

4.3.2. Thermal Aging Analysis

4.3.2.1. Cross-Section Analysis - Bulk

Bulk analysis was performed to confirm the effects that prolonged high-temperature aging of 740H has shown in previous works [36], [37], as no oxidation or carburization was observed deeper than about 10-15 μm into the material. Aging of 740H at 750°C results in grain coarsening [37] as well as the formation of M_{23}C_6 carbides along grain boundaries in base material [36]. Both of the latter effects individually increase strength – γ' as a high-strength precipitate, carbides by stabilizing dislocations – while decreasing ductility. However, the micro-segregation present in the fusion zone [60] could impact the formation and coarsening of both of these precipitates, and this may alter the mechanical properties of welded material in a different way relative to base 740H.

Figure 39 shows selective elemental distributions from an EDS mapping near grain boundaries of both the base material and fusion zone. Base material exhibited constant Cr-enrichment, presumably from Cr-carbide formation, along grain boundaries. However, there was little to no measurable Cr-depletion surrounding the grain boundaries due to this Cr-enrichment. Also shown is the presence of the previously

mentioned TiC particles, here located at a grain boundary in the bulk. The fusion zone, however, showed the segregation of Nb and Ti to the dendritic core and Cr and Co to the inter-dendritic regions. This segregation persisted through the high temperature aging, as was expected [60], because the exposure temperature was below the homogenization range for 740H. The presence of Cr-enrichment along grain boundaries was correspondingly inconsistent, with enrichment primarily occurring only where the inter-dendritic regions intersected with grain boundaries. The Al map is included to show that there was no micro-segregation of Al within the fusion zone, also consistent with previous work. In addition, the dendrite arm spacing was on the order of 10 μ m, matching that of previous analysis [60]. This indicated that the aging process appeared not to have affected the micro-segregation of elements, and that in fact this micro-segregation provided a significant barrier to the formation of Cr-carbides where the dendritic cores intersected grain boundaries. The lack of a continuous presence of carbides along grain boundaries, combined with larger grains relative to base material, reduced the stabilizing effect these carbides typically have on dislocations within the fusion zone, likely reducing the yield strength of the material. Additional exposure is not likely to alleviate this condition through the creation of a microstructure more typical of the base material. On the contrary, it is possible that the segregation-limiting Cr-content along grain boundaries was initially more continuous and that the aging process has coarsened them in discrete locations, meaning further aging would only reduce the total grain surface area covered by carbides.

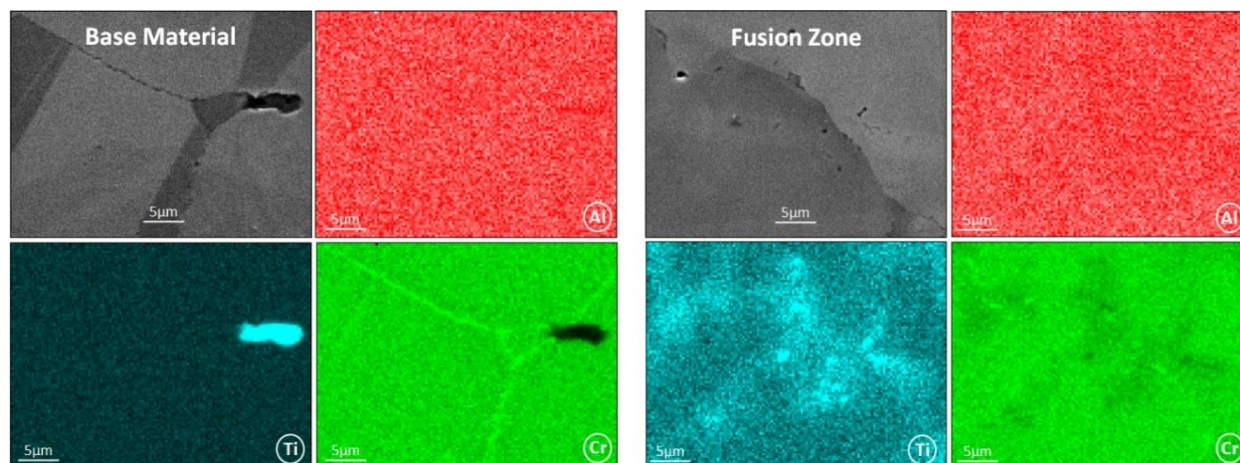


Figure 39 – Images in bulk of base material (left) and fusion zone (right) showing Ti segregation and lack of segregation of Al, along with showing that grain boundary Cr-carbide precipitation is more consistent in base material. The Cr map shows that dendrites were formed wide during weld solidification, forcing Ti into the relatively small inter-dendritic regions.

Analysis of the bulk material with SEM, seen in Figure 40, shows that γ' precipitates have increased in size to the 50-90nm range, consistent with previous work [36], [37]. This indicates that there will be hardening and embrittling of the base matrix which was seen in those previous studies. Further, there was no indication of PFZ formation along grain boundaries in either base or fusion zones. Consistent with the EDS scans in Figure 39 showing no measurable Cr-depletion, there was no observable change in γ' precipitate density as you approach the grain boundaries, even in the presence of Cr-carbides. This indicates that the depletion of Cr in the vicinity of these carbides, if any, was not sufficient to cause γ' to become unstable and dissolve back into the γ matrix. Previous work found that a PFZ formed along grain boundaries in 740H after long-term aging only when under creep conditions [34], [38]. This confirmed that work, as these samples were not under stress during exposure. In addition to this, previous analysis of the weld of 740H had shown PFZs along grain boundaries [62] or in dendritic cores [61]. Figure 40 indicates that this PFZ disappeared with prolonged aging at 750°C, a positive indicator for the creep and fatigue strength of the weld material. Further, the precipitate-poor inter-dendritic regions which were present after weld solidification [61] exhibited no visual evidence to either confirm or negate their presence after 1,000 hours at 750°C. However, given that all γ' coarsened to roughly the same size and that there was no

homogenization of key γ' -forming elements, it is inferred that these regions persisted. The estimation here is that they contained similar-sized precipitates which were less densely populated than the surrounding matrix, potentially weakening the matrix systematically every $10\mu\text{m}$. This could combine with the observed inconsistent grain boundary carbides to weaken welded material relative to base material after exposure at 750°C for 1,000 hours.

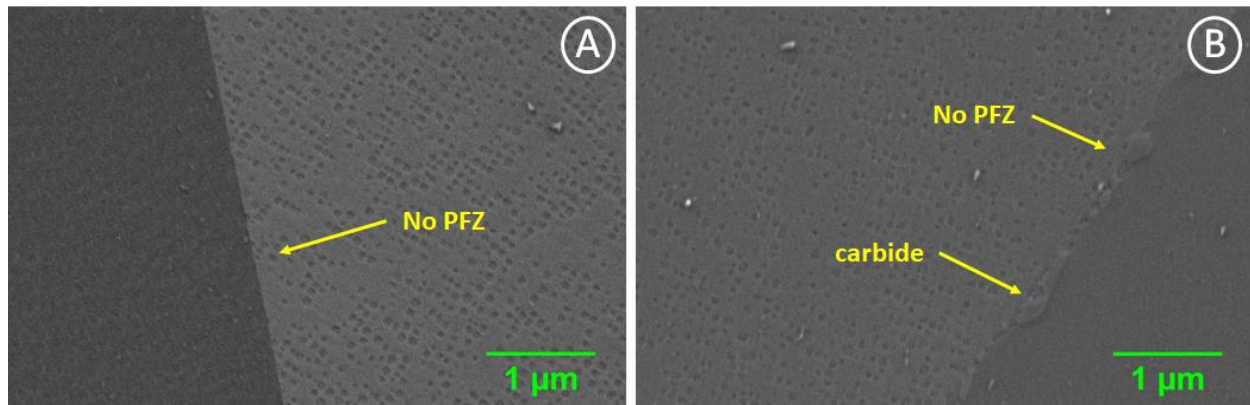


Figure 40 – Images of γ' precipitates in the bulk of base material (A) and in the fusion zone (B). Neither exhibits an apparent PFZ of any consistency, even when comparing grain boundaries with and without carbides inside the fusion zone.

4.3.2.2. Grain Size

It is important to analyze any potential grain alteration due to the aging process (or CO_2 corrosion), as this could have an effect on the material strength. Comparing the grain sizes of welded samples would yield no useful information about grain growth during exposure unless the same grains were measured both before and after exposure, as the grain sizes are dependent on the local energy density and cooling rates during the welding process. Because of this, base material was analyzed with EBSD for purposes of assessing grain size, with images shown in Figure 41. As is apparent from the images, there was no observed grain growth in the samples analyzed in this work: as-received ($82.0 \pm 40.2\mu\text{m}^2$), CO_2 -exposed ($76.2 \pm 39.3\mu\text{m}^2$), and aged ($89.2 \pm 68.9\mu\text{m}^2$) samples all had similar grain sizes. This contradicts previous work which observed grain growth in 740H [37], although that study measured grain size using a different

methodology (intercept method). However, for this study there was no observed grain growth, so grain size will make no impact on any change in mechanical properties.

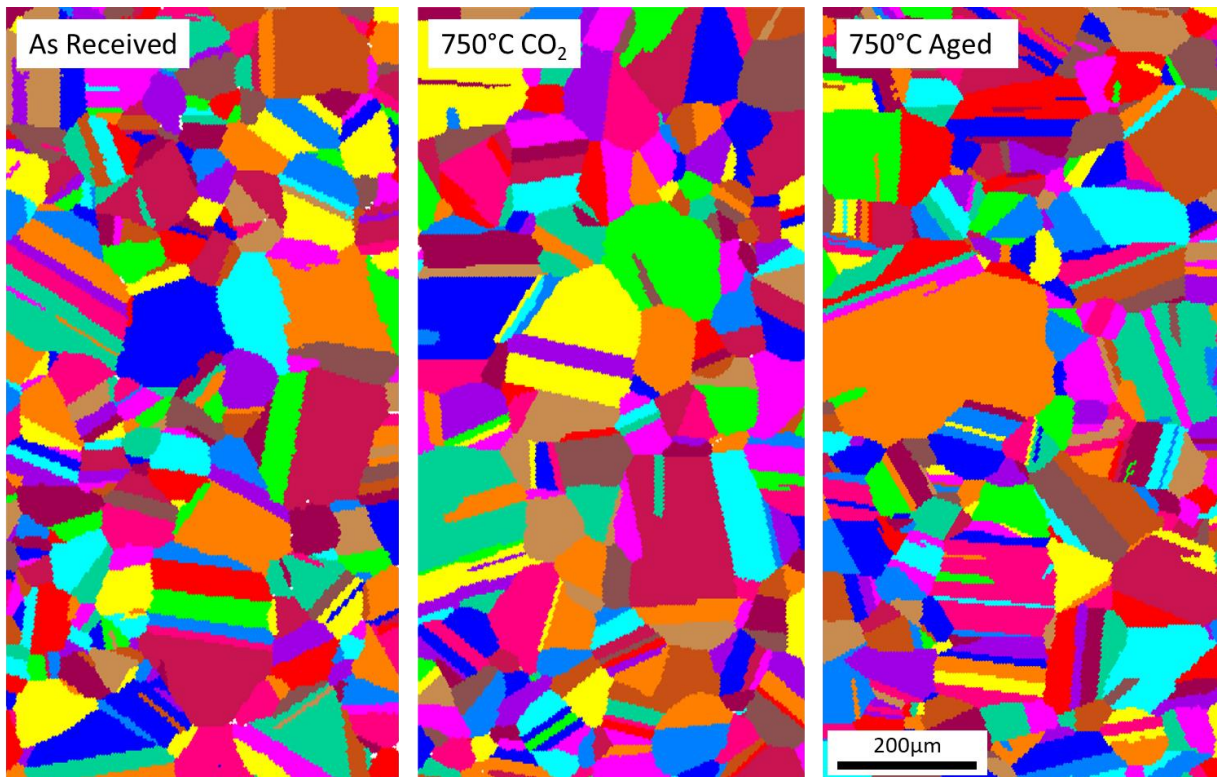


Figure 41 – EBSD for 740H base material in the following conditions (scales are equivalent): as-received (standard annealing + heat treatment); after 1,000 hours at 750°C, 20MPa in CO₂; and after 1,000 hours aging at 750°C

4.3.3. Mechanical Analysis

4.3.3.1. Tensile Results

Tensile results before and after exposure are given in Table 5. From literature, it was expected that exposure to CO₂ at 750°C should increase YS due to the coarsening of γ' precipitates, and this holds true for base material samples. Base material gained roughly 7% in UTS and 5% in YS while suffering a 31% loss of elongation relative to unexposed. 750°C neutral aging produced results which were very similar to that of CO₂-exposed samples, with any differences likely due to the limited number of samples which were tested. Welded samples responded differently than base material, however. For CO₂ exposed samples,

there was no change in UTS, YS dropped by 7%, and elongation dropped by 39%. Exposed samples experienced a very large drop in YS which combined with a drop in ductility to produce a much lower UTS. Similarly to base material, there was no statistically significant difference between welded samples which were exposed to CO₂ or neutrally aged. All samples appeared to fracture inside the fusion zone.

Table 5 – Tensile testing results for 740H (base material and welded)

	UTS (MPa)	YS (MPa)	Elongation (%)	Failure Location
Base Unexposed (UW)	1,111 ± 6	681 ± 3	38 ± 1.3	N/A
Base 750°C CO₂	1,188 ± 2	715 ± 3	26 ± 0.5	N/A
Base 750°C Aging	1,158 ± 4	718 ± 3	25.5 ± 0.2	N/A
Welded Unexposed	1,068 ± 22	759 ± 16	26 ± 2.6	Fusion Zone
740H-740H 750°C CO₂	1,063 ± 9	714 ± 9	16.5 ± 0.6	Fusion Zone
Welded 750°C Aging	1,084 ± 17	689 ± 19	17.1 ± 1.6	Fusion Zone

As can be seen in these tensile results – and was predicted with the above analysis – the thermal aging of both base and welded 740H dominated the evolution of bulk mechanical properties. The coarsening of both γ' precipitates and grain boundary carbides caused an increase in strength while decreasing ductility. This created competing factors for domination of overall mechanical properties. In the case of base material, grains are relatively small and equiaxed, and it was shown above that grain boundary carbides were essentially continuous. In contrast, the fusion zone was characterized with larger, oriented grains with inconsistent grain boundary carbides due to dendrite formation causing micro-segregation. It had been shown that M₂₃C₆ carbides function as barriers for dislocation movement [36]. It follows that – in the case of welded samples – both larger grains and inconsistent carbide formation on grain boundaries allowed for additional dislocation migration. Additionally, the likely presence of precipitate-poor regions in inter-dendritic regions created an inconsistent strength of the matrix. These effects combined to lower the yield strength of the material.

4.3.3.2. Microhardness Results

Microhardness was taken inside base material and the fusion zone before and after exposure to CO₂. As the grain size was roughly 80-90µm, a typical indentation (diameter ~10µm) provided values representative of the granular matrix, not overall material hardness. In addition, the 10µm indentation was of the same order as the dendritic arm spacing in the fusion zone, allowing all indentations to be representative of the combination of the dendritic and inter-dendritic sections of the fusion zone. This should provide an understanding of the interaction of the γ matrix with the coarsening γ' precipitates. In the base material, exposure increased microhardness from $367 \pm 5\text{HV}$ to $444 \pm 4\text{HV}$. This indicates the expected hardness increase from the coarsening of γ' precipitates observed previously [36] and with the SEM images shown in Figure 39. However, exposure did not increase microhardness in the fusion zone to the same degree, with measured values increasing from 366 ± 5 before exposure to 383 ± 5 after exposure.

While the γ' precipitates are discretely homogeneous in the γ matrix in base material, it can be recalled that micro-segregation has been shown to create inhomogeneities of γ' nucleation after initial PWHT [61]. These precipitate-poor regions in the inter-dendritic regions were not obviously apparent in SEM images (see Figure 39). However, as discussed above, the lack of elemental diffusion during exposure (and the obvious effect this had on Cr-carbide formation) indicates it is likely that these regions persisted throughout the exposure. The coarsening of existing precipitates in these regions could have left larger sections of the inter-dendritic regions precipitate-free, thus further lowering the local hardness and creating weak points in the matrix. These effects would only enhance the effects of inconsistent grain boundary carbides discussed above, lowering strength and ductility.

4.3.3.3. Fracture Surface Analysis

Fracture mechanisms were analyzed using SEM imaging of the post-tensile test fracture surfaces [77], [78]. Figure 42 shows the fracture surface of a base material sample that was tested in the unexposed condition. The surface indicates intergranular fracture combined with micro-void coalescence (MVC).

This fracture mechanism was expected, as the unexposed samples were heat treated at 800°C and had, therefore, formed brittle grain boundary carbides [37]. The relatively large dimples indicate a ductile mode of intergranular fracture. Figure 43 presents the fracture surface of a base material 740H sample which was exposed to CO₂. It can be observed that the same type of fracture surface occurred, but with a slight decrease in dimple size (note the figure scales). A decrease in the dimple size would indicate that the alloy was only slightly embrittled after exposure to CO₂ at 750°C for 1,000 hours, which is consistent with the elongation data acquired from tensile tests. The fracture surface of samples which were thermally aged matched that of CO₂-exposed, so images are not shown here.

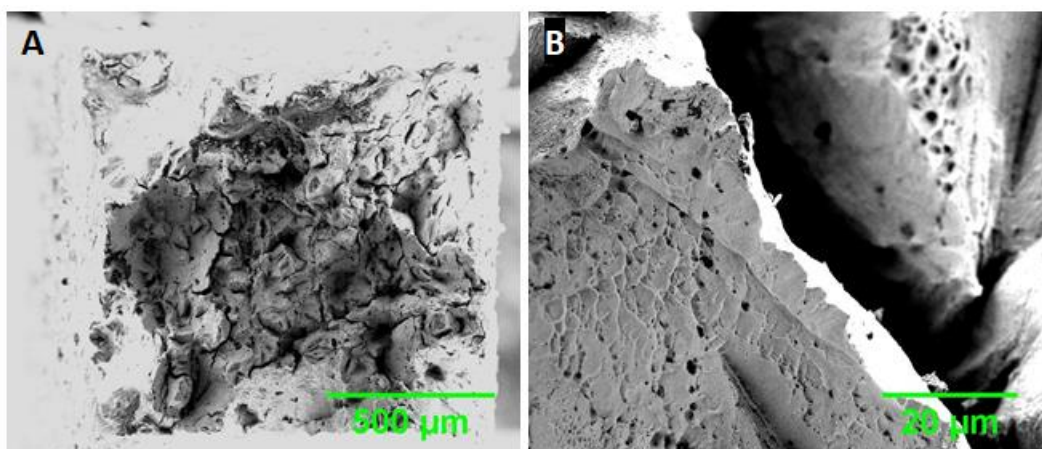


Figure 42 – SEM images of fracture surface of 740H base material unexposed sample. Clearly defined grains indicate intergranular failure, with MVC observed as large-scale dimples on the surface of the grains, size on the order of 10μm.

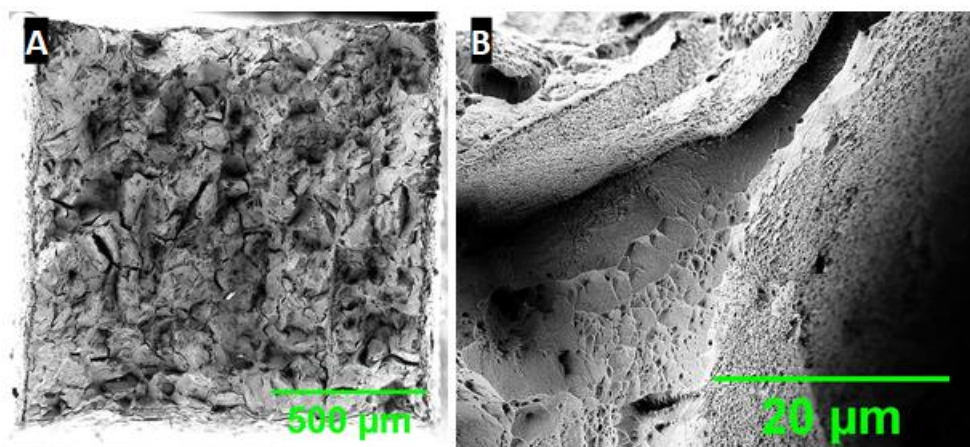


Figure 43 – SEM images of fracture surface of 740H base material CO₂ exposed sample. Clearly defined grains indicate intergranular failure, with MVC observed as dimples on the surface of the grains, with a size on the order of 1-5μm.

Figure 44 shows the fracture surface for an unexposed 740H welded sample (fractured inside the fusion zone). The fracture surface is very similar to that of the base material: intergranular fracture with large dimpled MVC (the grains within the weld are larger and directional). Figure 45 shows the fracture surface of a welded 740H sample exposed to CO₂ (also fractured inside the fusion zone). Figure 45 (A) shows the bulk of the failure occurred intergranularly. However, as observed in Figure 45 (B) and (D), the failure mode was mainly micron-scale cleavage (B, likely occurring within grain boundary carbides) or grain boundary cracking (D). Both of these observed failure modes resulted from more brittle fracture than that of unexposed, and they reflect the loss of elongation observed in tensile results. Grain boundary cracking, in particular, indicates that the grain boundary sheared with a very low energy failure – so low that the underlying dendritic structure can be observed on the fracture surface (Figure 45, D). In addition, the inhomogeneity of fracture mode after exposure indicates that the intermittent grain boundary carbides had a profound effect of mechanical properties, as inferred above from cross-sectional analysis. As with base material, the fracture surface of welded samples which were thermally aged matched that of CO₂-exposed, so images are not shown here.

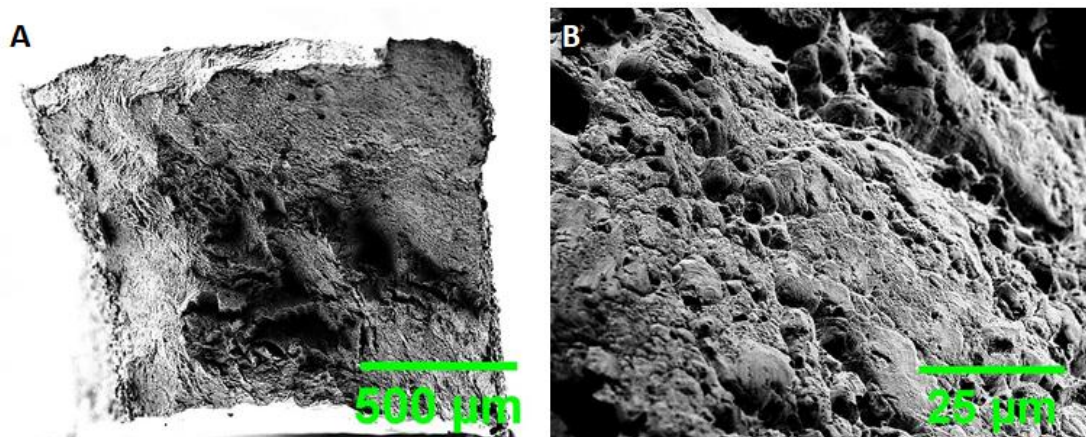


Figure 44 – SEM images of fracture surface of 740H welded unexposed sample. Large-dimpled MVC observable with dimples on the order of 10 μ m in diameter.

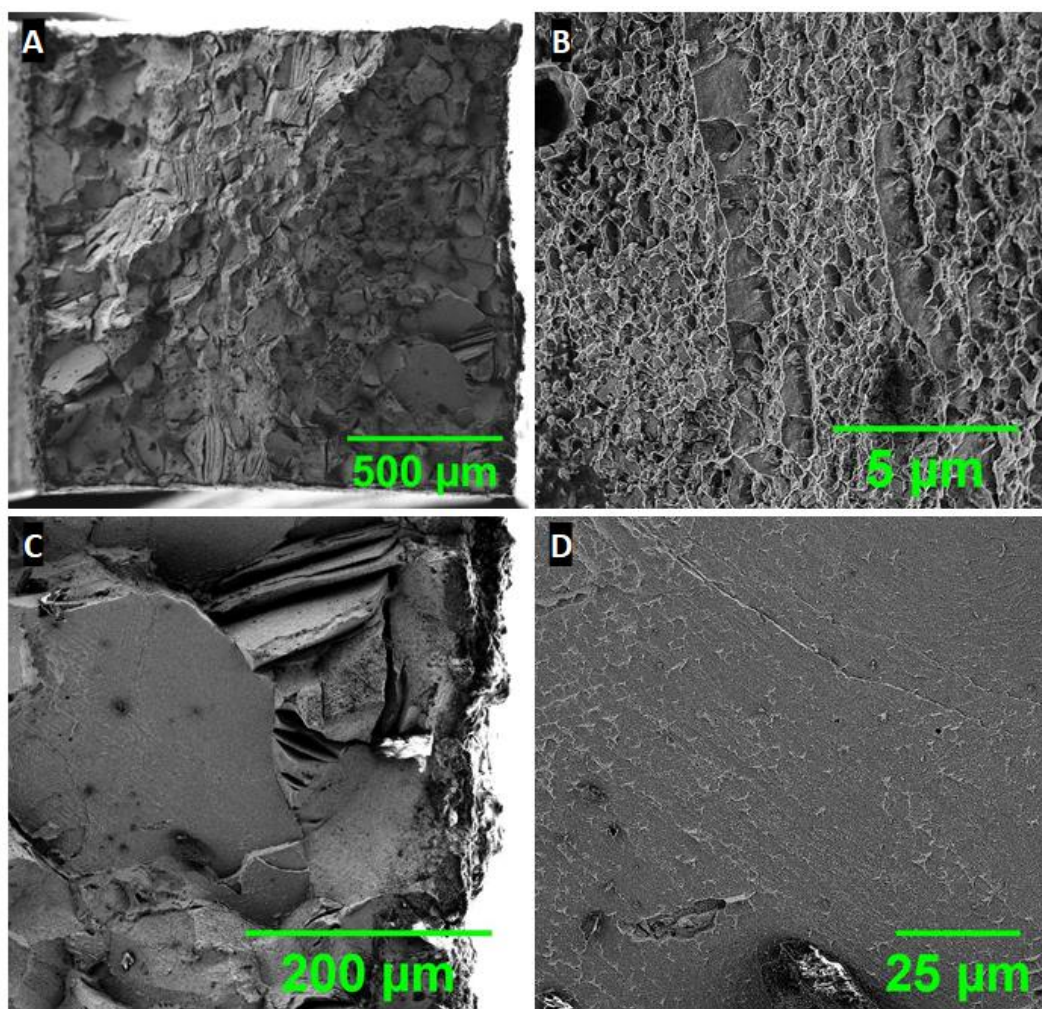


Figure 45 – SEM Images of Fracture Surface of 740H Welded RG CO₂ Exposed at 750°C for 1,000h; a) Entire rupture area, b) micron-scale cleavage, c and d) grain boundary cracking (with inter-dendritic regions observable on the grain surface).

4.3.4. 740H Performance Summary:

740H exposed to CO₂ produced a protective Cr-rich scale of 1-2µm in thickness. This scale prevented carburization and limited oxidation such that 740H did not experience any observable negative effects from the CO₂ fluid beyond a depth of 4µm from general corrosion, and 10-15µm from internal oxidation. The mechanical effects of exposure to the CO₂ environment are attributed to the prolonged aging of the material at 750°C, and this is supported by the tensile results of thermally aged samples. The strengthening γ' precipitates were observed to coarsen to a size consistent with previous work [36], [37] in both base material and the fusion zone. This coarsening during exposure caused a reduction in ductility of both base material and welded samples. Microhardness measurements showed that significantly more hardening occurred in base material than in the fusion zone, indicating that the precipitate-poor dendritic cores inside the fusion zone observed in previous work [61] may have persisted through aging and negatively affected strength on the scale of inter-dendritic spacing (roughly 10µm).

Cr-rich carbides were present on all grain boundaries in the base material, but inconsistent in the fusion zone due to micro-segregation of Cr out of the dendritic cores. This led to base material exhibiting increased strength from prolonged aging, while welded samples exhibited significantly decreased yield strength. The effect may have been magnified in both CO₂-exposed and thermally aged welded samples due to coarsening of grain boundary carbides, increasing their size by reducing the surface area they covered, thereby reducing their ability to stabilize dislocations. Additionally, EBSD confirmed that there was no grain growth in base material, so it is supposed that there was also no grain growth in the fusion zone, removing that variable from any impact on tensile results.

The weld appears to be the major mechanical concern with prolonged application of 740H at 750°C. Corrosion performance was very good, such that the CO₂ environment seems not to make any impact beyond about 15µm from the surface. Additionally, there was no PFZ observed along grain boundaries –

likely due to the local Cr-content not depleting below the γ' -dissolution composition – indicating good creep and fatigue strength. However, the elemental micro-segregation in the fusion zone, specifically of Cr and Ti, appears to create heterogeneities in γ' and grain boundary carbide distribution which severely impacted mechanical properties. It is anticipated that additional exposure at 750°C would have little impact on fusion zone grain boundary morphology, though the material should continue to embrittle as γ' precipitates in the matrix continue to coarsen.

The work presented here identifies a specific correlation between microscopic phenomena and macroscopic properties. The observed corrosion-affected zone indicated that corrosion would play a negligible role in the evolution of mechanical properties in CO₂. This was proven through the comparison of measured mechanical properties after 750°C exposures: one in CO₂ and the other in a neutral environment. In addition, the analysis of aging effects in the bulk material – including microhardness testing and SEM imaging, combined with studies from literature – identified that there should be strengthening in base material, but the potential for a divergent response from the fusion zone. These predictions were also proven to be accurate when mechanically tested. This indicates that if one is provided with a thorough understanding of the strengthening mechanisms of an alloy, combined with the ability to observe their evolution, an estimate of mechanical properties can be achieved. While mechanical testing is necessary in order to quantify these effects, the number of potential alloys to pursue can be effectively whittled down by applying strictly micro-scale analysis techniques. While this is not a groundbreaking conclusion, it can be clearly stated that the analysis of 740H can be completed with a microscopic characterization, as the macroscopic testing supports this characterization, and further analysis of this alloy can proceed without macroscopic testing unless specifically requested.

5. 282 – Precipitation-Hardened Ni-Based Alloy:

5.1. Sample Fabrication

Samples of 282 were acquired from the manufacturer, Haynes International. Base material samples were acquired in the form of 1/16" thick plate which was in the annealed condition (at a temperature of 1,121-1,149°C). The plate was then heat treated in Ar at UW-Madison at conditions of 800°C/4hr/furnace cooled, a heat treatment which Haynes advised for 282 which will be in service below 760°C. Welded samples were produced by Haynes through the welding of 1/8" thick plate (specifications listed in Table 20). Haynes then performed the PWHT (800°C/4hr/air cooled). Plates were milled down to 1/16" thickness to remove the weld bead and any other surface defects. The plates were then etched with glyceresia (see Table 1) to identify the location of the fusion zone on the now flat plates. Each plate was dimensioned and entered into AutoCAD to ensure that samples would be located correctly on the plate to get the different sections (base material, HAZ, fusion zone) present in the gauge. Tensile samples for both base and welded material were then acquired by sending them off site to get EDM cut (transversely relative to the weld), along with the corrosion samples mentioned in section 3.2. Samples were then polished to 800-grit before either exposure or tensile testing. The number of samples utilized for tensile testing in each condition are given in Table 6.

Table 6 – Number of 282 tensile samples tested in each condition

	Base Material	Welded
Unexposed	2	2
750°C CO ₂	2	2
750°C Ar	4	3

5.2. Pre-Exposure Tensile Results

In order to identify the location of failure of the unexposed welded samples, they were again etched with glyceresia until the fusion zone was visibly identifiable, then images were taken of every sample. Sample

gauge cross-sections were measured using a micrometer (mentioned in section 3.2) with five measurements for each thickness and width. Samples were marked according to the procedure given in section 3.4.3.2 and then pulled in a calibrated tensile machine with the video extensometer noted in section 3.4.3.2 accounting for strain measurements. In order to assess the quality of the weld used in this experiment, unexposed welded samples were tested and compared to the standard values reported by Haynes in Table 7.

Table 7 – 282 pre-exposure tensile results for welded samples, compared to those provided by Haynes, * = [79]

	UTS (MPa)	0.2% YS (MPa)	Elongation %
Haynes – Weld*	1,160	733	22.3
UW – Welded Samples	984 ± 8	634 ± 8	18.1 ± 0.6
Haynes – Welded Sample	934	680	10.4

As can be seen, the weld was of lower quality than the reported standard. Haynes was consulted on this point and a sample of the weld was sent back for them to test in their standard procedure. This result, also given in Table 7, agree with the tested results that the weld is of lower quality than reported by the Haynes 282 brochure [79]. However, Haynes said that while this was on the lower range of mechanical performance, the result was well within an acceptable range for the strength and ductility of their 282 weldments. With this assurance, work was conducted to analyze the performance of these welds in CO₂, with the caveat that no weld is perfect – especially with Ni-based alloys – and that the result will need to be analyzed relative to the unexposed performance.

5.3. Exposure Results

Once the weld was confirmed to be of sufficient quality, exposure to CO₂ was begun. Samples of 282 and its weld were exposed in one of two environments at 750°C for 1,000 hours continuously: CO₂ at 20MPa and Ar at 0.02MPa. Samples were then analyzed using mass change, RAMAN, and SEM analysis to understand the effects that the environment had on the material. Tensile samples were pulled in a tensile

test, and the fracture surfaces were subsequently analyzed with SEM to identify failure modes. The combination of this data provides a thorough understanding of the base material and the weld performance after exposure in the above environment.

5.3.1. Corrosion Analysis

5.3.1.1. Mass Change

Mass change (normalized by surface area) was measured for all samples and compared with previous work, revealing consistency with previous work within 10% in the same conditions and time for base material [17]. Similar to 740H, there was no apparent spallation for either base material or welded, so mass change will be used as representative of the amount of carbon and oxygen uptake. Base material gained $0.4864 \pm 0.0352 \text{ mg/cm}^2$ while welded samples gained $0.4158 \pm 0.0146 \text{ mg/cm}^2$. This would indicate that welded material performs slightly better from a corrosion standpoint than base material. It should be noted, however, that the fraction of base material to fusion zone present on each sample varied somewhat (and was not near 100%), so no quantitative analysis is possible from these numbers. In addition, the difference was relatively small, so it may simply be a function of inherent experimental error (location in the autoclave relative to the inlet of CO_2 , for instance) and not indicative of a change in corrosion performance. As a quality assurance check, mass change was measured for the neutral aging exposure and found to be negligible: $0.0352 \pm 0.0694 \text{ mg/cm}^2$ for base material and $0.0686 \pm 0.0051 \text{ mg/cm}^2$ for welded samples.

5.3.1.2. Surface Characterization

RAMAN spectroscopy was performed to characterize the oxide through acquiring bonding information. RAMAN was acquired using a 532nm laser and compared using the online database rruff.info (Cr_2O_3 is eskolaite). Figure 33 shows a comparison between 282 and the reference value for pure Cr_2O_3 , indicating that it is the dominant surface phase of oxide. Additionally, this analysis provided indications that there

is also some TiO_2 present in the oxide. This is expected, as it matches with previous work on the alloy after high temperature oxidation [17], [20].

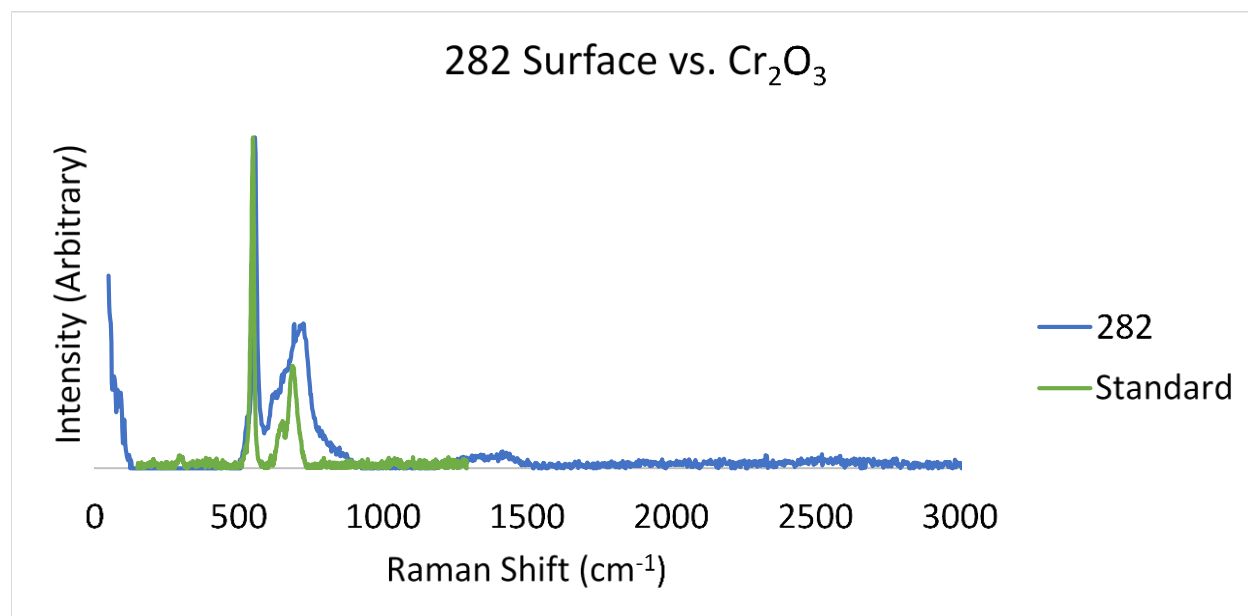


Figure 46 – Comparison of the surface of 750°C CO_2 exposed 282 to the reference for Cr_2O_3 (Eskolaite)

SEM was also performed on the surface of 282 and found a surface covered in Cr-rich oxide. In addition to this, raised topography was observed in isolated, contiguous lines, see Figure 47, which matched the expected appearance of grain boundaries. This indicates enhanced corrosion along grain boundaries occurred in 282. An EDS scan of the surface, shown in Figure 48, revealed that this enhanced corrosion corresponds to enrichments of Ti, while other potential oxidizing elements and oxygen remain constant. This indicates that Ti is oxidizing preferentially along grain boundaries, presumably because it is a trace alloying element (2.1 wt%) so it benefits from the easier diffusion pathway to the surface provided in these locations. This also suggests a possible explanation for increased mass gain in base material relative to welded samples: base material contains smaller grains and, correspondingly, a higher density of grain boundaries on the surface than the fusion zone. A higher density of grain boundaries would correspond to additional pathways for Ti diffusion, and subsequently additional oxidation and mass gain.

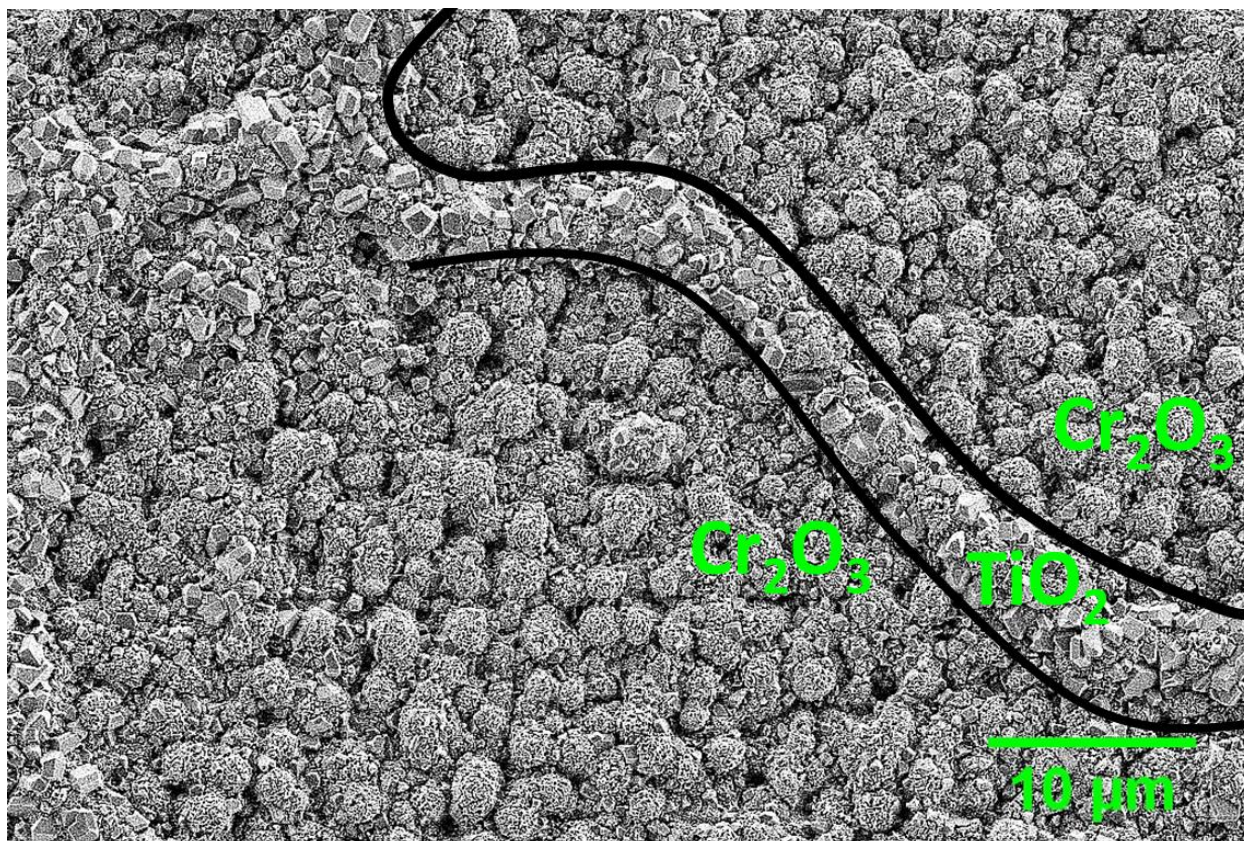


Figure 47 – Surface image of 282 showing typical Cr_2O_3 oxide in small grains, but with enhanced corrosion running along a grain boundary with larger oxide grains. This enhanced corrosion is thought to be due to additional Ti oxidation into TiO_2 .

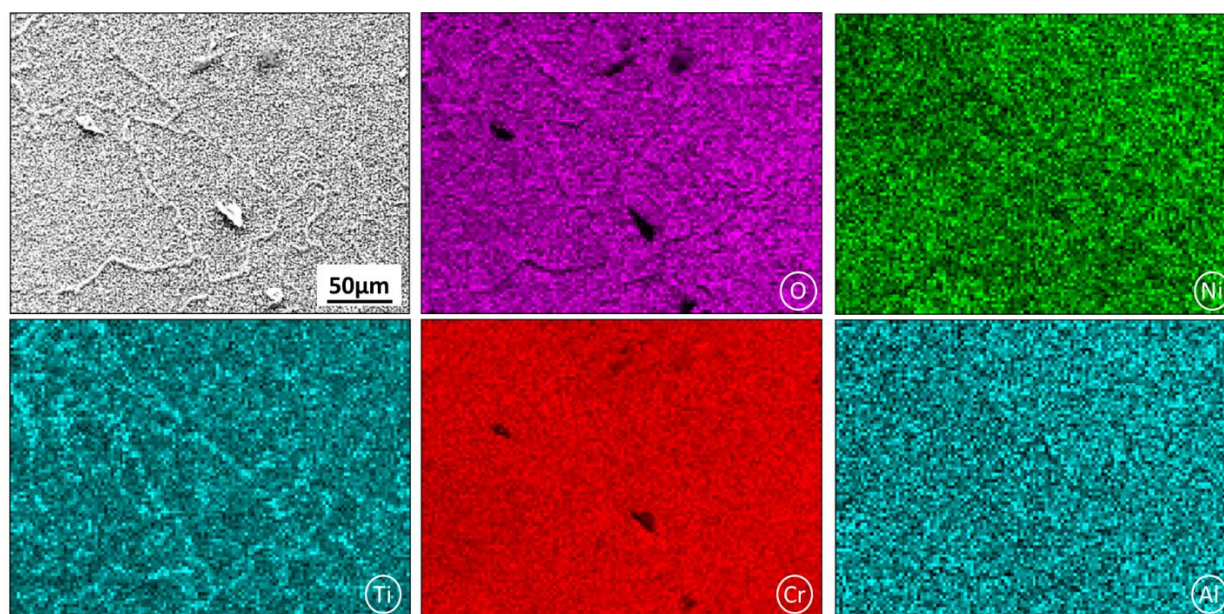


Figure 48 – EDS of the surface of 282 showing Ti-enrichment in strips which appear to be grain boundaries. No other primary elemental segregation is evident to explain this topography.

5.3.1.3. Cross-Section Analysis - Surface

Corrosion samples, described earlier in section 3.2, were formed into cross-sections and analyzed to observe the depth-dependent effects of corrosion as well as the bulk effects of heat treatment. As can be seen in Figure 49, cross-sectional analysis revealed very similar oxidation in both the fusion and base material regions. In both cases, a thin protective oxide covered the majority of the surface. Oxide thickness measurements, performed from three SEM images of each region taken from various locations, indicated an oxide of mean thickness $1.86 \pm 0.23\mu\text{m}$ for base material, and $1.40 \pm 0.04\mu\text{m}$ for the fusion zone. These values support the indication from mass change measurements that there is less oxidation in the fusion zone. Additionally, Figure 49 shows internal oxidation in both regions, and there is a corresponding increase in thickness, confirming the hypothesis from observations in the surface image in Figure 47 that oxidation of Ti along grain boundaries leads to increased oxide thickness. The internal oxidation was observed to extend up to $20\mu\text{m}$ from the oxide-metal interface.

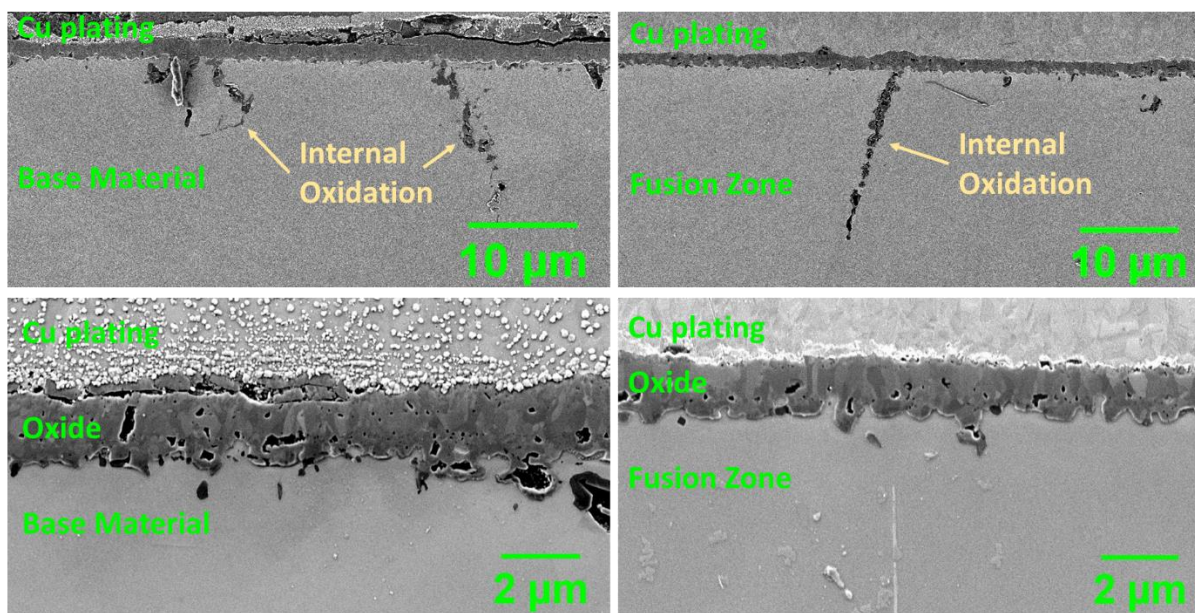


Figure 49 – Cross-sectional SEM of base material (left) and the fusion zone (right). Top images show internal oxidation which results in a thicker oxide. Bottom images show that oxide morphology of Cr-scale is very similar between fusion and base zones.

EDS analysis was performed and is shown in Figure 50 for the fusion zone. This shows a protective oxide of primarily Cr, with some evenly distributed Ti and a small amount of underlying Al. In addition, internal oxidation along a grain boundary is shown to incorporate all of these elements, but with a preference for Al and Ti. This oxide morphology confirms findings from previous studies [20], [22]. As this internal oxidation approached the surface, the Al-enrichment stopped, but the Ti-enrichment continued to the surface of the oxide. This confirms with elemental analysis the indications from both Figure 47 and Figure 49 that internal oxidation along grain boundaries led to additional surface oxidation of Ti into TiO_2 . In addition, there was an observed depletion in Ti, Al, and Cr below the oxide with a thickness of 1-4 μm , from which the elements diffused to form the oxide and have not been replaced from the bulk of the alloy. This depletion continued along internal oxidation, extending 1-2 μm around the oxides as they grew into the material. The morphology was similar in the base material region, so analysis was not deemed necessary to include here. It should be noted, however, that the internal oxidation sites are more common in base material, as speculated above.

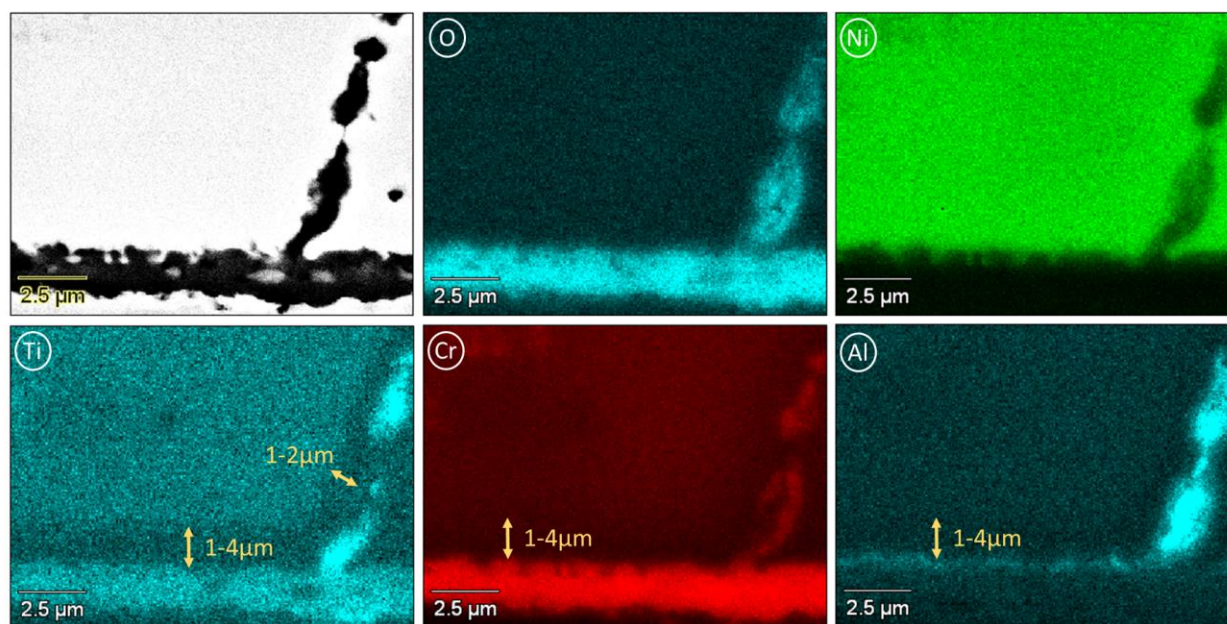


Figure 50 – 282 CO_2 exposed sample inside the fusion zone. Shows Cr, Ti and Al depletion zone underneath oxide, as well as internal oxidation via Al along grain boundary. Cr, Ti, and Al maps have the depletion zones marked.

Samples were also etched with HCl + 1% H_2O_2 for 10 seconds (by submersion) to reveal the presence of γ' precipitates. Images of both the base material and fusion zone in this etched condition are shown in Figure 51. These show a γ' -denuded region of 1-4 μm in thickness – corresponding to the Cr, Al, and Ti-depleted regions – directly beneath the oxide. Further imaging showed that this γ' -denuded region was also present surrounding internal oxide formation, shown to be present at depths of up to 20 μm , corresponding to the Al and Ti-depleted regions. Both of these phenomena were also observed in 740H after exposure to CO_2 at 750°C for 1,000 hours – as was detailed in section 4. Similarly, for 282 the lack of γ' in these regions can be attributed to one or a combination of the following: the depletion of Cr could have caused γ' to be unstable in the γ matrix; and/or the depletion of primary γ' -forming elements reduced the total amount of γ' which could form [20]. The determination for 282, regardless of base material or fusion zone, is that the formation of an oxide creates the conditions for a typically 1-4 μm thick γ' -denuded region after 1,000 hours of exposure to CO_2 at 750°C, 20MPa, with internal oxidation along grain boundaries extending this region to up to 20 μm from the oxide-metal interface.

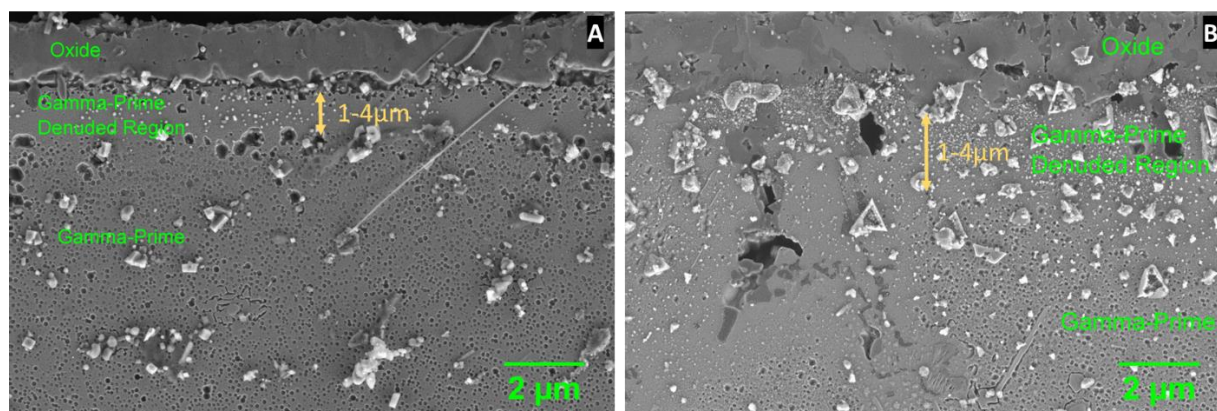


Figure 51 - 282 sample etched with HCl-1% H_2O_2 solution showing γ' density in the near-surface region for base material (left) and inside the fusion zone (B). γ' -denuded region is of similar thickness for both regions, and correspond to the depleted regions of Al, Ti, and Cr.

This surface analysis allows for a projection of the mechanical response of 282 due to corrosion from the s- CO_2 environment at 750°C, 20MPa for 1,000 hours. There is an oxide of negligible thickness for most applications (1-3 μm thick) which appears to grow primarily outward from the surface. The depletion of

Cr and γ' -forming elements creates a γ' -denuded region which leaves only the un-strengthened γ matrix in its place. However, this region is only present 1-4 μm below the majority of the oxide surface, and extending up to an observed maximum of 20 μm into the material from the metal-oxide interface. This should be of concern only if the 20 μm makes up a substantial portion of the test section, which in the case of this study it does not (attack of 20 μm represents <5% of the gauge cross-section). Therefore, the prediction from this analysis is that, similar to 740H, the mechanical response of 282 to exposure at 750°C, 20MPa for 1,000 hours will be dominated by effects from thermal aging.

5.3.2. Thermal Aging Analysis

5.3.2.1. Cross-Section Analysis - Bulk

Bulk analysis was performed to observe the effects of prolonged high-temperature aging of 282, and to see how it compares to 740H. As of this writing, no published study has thoroughly analyzed the development of γ' in 282. Similar to 740H, 282 is a precipitation-hardened alloy which has a standard heat treatment at 800°C in order to ensure proper strength from precipitation and growth of γ' , so it was anticipated that the γ' precipitates should coarsen during exposure at 750°C (in either CO₂ or Ar). If this occurs, it is expected to harden the base matrix similarly to that of 740H. In addition to γ' , the development of grain boundary carbides and possible grain growth were analyzed to provide insight to the mechanical development of both the base and fusion regions of 282.

Images of 282 – etched to show the γ' precipitates – are shown in Figure 52. While it is not possible to confirm a well-defined range on the scale of SEM analysis, γ' precipitates appear to have coarsened to the roughly 30-90nm that has been observed in 740H after this amount of aging [36], [37]. This indicates that the γ - γ' matrix was likely hardened from the aging process. Additionally, intermittent carbides were visible along grain boundaries in the base material. These carbides corresponded to a PFC of roughly 100nm, while there was no PFZ observed in the sections without carbides. EDS analysis, see Figure 53,

shows that these sections of grain boundaries which don't have Cr-rich $M_{23}C_6$ carbides are enriched in Ti and Mo, possibly creating MC-type carbides. Whatever the form of the Ti and Mo enrichments, they are not creating a corresponding PFZ.

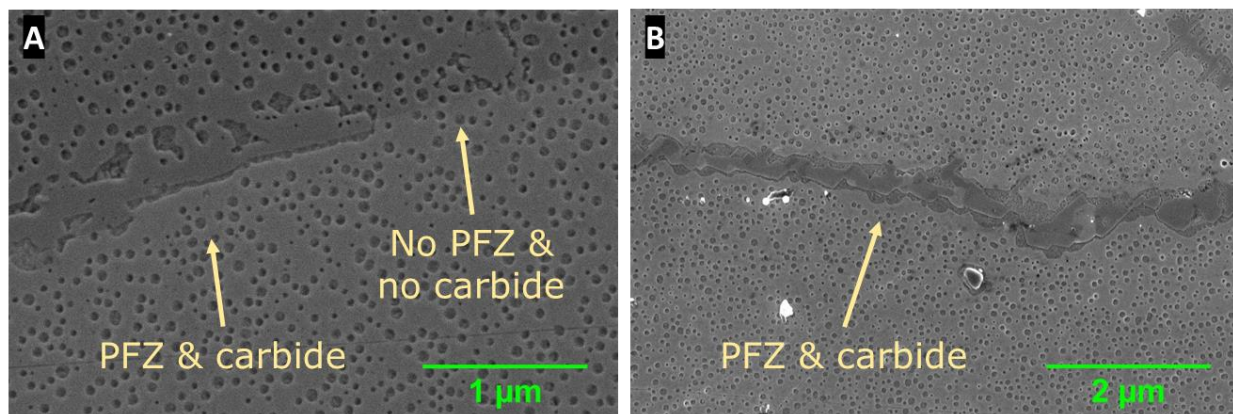


Figure 52 – Images of 282 in the bulk of base material (A) and in the fusion zone (B), etched to reveal the γ' precipitates. Grain boundary carbides appear to cause a PFZ of roughly 100nm thickness. These grain boundary carbides are consistently present in the fusion zone, but only intermittent in base material.

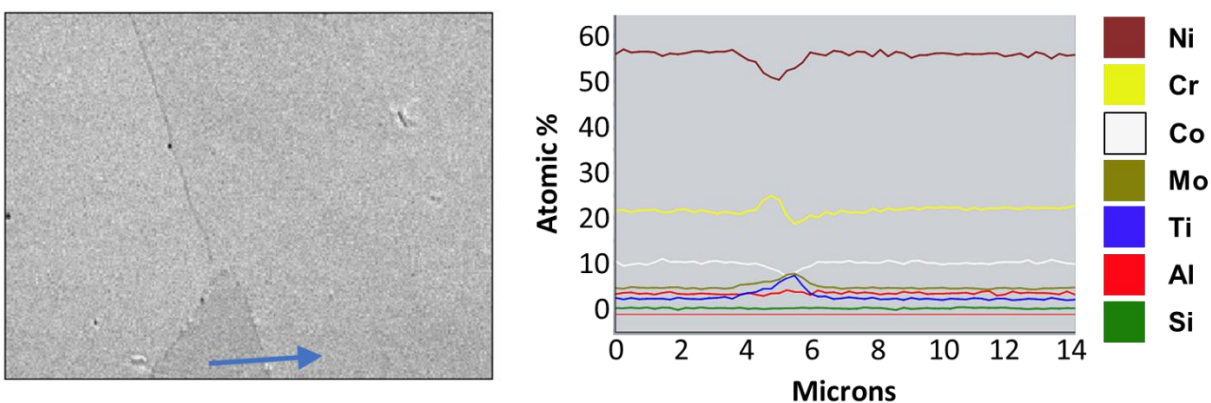


Figure 53 – EDS line scan over section a section of grain boundary in base material which has inconsistent Cr-enrichment, with Ti and Mo enrichment in its place.

In the fusion zone, however, carbides were observed to be present along all grain boundaries. Similar to base material, there was a PFZ surrounding the carbides, resulting in a continual PFZ along all grain boundaries inside the fusion zone. This PFZ, not observed in the bulk of 740H after exposure, easily projects toward a negative mechanical response of 282. The presence of a PFZ along grain boundaries sticks a soft, weak γ matrix between the hard grain boundary carbides and the hardened γ' -infused γ

matrix. This weak layer is a common failure point during creep and fatigue testing, and it projects to weaken the overall material.

In addition, the micro-segregation in the fusion zone mentioned above in section 2.3.1 remained after exposure. As can be seen in Figure 54, Mo and Ti enrichment – likely as MC-type carbides – are observed in rows with roughly 10 μ m spacing between them. There was no other micro-segregation detectable with EDS – unlike 740H, Cr and Co did not migrate into or out of dendrites. Also, while there was no Cr-depletion zone observed with EDS (see Figure 54 line scan), the anticipated Cr-depletion is only 100nm in size (corresponding to the observed PFZ) and therefore is too small to be observed in SEM EDS.

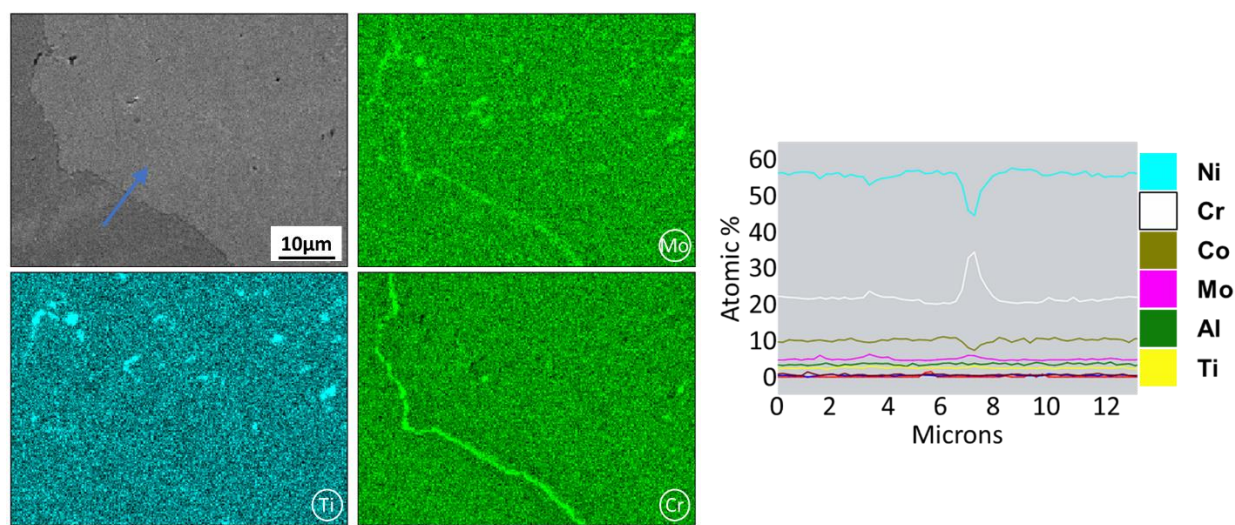


Figure 54 – EDS of 282 fusion zone, showing Cr and Mo-enrichment along grain boundaries as well as Mo and Ti-enrichment in interdendritic carbides. No preferential segregation of other elements observed. Line scan across a grain boundary shows Cr and Mo enrichment.

5.3.2.2. Grain Size

Grain growth was analyzed using EBSD in order to understand the impact that grain growth may have on mechanical performance. As covered above, internal oxidation occurred along grain boundaries, meaning that grain growth may mitigate this growth somewhat by reducing the number of grain boundaries that are available. Base material was utilized for the analysis of grain evolution during exposure, and images are shown in Figure 55. As-received 282, which was annealed and then given a one-step aging at

800°C/4h/FC, resulted in an average grain size of $57.1 \pm 34.0\mu\text{m}$. This value was very comparable with the values of samples which were exposed to CO₂ at 750°C ($70.9 \pm 46.1\mu\text{m}$) and aged at 750°C ($54.0 \pm 31.1\mu\text{m}$). Therefore, no grain growth was observed after either exposure at 750°C, so grain size did not play a role in affecting the mechanical response of 282 to either the CO₂ environment or thermal aging.

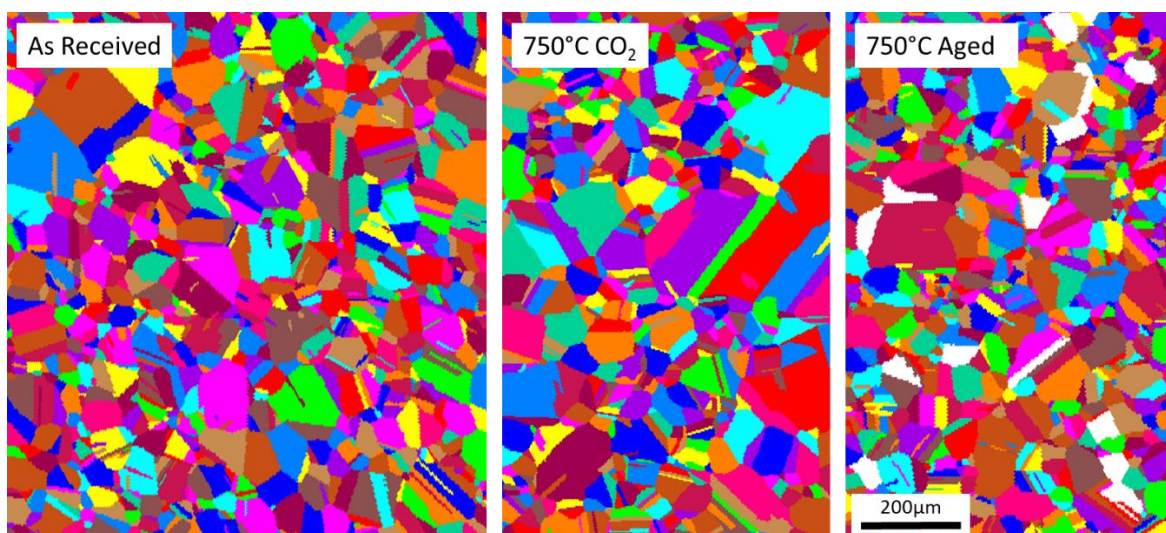


Figure 55 – EBSD for 282 in three conditions: as-received, 750°C CO₂-exposed, and 750°C aged. No grain growth after exposure was observed.

5.3.3. Mechanical Analysis

5.3.3.1. Tensile Results

Tensile results before and after exposure are given in Table 8. In contrast to 740H, exposure of 282 had a neutral or negative impact on strength, with a much greater effect on elongation. The exposures at 750°C, one in CO₂ and one in Ar, resulted in similar effects for both base material and welded samples. Base material exhibited a 2% increase in UTS, a similarly moderate increase in YS (5% for CO₂, 1% for aged), while suffering a significant loss of elongation relative to unexposed. Welded samples exhibited a small increase in YS (9% for CO₂, 7% for aged), but this was offset by a drastic decrease in elongation to result in a loss of UTS from both exposures (6% for CO₂, 4% for aged). All welded samples failed near the fusion and base interface (there is no clearly defined HAZ for 282).

Table 8 – Tensile testing results for 282 (base material and welded)

	UTS (MPa)	YS (MPa)	Elongation (%)	Failure Location
Base Unexposed (UW)	1,119 ± 2	734 ± 1	43.2 ± 0.3	N/A
Base 750C CO ₂	1,139 ± 2	769 ± 1	20.8 ± 0.7	N/A
Base 750C Aging	1,138 ± 5	743 ± 2	19.6 ± 0.9	N/A
Welded Unexposed	984 ± 7	634 ± 8	18.1 ± 0.6	Fusion/Base Interface
Welded 750C CO ₂	925 ± 2	692 ± 5	7.5 ± 0.3	Fusion/Base Interface
Welded 750C Aging	949 ± 23	677 ± 5	8.9 ± 1.2	Fusion/Base Interface

There were small differences between samples which were exposed to CO₂ or neutrally aged. The main observed difference is that the YS for CO₂-exposed samples was shown to be slightly higher than for aged samples in both base and welded samples. While there was no significant carburization for this alloy, this could be a result of either of the following possibilities: small sample sizes, or a slight hardening effect from internal oxidation. Whatever the reason for these small differences, the trends for exposed versus unexposed are consistent with both conditions. Alloy 282 was thermally aged at temperature, and this increased the YS and severely decreased ductility. All samples experienced a 50-60% decrease in elongation, and this in turn resulted in a reduced UTS. This increased macro hardness and decreased ductility can be observed in the divergence of both exposures from that of unexposed in the stress-strain curves shown in Figure 56. The magnified decrease in ductility after exposure compared to that of 740H is likely a result of the PFZs present in both regions of 282 (which were absent from 740H).

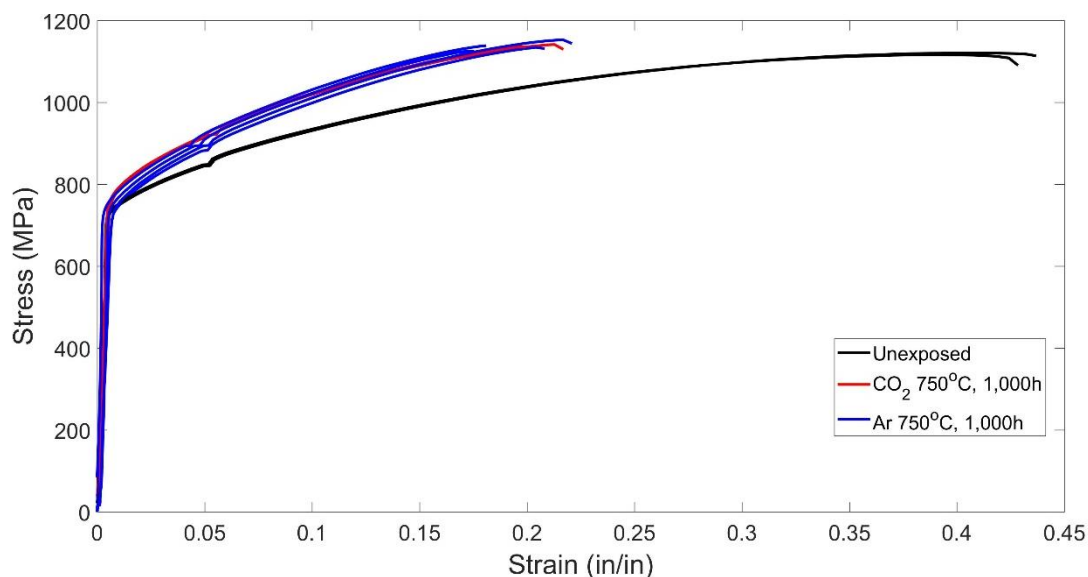


Figure 56 – Stress-strain curves for 282 base material before and after exposure at 750°C.

5.3.3.2. Microhardness Results

Microhardness was taken inside base material and the fusion zone before and after exposure to CO₂. As the grain size was roughly 50-70μm, a typical indentation (diameter ~10μm) provides values representative of the granular matrix, not overall material hardness. In addition, the 10μm indentation is of the same order as the dendritic arm spacing in the fusion zone (seen above in Figure 54), allowing all indentations to be representative of the combination of the regular matrix and the interdendritic regions rich in Ti and Mo carbides. In the base material, unexposed hardness was measured at $411 \pm 4\text{HV}$, while CO₂ exposure resulted in $399 \pm 5\text{HV}$ and thermal aging resulted in $408 \pm 5\text{HV}$. In the fusion zone, unexposed hardness was found to be $379 \pm 3\text{HV}$, and exposures resulted in values of $393 \pm 5\text{HV}$ (CO₂) and $406 \pm 3\text{HV}$ (aging). This indicates that for both exposures the expected hardness increase from γ' coarsening (observed in SEM images above - Figure 51 and Figure 52) and increased YS was not reflected on the micro-scale. For base material, there was effectively no hardening, and the fusion zone hardened only slightly – achieving equal hardness to that of base material.

The effectively equal hardness of the base and fusion regions indicates that there likely were not the precipitate-poor regions in the 282 fusion zone that there were in 740H. The 282 fusion zone actually exhibited higher hardness than did 740H, but shows reduced mechanical properties relative to 740H after exposure. The likely culprit for this decrease is the PFZ that covers all grain boundaries in 282, but is non-existent in 740H after exposure.

5.3.3.3. Fracture Surface Analysis

Fracture mechanisms were analyzed using SEM imaging of the post-tensile test fracture surfaces [77], [78]. Figure 42 A and B show the fracture surfaces of 282 base material which was pulled in the unexposed condition. This shows a fracture surface which was comprised entirely of intergranular fracture, as was expected from the formation of brittle carbides during initial heat treatment. On the faces of the grains, MVC with micron-scaled dimples was observed, indicating a moderately ductile mode of intergranular fracture. Conversely, Figure 42 C and D show the fracture surface of 282 base material that was exposed to CO₂ at 750°C, 20MPa for 1,000 hours. This fracture was observed to be very similar on the macro level, comprised of intergranular fracture, but a closer look revealed the grain surfaces to be a mixture of MVC with micron-scale dimples (similar to unexposed) and sub-micron-scale cleavage. This dual-phase fracture matches the intermittent grain boundary carbides (and subsequent PFZ) observed in Figure 52 A. Cleavage indicates a more brittle form of fracture, and its presence was representative of the embrittlement observed in the lowered elongation during tensile testing. The fracture surface of samples which were thermally aged matched that of CO₂-exposed, so images are not shown here.

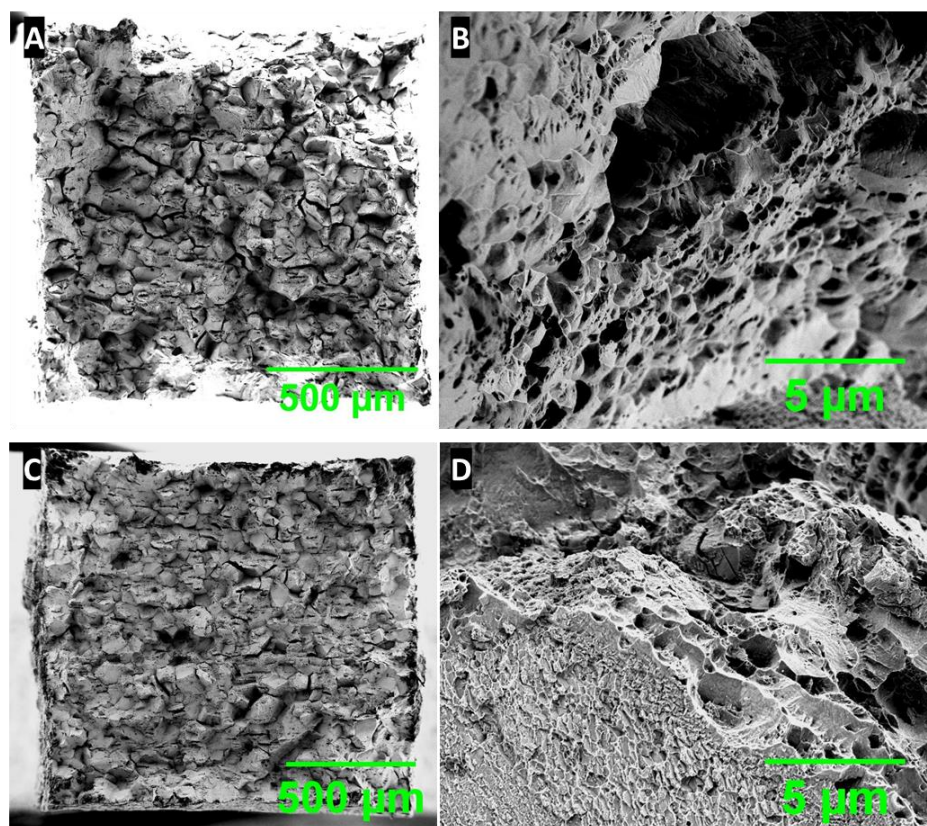


Figure 57 – SEM images of fracture surface of 282 base material tested in the unexposed condition (A,B) and after exposure to CO₂ at 750°C, 20MPa for 1,000 hours (C,D). Clearly defined grains indicate intergranular failure.

The fracture surface of welded samples, which failed near the base-fusion interface, as noted above in section 5.3.3.1, exhibited a similar shift towards brittle fracture modes. Figure 44 A and B shows the fracture surface of an unexposed welded sample. This fracture was characterized by intergranular fracture – similar to that of base material – but the grain surfaces were covered with sub-micron-scale cleavage. This indicates a more brittle fracture than observed in base material, even after exposure, and this was reflected in the tensile results. Figure 44 C and D show that exposure at 750°C, 20MPa for 1,000 hours has embrittled the fusion-base interface still further. Figure 44 D shows more brittle cleavage, but this time with enlarged facets which correspond to an increasingly embrittled fracture mode. This consistent fracture mode – as opposed to that of exposed base material – is likely due to the coarsening of continual grain boundary carbides in the fusion zone and their corresponding PFZs.

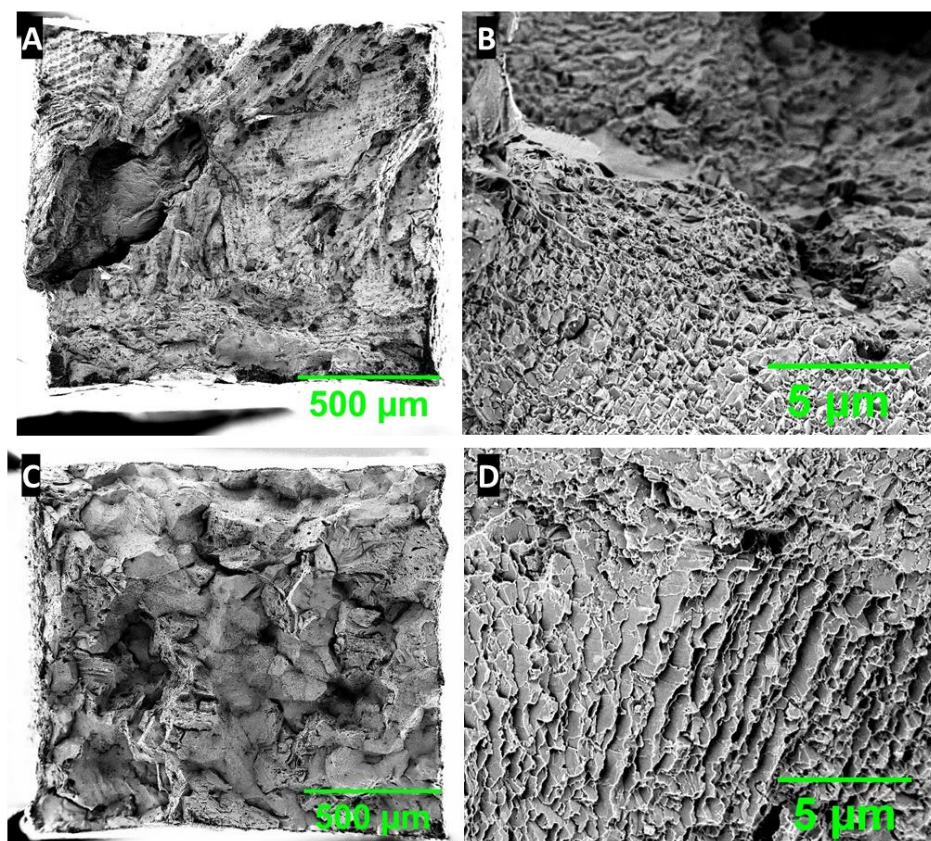


Figure 58 – SEM images of fracture surface of 282 welded samples, pulled in the unexposed (A,B) or the CO₂-exposed condition (C,D). Characterized by intergranular fracture with varying degrees of brittle cleavage.

5.4. 282 Performance Summary

Exposure to CO₂ at 750°C, 20MPa for 1,000 hours resulted in very little corrosion for both welded and base 282. The majority of the surface of both regions was covered with a 1-3μm Cr and Ti-rich, protective oxide with an underlying, intermittent layer of Al-oxide. Below this, a corresponding depletion of the oxide-forming elements created a region without the strengthening γ' precipitates, but this region was largely limited to a depth of 1-4μm. Internal oxidation was observed along grain boundaries in both regions, with the PFZs continuing into the material to surround these oxides. The deepest observed oxidation was roughly 20μm in both base and fusion zones, indicating the maximum depth of corrosion effects for the 282 alloy in these conditions. While the yield strength was observed to be slightly higher

in CO₂-exposed rather than in aged samples, it is not clear if there was a definitive mechanism for this, and it may be explained by the utilization of small sample sizes in this work.

In a similar fashion to the other Ni-based precipitation-hardened alloy in this study, 740H, the majority of the mechanical response to exposure for 282 was due to thermal aging. Aging allowed γ' precipitates to coarsen throughout the matrix, achieving a range of sizes that is comparable to that which was found for equally aged 740H (and reported in other studies as well [36], [37]). However, the hardness of the matrix was not observed to increase to the same degree that was observed in 740H.

Another important factor of thermal aging was analyzed: the coarsening of grain boundary carbides. These carbides, intermittent in base material and continuous in fused material, were found to create sufficient depletions of Cr surrounding them that it destabilized γ' in the area, causing PFZs on the order of 100nm in thickness. These PFZs, containing only the soft γ matrix, are weak points during tensile testing, as well as being likely crack initiation sites during creep or fatigue. They were likely the cause of the lower hardness and YS, relative to unexposed, than was observed in 740H. They were definitely a leading cause of embrittlement, as the prevalence of the PFZs was seen to correlate to an embrittled fracture mode. Brittle cleavage was observed in both welded and base exposed samples, where it was not seen in samples without the PFZs (unexposed base material, and all 740H samples).

282 welded mechanical properties, while within the reported specifications of the manufacturer, were initially lower than reported values. This indicates that a more thorough study of welding procedures and expected strength should be applied to the use of 282 welds in pressure vessels. However, once the quality of the welds was understood, both base and welded 282 performed well in CO₂ in terms of corrosion. Internal oxidation was seen, but no corrosion phenomena was observed below roughly 20 μ m from the oxide-metal interface. Of larger concern was the performance of 282 during aging, as it has been shown to produce a PFZ in both base material and the fusion zone which projects as problematic for long-

term use as part of a pressure vessel. As was true for 740H, the study of 282 for use at high temperatures is dominated by the effects of thermal aging, and the corrosion analysis of the alloy should only be meaningful in these environments if the pipe wall thickness approaches the scale of the corrosion-affected region.

6. 316 Austenitic Stainless Steel:

316 is a stainless steel widely used in industry. As such, it is a prime example of how a 16-18%Cr austenitic stainless steel will perform in the CO₂ environment. A primary concern for this alloy is the formation of Cr-rich carbides along grain boundaries. These carbides are known to cause both sensitization – the removal of Cr from the matrix surrounding grain boundaries, thereby reducing the local corrosion resistance – and grain boundary embrittlement. As covered in section 2.2.2, this concern is such that the carbon content of the alloy is highly controlled, leading to the creation of several types of 316 in order to balance the limiting of carbon with desirable mechanical properties. Of interest here is the interaction of 316 with the CO₂ environment and the mechanical effect of different amounts of carburization. As such, two types of 316 were utilized in this work, and they were chosen for their specific carbon contents: 316L (maximum of 0.03wt% C) and 316H (0.04-0.10wt% C). The actual chemical compositions are given in Table 19, and the 316L used here had 0.019wt% C while the 316H had 0.0523wt% C.

Both allowable stress at temperature, covered in section 2.3.2, and previous corrosion studies of 316 and similar alloys, covered in section 2.1.3.2, indicated that 316 application in CO₂ environments was limited to a temperature of roughly 550°C. Therefore, the primary analysis temperature chosen for these materials was 550°C. Two 1,000 hour exposures were performed at this temperature, with one in CO₂ at 20MPa, and the other in UHP Ar at 0.02MPa. Additionally, the alloys were aged in UHP Ar for 1,000 hours at 750°C, 0.02MPa. The two 550°C exposures were designed to isolate the effect of the CO₂ fluid on each variant of 316, while the 750°C aging was purposed to find the mechanical effect of creating carbides with as much alloying carbon as possible. All exposures were performed straight through, with the only thermal cycling due to experimental failures.

6.1. Sample Procurement

Samples were purchased from standard vendors. 316L was purchased in 1/8" sheet and then either milled to 1/16" thickness from which to cut base material samples, or directly welded. 316H, being more difficult to find, was acquired in 1/2" bar. EDM was then used to directly cut base material samples, as well as to produce 1/8" plates for welding. After the welding of the 1/8" thick plates, both 316H and 316L samples were milled to 1/16" to remove surface effects and then sent off-site for EDM to cut out tensile samples and corrosion coupons. All welding procedures are given in Table 20. The number of samples tested for each material in each condition are given in Table 9.

Table 9 – Total number of 316 tensile samples tested at each analysis condition

Type of Sample	Unexposed	550°C CO ₂	550°C Ar	750°C Ar
316L Base	2	5	2	2
316L Weld	4	3	3	2
316H Base	2	2	3	2
316H Weld	2	2	3	2

6.2. Corrosion Results

6.2.1. Mass Change

Mass change for each alloy was measured for the CO₂ exposure as well as for each aging exposure (for quality assurance), and is shown in Figure 59. Interestingly, after 550°C CO₂ exposure there was higher mass change in base material samples than in welded ones. While this was only statistically significant in the case of 316L, 316H base material tensile samples consistently exhibited a higher mass gain than those of 316H welded samples. There was an outlier from using the 316H base material corrosion samples, which were square as opposed to ellipsoidal (like the rest of the corrosion samples in this experiment), and comprised roughly twice the surface area (~500mm² vs. 250mm²). If this is ignored (to correct for different geometries), then 316L and 316H performed equally well, and each weld out-performed the base alloy. This is especially interesting in the case of 316H, as sensitization during the welding process

has been shown to decrease its corrosion performance near grain boundaries, as discussed in section 2.3.2.

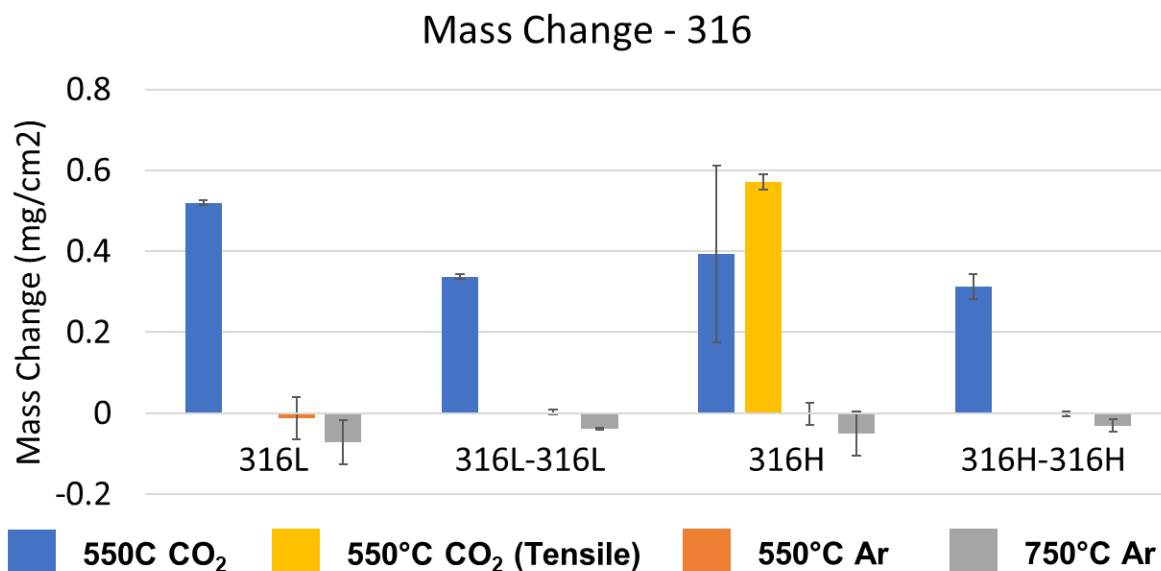


Figure 59 – Mass change for 316L and 316H exposures. 550°C CO₂ tensile sample mass change data provided separately for 316H because corrosion samples had unique geometry and performed much different than all other samples exposed to CO₂ at 550°C, 20MPa for 1,000 hours.

6.2.2. Surface Characterization

The surface of both 316 variants was dominated by a Cr-rich oxide. This oxide was very thin – on the order of 100s of nanometers – and protective. There were also occasional nodules of dual-phase Fe-based oxide, which likely formed in locations where Fe-oxidation dominated initially and Cr was not given time to form the protective layer. These two distinct oxide growths are observed from the surface EDS scan shown in Figure 60. Cr was not present in the magnetite layer which was found on the surface of the Fe-oxide nodules. In addition, as can be seen by the point scans of Figure 60, the Cr-rich oxide layer was less than 1µm thick and the EDS scan incorporated a significant amount of the underlying alloy in its measurement (which it did not for the thicker Fe-oxide). This is because the interaction volume with EDS is much larger and deeper than what the few hundred nanometer-thick oxide could support, so the underlying alloy made up the bulk of the received information.

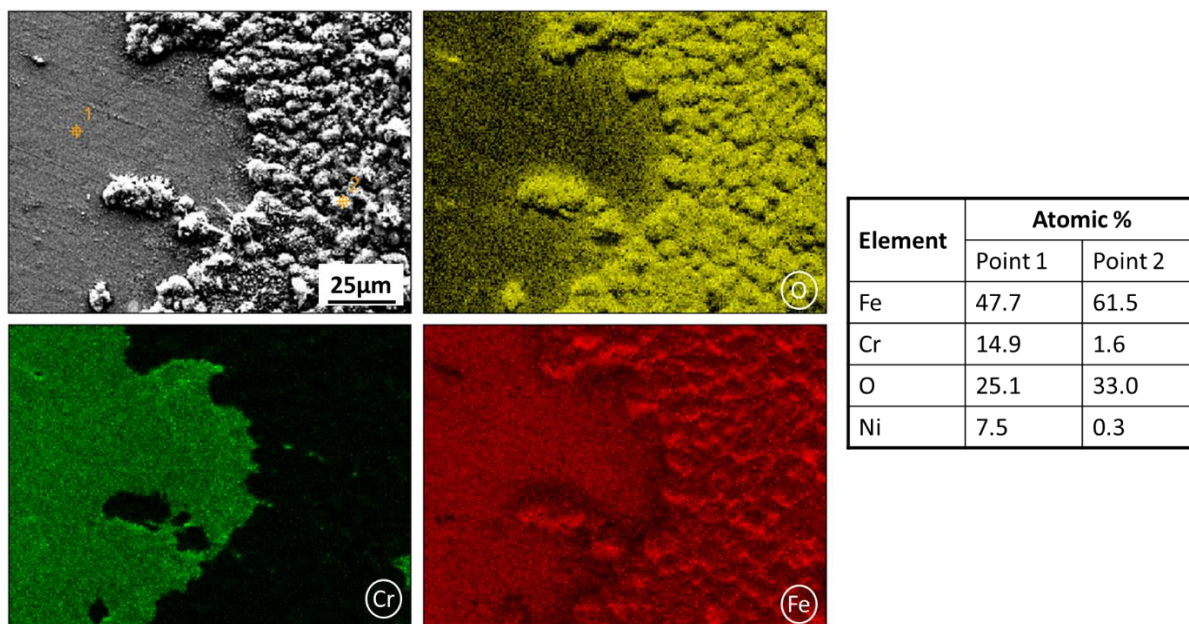


Figure 60 – Surface EDS of 316L exposed at 550°C, 20MPa for 1,000 hours. Image includes two point scan locations, whose primary measured constituent values are given to the right.

6.2.3. Cross-Section Analysis - Surface

The corrosion which occurred for 316 in CO₂ at 550°C after 1,000 hours was, as has been shown in section 6.2.2 and previous work, very minor. The oxide and near-surface region can be seen in Figure 61 for both base and fusion regions. The majority of both regions was indeed covered by a thin Cr-scale (<1µm, as observed in both Figure 61 A and B), and occasional nodules of Fe-rich oxide (Figure 61 A) have been observed to be up to 5µm thick. This represented a very small amount of total oxidation. Based on the theory that carbon is liberated through the oxidation process in the CO₂ environment (from section 2.1.2), it can be projected that very little carbon was deposited. Therefore, similar to the analysis of 740H and 282 at 750°C discussed earlier, the major effect on mechanical properties for 316 (either L or H) at this temperature will be thermal aging.

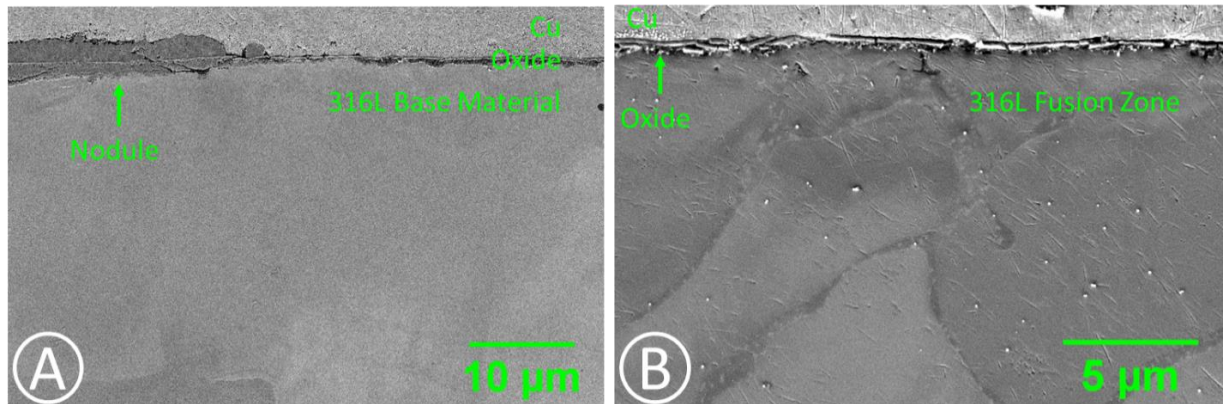


Figure 61 – XS image of 316L base and fusion material after exposure to CO₂ at 550°C, 20MPa for 1,000h. Base material shows a thick nodule, while the majority of the surface (both base and fusion zones) resembles that shown in the fusion image.

6.3. Thermal Aging Analysis

6.3.1. Grain Size

One cause of altered mechanical properties could be the coarsening of grains. Grains tend to grow when the material is aged at high temperature. In order to assess if coarsening has occurred in 316, EBSD images of 316L base material – shown in Figure 62 – were taken in three different conditions: as-received; exposure in CO₂ at 550°C, 20MPa for 1,000 hours; and aging in Ar at 750°C, 0.02MPa for 1,000 hours. Similar to previous work [47], results for base material showed very little, if any, grain growth, with the following measured grain sizes: $17.8 \pm 7.5\mu\text{m}$ for unexposed; $20.9 \pm 9.2\mu\text{m}$ for 550°C CO₂ exposure; and $21.7 \pm 9.7\mu\text{m}$ for 750°C aging. Exposure at 750°C – which is well over the plausible application temperature for 316 in CO₂ – would be expected to magnify and accelerate any grain growth that would occur at 550°C. However, since no grain growth occurred, it can be assumed that grain growth will not be a problem for 316 at 550°C, and will definitely not be a factor in the results presented in this work.

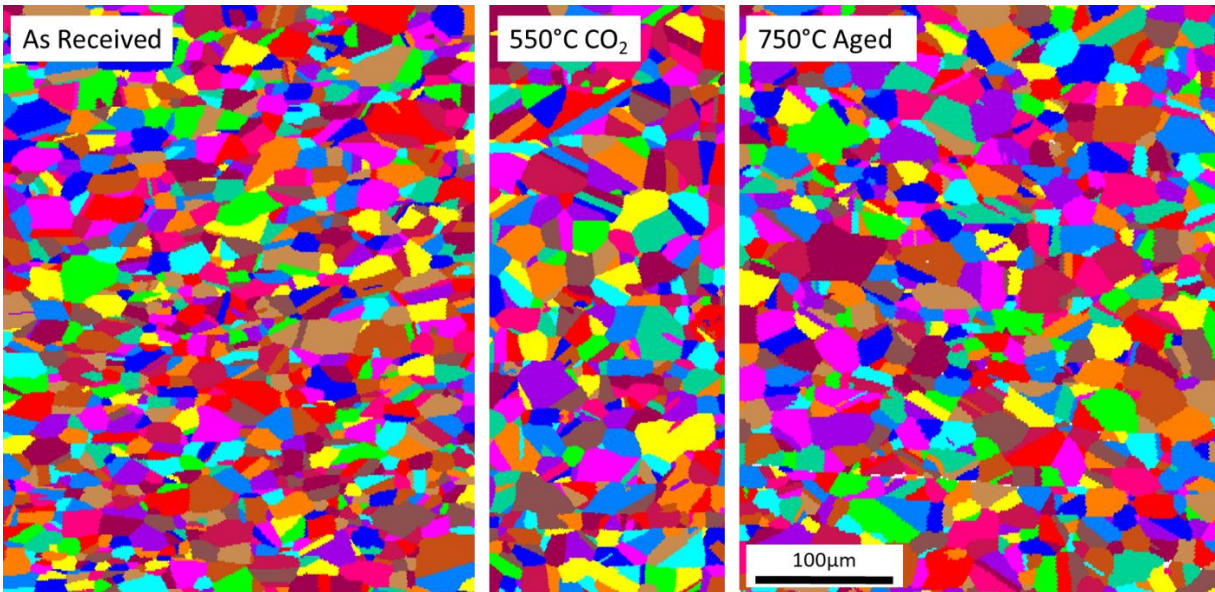


Figure 62 – EBSD images for 316L in the unexposed, 550°C CO₂-exposed, and 750°C aged conditions. Results indicate there was no difference in grain size, but possibly a shift in grain geometry.

6.3.2. Microstructural Alignment and Precipitation

It is important to note that grains were originally equiaxed and randomly distributed, with no noticeable alignment. After spending 1,000 hours at either 550°C or 750°C, some alignment was seen. It can be observed in both exposures that grains began to congregate along lines which were all somewhat parallel to each other (they appear horizontal in Figure 62). It is possible that this was due to grain movement to align along lamellar inclusions left over from rolling the steel and creating the original plate from which samples were manufactured [66]. An example of these inclusions is observed in the bulk of 316L in Figure 63. Whatever the original cause, the result does not appear to indicate grain coarsening to a measurable level and it is not believed that it will get more exaggerated with time (both temperatures resulted in a similar partitioning).

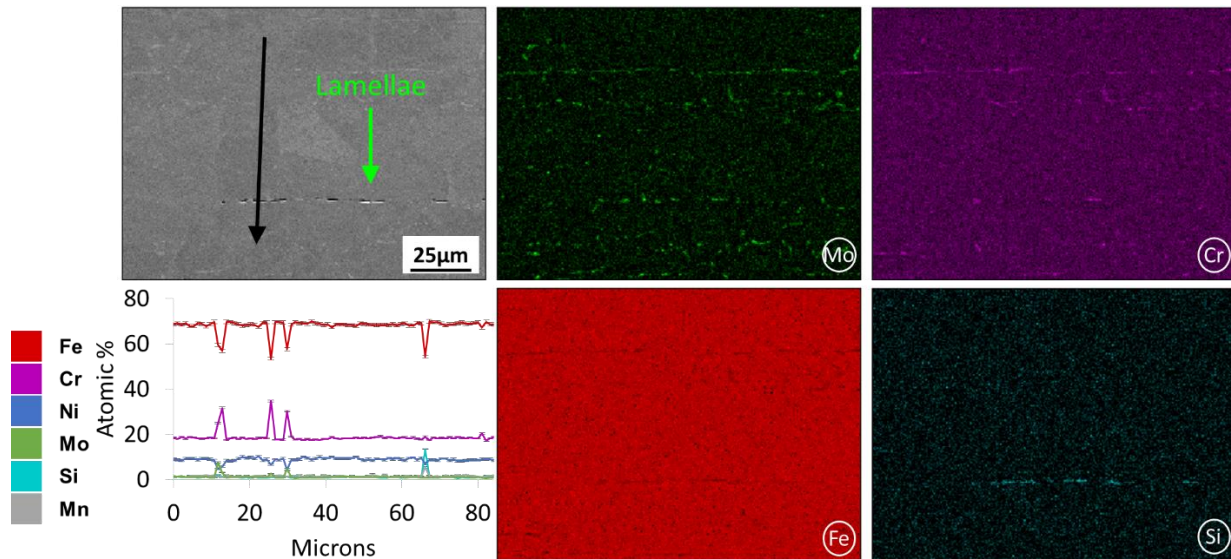


Figure 63 – EDS mapping and line scan of base 316L after aging at 750°C, 0.02MPa for 1,000 hours. Shows Cr and Mo-enrichments along horizontal planes, and Si lamellar inclusions.

However, 316H base material showed a somewhat different microstructure after aging. Figure 64 shows Si and Mo inclusions in the form of spherical precipitates which do not appear to congregate in lamellae. It should be noted that the 316H acquired for this work was in ½" bar, while the 316L was 1/8" plate, so the same Si lamellae may not be expected due to differences in manufacturing. Of more interest is the Cr-enrichment observed along grain boundaries, which was not observed in 316L, and is due to the added C content of 316H, drawing Cr into forming carbides. This has likely led to embrittlement along grain boundaries, which would be exhibited by intergranular failure and lower fracture strain in tensile samples.

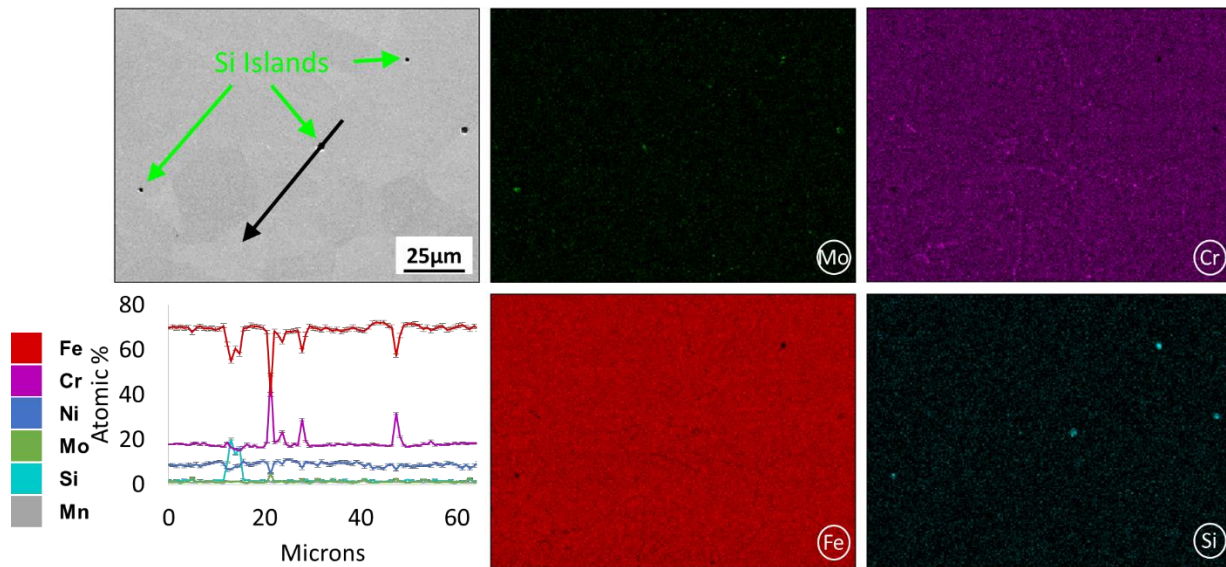


Figure 64 – EDS mapping and line scan of base 316H after aging at 750°C, 0.02MPa for 1,000 hours. Shows Cr-enrichments along grain boundaries, and Si and Mo spherical inclusions.

Conversely, the fusion zone of both variants of 316 aged similarly, regardless of C content. As can be seen from Figure 65 and Figure 66, there were Cr and Mo-enrichments along with Ni-depletions (not shown) in interdendritic regions. As discussed in section 2.3.2, this was a result of micro-segregation during the welding process and corresponded to δ -ferrite formed along the dendritic axes. These enrichments of Cr and Mo are likely to have formed carbides during the prolonged aging at either temperature, but especially at 750°C. It is anticipated that 316H has experienced additional embrittlement from this process relative to unexposed due to the formation of additional carbides. As EDS cannot measure carbon accurately, this hypothesis will be checked through tensile testing.

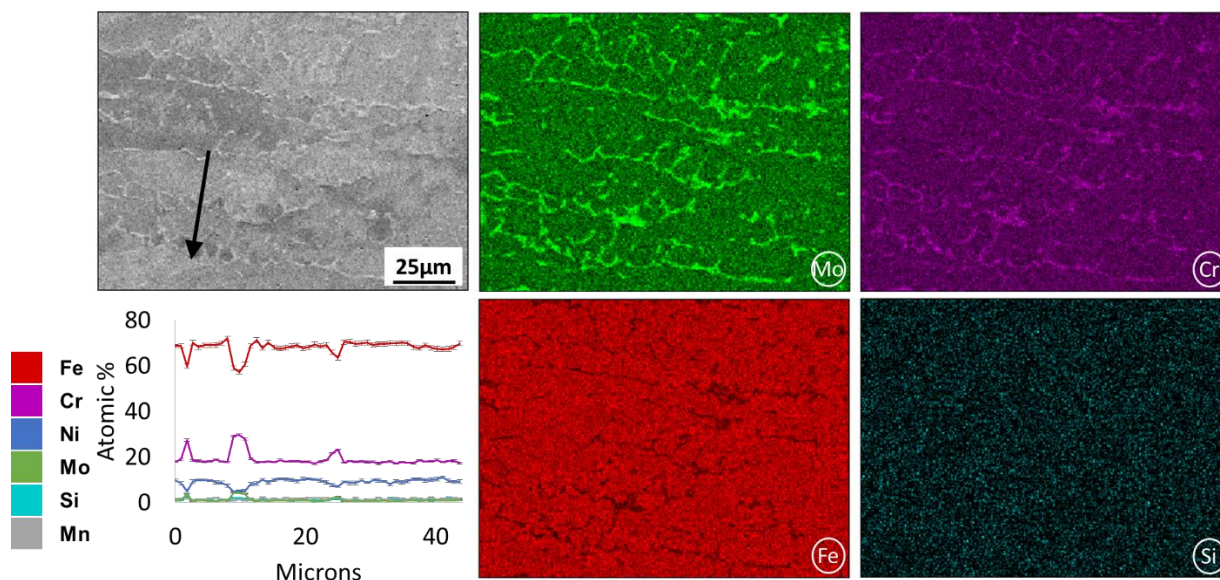


Figure 65 –EDS mapping and line scan of the 316L fusion zone after aging at 750°C, 0.02MPa for 1,000 hours. Shows Cr and Mo-enrichments in interdendritic regions, likely in the form of $M_{23}C_6$.

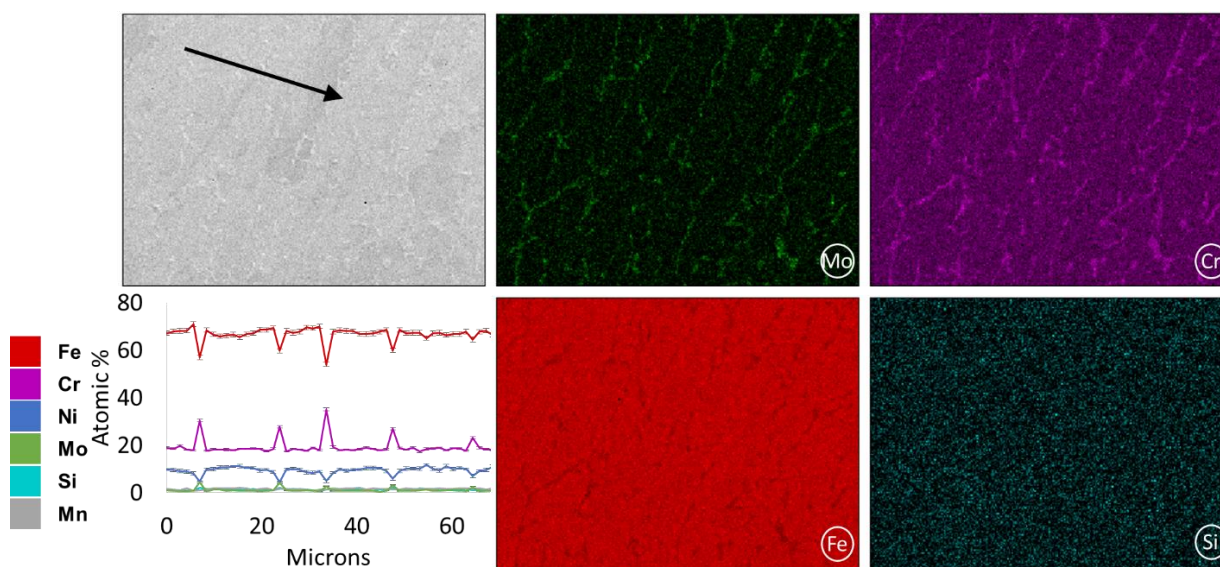


Figure 66 – EDS mapping and line scan of the 316H fusion zone after aging at 750°C, 0.02MPa for 1,000 hours. Shows Cr and Mo-enrichments in interdendritic regions, likely in the form of $M_{23}C_6$.

While 550°C exposures are not imaged here, it is expected that a similar carbide formation process may have occurred in both base and fusion zones as observed here for 750°C. The carbide formation process was likely less developed, however, so there is expected to be less of an effect after exposure at 550°C. As shown in section 6.2.3, the impact of the CO₂ environment was very minimal, so the overall effect of the 550°C environment is projected to be equivalent in both Ar and CO₂. One thing to note, however, is

that the solubility of C in 316 is much lower than the alloying C of the alloy [80]. This means that the long-term aging of either 316L or 316H will result in precipitation of carbides with the majority of alloying carbon. Therefore, the higher temperature aging should provide insight into the precipitation and coarsening which would be observed at lower temperature after a much longer period of time.

6.3.3. Microhardness Testing

In order to better understand the effects of the microstructural changes in 316 during aging, microhardness measurements were performed on 316L before and after aging. Prior to exposure, the 316L used in this experiment was measured and found to be 188 ± 2 HV, well within the typical hardness for this material [81], [82]. As the majority of the mechanical effects on 316 in CO₂ at 550°C are likely attributable to thermal aging, 316L was measured after 1,000 hours of aging at both 550°C and 750°C. Exposure at 550°C resulted in a very slight increase to 197 ± 2 HV. 750°C exposure, meanwhile, resulted in a more significant increase in hardness: up to 212 ± 3 HV. Both increases are indicative of an effect of thermal aging, likely due to the precipitation of M₂₃C₆ carbides and other intermetallic phases [18]. The larger increase after aging at a higher temperature is likely due to additional coarsening of carbides, as well as the precipitation of intermetallic phases, relative to that of lower temperature. The effect of this on tensile properties is expected to be mild, though a slight increase in yield strength would fit this effect.

6.4. Mechanical Analysis

6.4.1. Tensile Results

Tensile results for base material are given in Table 10. Of note here is that, as expected from the analysis above and literature review from section 2, there was very little effect of either CO₂ exposure or aging at 550°C for 1,000 hours. Results for 316L and 316H, while differing slightly from each other in strength and ductility, were not individually affected from these exposures – the small differences in values can likely

be attributed to small sample sizes. However, both 316L and 316H were mechanically altered after aging at 750°C for 1,000 hours. In both alloys, this lowered yield strength and elongation, and in 316H it led to an increased UTS.

Table 10 – Tensile results of 316 base material

	UTS (MPa)	YS (MPa)	Elongation (%)
316L Base Unexposed	624 ± 7	302 ± 2	76.1 ± 0.7
316L Base 550°C CO₂	627 ± 6	296 ± 3	74.8 ± 0.6
316L Base 550°C Aging	635 ± 2	305 ± 2	73.6 ± 0.4
316L Base 750°C Aging	630 ± 12	244 ± 4	60.9 ± 0.9
316H Base Unexposed	574 ± 1	274 ± 3	92.2 ± 1.0
316H Base 550°C CO₂	575 ± 2	282 ± 2	87.1 ± 5.9
316H Base 550°C Aging	579 ± 1	270 ± 1	83.6 ± 2.3
316H Base 750°C Aging	617 ± 2	243 ± 1	67.6 ± 1.3

Welded samples paint a somewhat more muddled picture. For 316L, both exposures at 550°C increased UTS, while having little total effect on yield strength or elongation. For 316H, 550°C had an overall minimal effect, similar to that of base material. Also similar to base material, aging at 750°C increased UTS while lowering yield strength. Where these welded samples differ from base material is that the overall elongation was not affected from this high temperature aging. All samples ruptured in the fusion zone, and this was not altered by exposure in either 316L or 316H.

Table 11 – Tensile results of 316 welded material

	UTS (MPa)	YS (MPa)	Elongation (%)	Failure Location
316L Welded Unexposed	544 ± 3	282 ± 1	40.4 ± 0.3	Fusion Zone
316L Welded 550°C CO₂	592 ± 2	294 ± 5	40.0 ± 0.5	Fusion Zone
316L Welded 550°C Aging	560 ± 2	276 ± 2	36.2 ± 0.5	Fusion Zone
316L Welded 750°C Aging	627 ± 2	241 ± 2	40.1 ± 2.5	Fusion Zone
316H Welded Unexposed	583 ± 10	303 ± 1	49.0 ± 2.0	Fusion Zone
316H Welded 550°C CO₂	598 ± 5	291 ± 3	41.6 ± 0.8	Fusion Zone
316H Welded 550°C Aging	570 ± 11	278 ± 6	34.3 ± 3.8	Fusion Zone
316H Welded 750°C Aging	648 ± 4	260 ± 2	40.0 ± 2.9	Fusion Zone

Based on the analysis above, that there was very limited oxidation in CO₂ at 550°C – and given the equal mechanical values of the unexposed and 550°C exposures – it follows that there was likely negligible

internal carbide formation in base material, either from the environment or from alloy carbon. This matches the discussion from section 6.2. Welded samples exhibited higher UTS after exposure at 550°C in CO₂ relative to neutral aging. This could be either an indication of the larger, more contiguous grains of the fusion zone being more affected by carbide or intermetallic precipitation than the smaller grains of base material, or a figment of small sample sizes.

After 750°C aging, however, there was a significantly higher UTS for both alloys, with the exception of 316L base material, combined with a lowered yield strength. Additionally, there was lowered ductility in base material, but not in welded samples. This indicates that precipitation of carbides and intermetallic phases might have caused strengthening and embrittlement. However, given that there was no strengthening in 316L base material, there is likely an upper limit to the strength addition from this precipitation around 630-650MPa. In addition, this heat treatment-induced precipitation was only ductility-limiting in base material, so there is a similar limit to the reduction in ductility which has occurred at this stage in the aging process.

Further, while the microhardness results indicated a mild hardening could be expected from exposure, perhaps only noticeable in the 750°C aged samples, results for yield strength indicate the opposite. Exposure at 550°C caused essentially no change in YS, while 750°C aging consistently resulted in yield occurring at lower strength values. Because this result is the opposite of that of microhardness, it is inferred that some development has separated the micro-strengthening of the matrix from the macro-weakening of the overall material.

6.4.2. Fracture Surface Analysis

6.4.2.1. 316L

Analysis of the fracture surface of unexposed 316L base material shows the effects of changing ductility. Figure 67 A and B show the fracture surface for 316L which was pulled in the as-annealed condition. This

sample showed its high ductility in localized necking before fracture, as well as its transgranular fracture mode. Further, Figure 67 B shows that the MVC which characterized this fracture surface had dimples which were typically 5-25 μm in size. This was a highly ductile fracture surface which reflected the elongation measurement. Figure 67 C and D show the fracture surface of a 316L sample which was aged at 750°C, 0.02MPa for 1,000 hours. The decrease in localized necking as well as the reduction in dimple size down to 1-5 μm shows that this surface was embrittled compared to that of as-received base material. In addition, horizontal striations were observed on the fracture surface. These could be due to the effect of grain alignment along inclusions discussed in section 6.3. However, another explanation is that these horizontal striations represent the formation of σ -phase in the horizontal islands of delta-ferrite which were left over from the manufacturing process. As discussed in section 2.2.2, σ -phase is embrittling at room temperature, so it is likely to be the limiting factor in the material's ductility after exposure. In addition, this means that the ductility should not be affected by this development while at temperature. Therefore, even aging at 750°C may have had no effect on 316L at potential operating conditions of an s-CO₂ Brayton cycle.

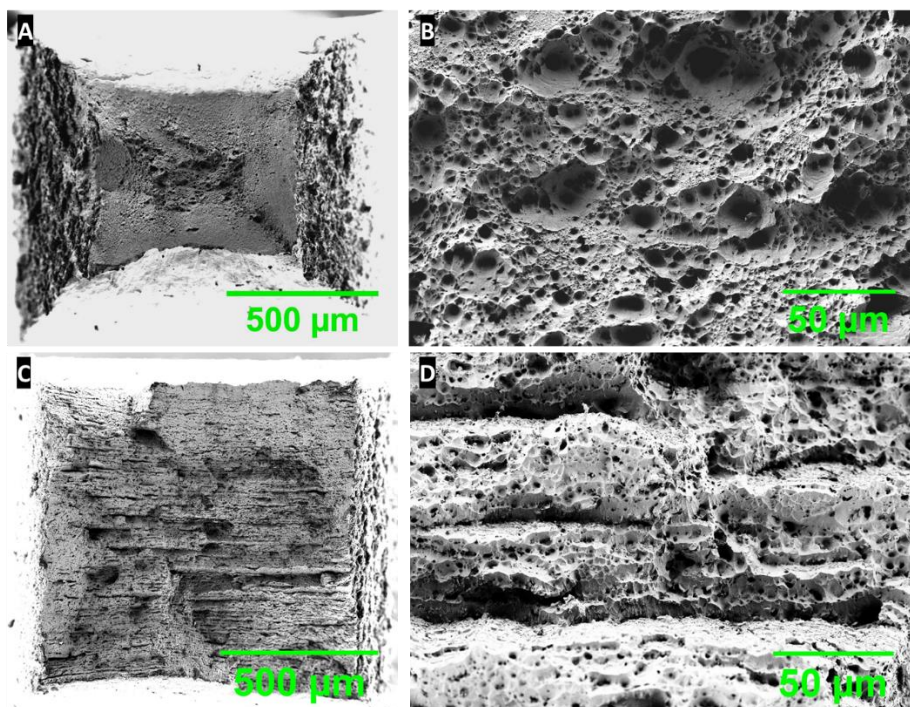


Figure 67 – Fracture surface images of base 316L samples pulled in the unexposed (A,B) and 750°C aged (C,D) conditions. Loss of ductility after aging observed in lack of necking and decrease in dimple size.

The fracture surface images for 550°C aged samples are given in Figure 68 A and B, while those for 550°C CO₂-exposed samples are shown in Figure 68 C and D. These fracture surfaces show that while the fracture mode was altered after both exposures, there was no difference between them. The majority of the gauge cross section during both exposures was aged and not affected by the CO₂ environment. Both samples exhibited a slight reduction in both localized necking and dimple size relative to as-received material. Horizontal striations were observed in these samples as well, with the same inference that they were likely due to σ -phase embrittlement. It is likely that these samples were not embrittled as much as those aged at 750°C because lower temperature resulted in less σ -phase precipitation and coarsening.

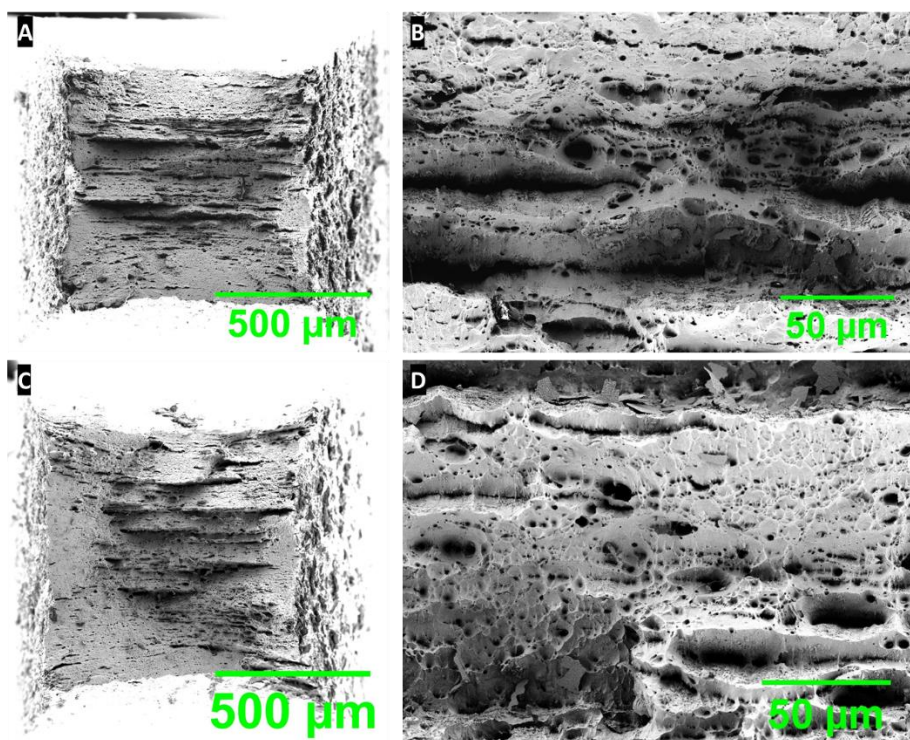


Figure 68 – Fracture surface SEM of base 316L samples which were exposed to 550°C in Ar (A,B) or CO₂ (C,D) for 1,000 hours. Fracture surfaces show no discernable differences.

Welded 316L pulled in the unexposed condition exhibited a fracture surface similar to that of base material. Shown in Figure 69 A and B, it was characterized by localized necking, with transgranular fracture and MVC consisting of 5μm dimples. The localized necking caused a smaller reduction in area than that observed in base material, and the dimples were significantly smaller, and this reflected the lower strain at fracture observed in tensile results. Results after aging at 750°C, see Figure 69 C and D, show that while the measured elongation did not change, the fracture mode changed considerably. 750°C aged samples exhibited no necking, while failing in a mixture of MVC with micron-scale dimples and micron-scale cleavage. This is a significantly embrittled form of fracture compared to unexposed as well as to base material in the same aged condition. It appeared that there was σ -phase embrittlement after 750°C, as observed in base material, but because the failure occurred in the fusion zone, the orientation of the characteristic lines were along the weld direction instead of the rolling direction. It was also likely that the σ -phase formed within δ -ferrite, and the shape of the lathes in the fracture surface matched the

description of δ -ferrite formation in vermicular or lathy shapes along the axes of dendrites, as discussed in section 2.3.2.

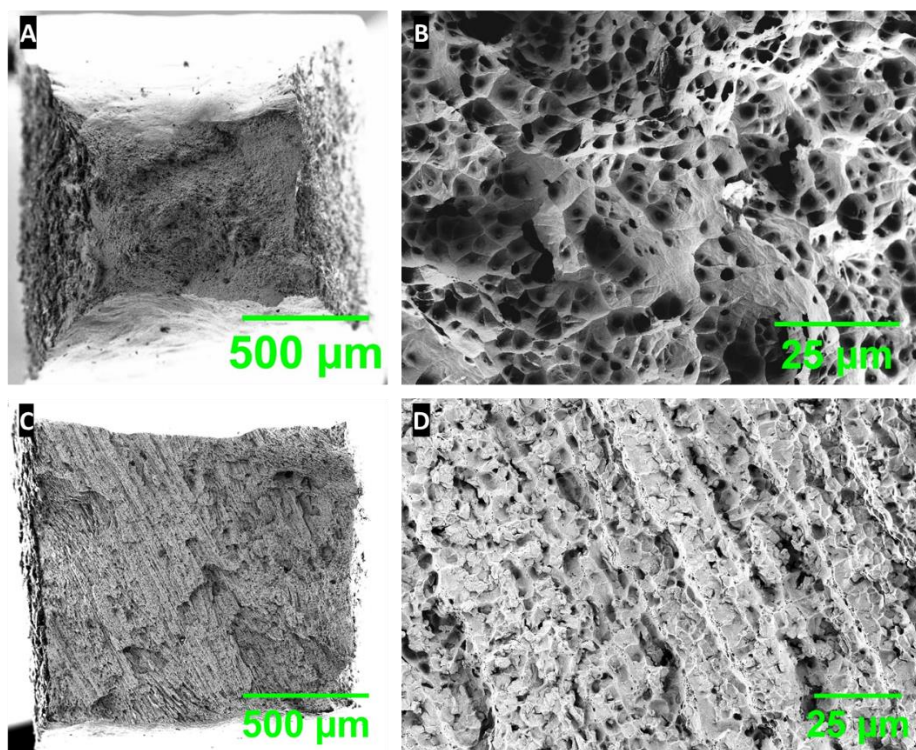


Figure 69 – Fracture surface images of welded 316L samples pulled in the unexposed (A,B) and 750°C aged (C,D) conditions. Loss of ductility after aging observed in lack of necking and shift to smaller dimples and micron-scale cleavage.

Similar to base 316L, the fracture surfaces of welded 316L, shown in Figure 70, appeared nearly identical. There was moderate localized necking in both which was slightly below that observed in the as-welded samples. Also, they both produced surfaces with transgranular fracture and MVC with dimples in the range of 5 μ m in size. The odd shape of fracture observed in Figure 70 C does not seem to provide any useful information, as it was likely just a sample-specific phenomena.

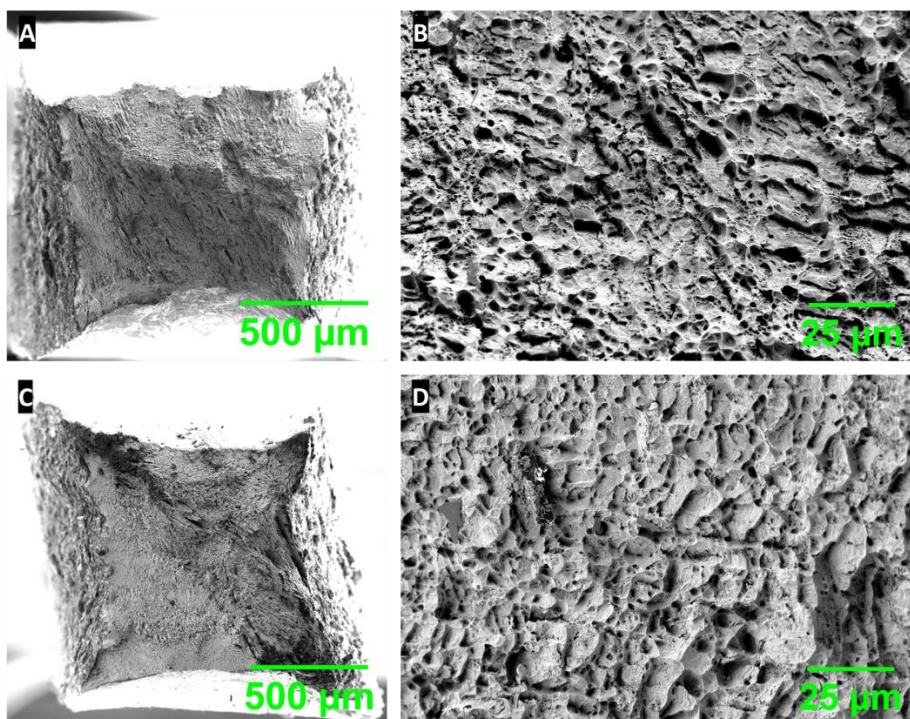


Figure 70 – Fracture surface SEM of welded 316L samples which were exposed to 550°C in Ar (A,B) or CO₂ (C,D) for 1,000 hours. Fracture surfaces show no discernable differences in fracture mode.

In addition to the above, fracture occurred in the fusion zone for all 316L samples. While the fracture remained transgranular after exposure, it was oriented along parallel lines. As this was not observed in as-welded samples, it is likely to be a similar phenomenon to that observed in base material samples: growth of σ -phase precipitates. In contrast to base material, whose precipitates grew along the rolling direction, these precipitates grew along solidification direction, on the axes of dendritic cores. This had the same effect as it did with base material: eliminating localized necking in 750°C aged samples and limiting it after both 550°C exposures. This decrease in ductility did not prove limiting from an elongation perspective but, as was seen in these fracture surfaces, is still present. Also, as was the case with base samples, this ductility decrease is not anticipated to affect the material strength at temperatures above 150°C.

6.4.2.2. 316H

Analysis of the fracture surface for 316H samples revealed many similarities to that of 316L, but some notable differences. Base, as-received 316H, as seen in Figure 71 A and B, exhibited an equivalent fracture surface to that of 316L: significant necking, transgranular fracture, and MVC with dimples of 1-10 μ m microns in diameter. However, aging at 750°C for 1,000 hours produced a significant change in fracture mechanism. Similar to 316L, the fracture surface seen in Figure 71 C and D exhibited little-to-no necking, along with MVC featuring much-reduced dimple size. However, in contrast to 316L, the primary fracture mode changed from transgranular to intergranular, with the sample rupturing along grain boundaries. This is consistent with previous work which showed that increased carbon content in 316 increases the precipitation of grain boundary carbides, while decreasing the precipitation of intermetallic phases such as σ -phase (which dominated fracture in 316L) [80]. While the measured elongation of 316H after 750°C aging was higher than that for 316L, the difference relative to unexposed was greater for 316H. This fracture surface shows why that relative change was greater: the added carbon in 316H has embrittled the material along grain boundaries – likely through the production of $M_{23}C_6$ carbides, as discussed in section 2.2.2. These precipitates, unlike the σ -phase precipitated in 316L, are embrittling at both high and low temperatures.

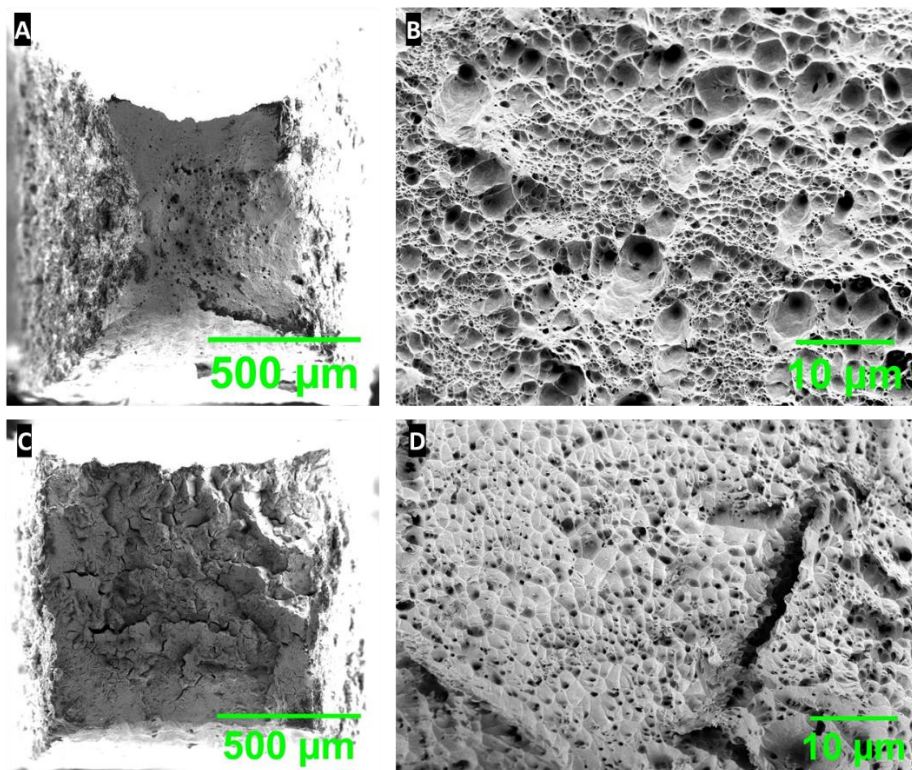


Figure 71 – Fracture surface images of base 316H samples pulled in the unexposed (A,B) and 750°C aged (C,D) conditions. Loss of ductility after aging observed in lack of necking, decrease in dimple size, and primary fracture mode changing from transgranular to intergranular.

The fracture surfaces for base 316H after exposure at 550°C tells a diverging story. Samples exposed to CO₂ at 550°C for 1,000 hours, see Figure 72 C and D, had similar fracture as that in unexposed samples: significant necking with largely transgranular fracture incorporating dimples on the order of 5-10μm. In addition, there were a few locations of rupture which appeared to have occurred along grain boundaries, and this was likely due to a smaller amount of grain boundary carbide precipitation than that in 750°C aged samples (Figure 71 C and D). However, samples aged at 550°C, observed in Figure 72 A and B, resulted in a very different fracture surface from any other exposure for 316. Compared to unexposed, the fracture mode changed from transgranular to intergranular, but the intergranular fracture did not occur via MVC. While there were occasional dimples on the surface, the dominant effect was that of grains separating into small groups and then necking separately from the rest of the sample. This mode of fracture could be an indicator of incomplete grain boundary embrittlement, where some sections of

grains elongated and necked, and other sections remained rigid. In this way, although it would appear as if the grains were cracking apart, they were actually elongating separately. The tensile result was a measured elongation similar to that of both unexposed and 550°C CO₂-exposed samples, indicating that, although the mode of fracture appears different, the grain boundary hardening has not yet caused embrittlement of the overall sample. In that way, the incomplete grain boundary embrittlement in both 550°C exposures can be seen as two sides of the same effect, and the observed differences were likely due to disparities in local composition and grain structure. Further, in both cases there was no observed effect of σ -phase embrittlement. This supports the hypothesis that the extra carbon suppressed intermetallic precipitation in 316H. The (slight) additional ductility loss of 316H after 550°C exposure reinforces that this morphology is more embrittling than that of 316L

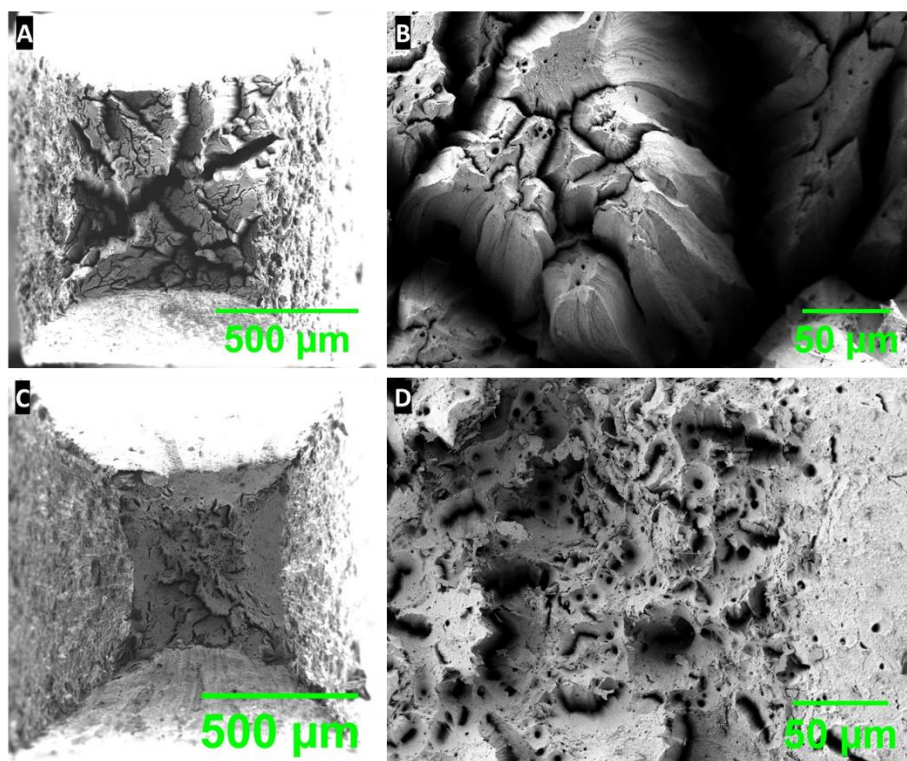


Figure 72 – Fracture surface SEM of base 316H samples which were exposed to 550°C in Ar (A,B) or CO₂ (C,D) for 1,000 hours.

The fracture surfaces of welded 316H appeared very similar to those of welded 316L. Unexposed, viewed in Figure 73 A and B, fractured transgranularly, with dimples on the order of 1-5µm. As seen in 316L, aging

at 750°C for 1,000 hours led to a loss of localized necking, along with a shift to a combination of MVC with micron-scale dimples, and micron-scale cleavage. Additional embrittlement relative to that of 316L was not observed, as shown in the tensile results.

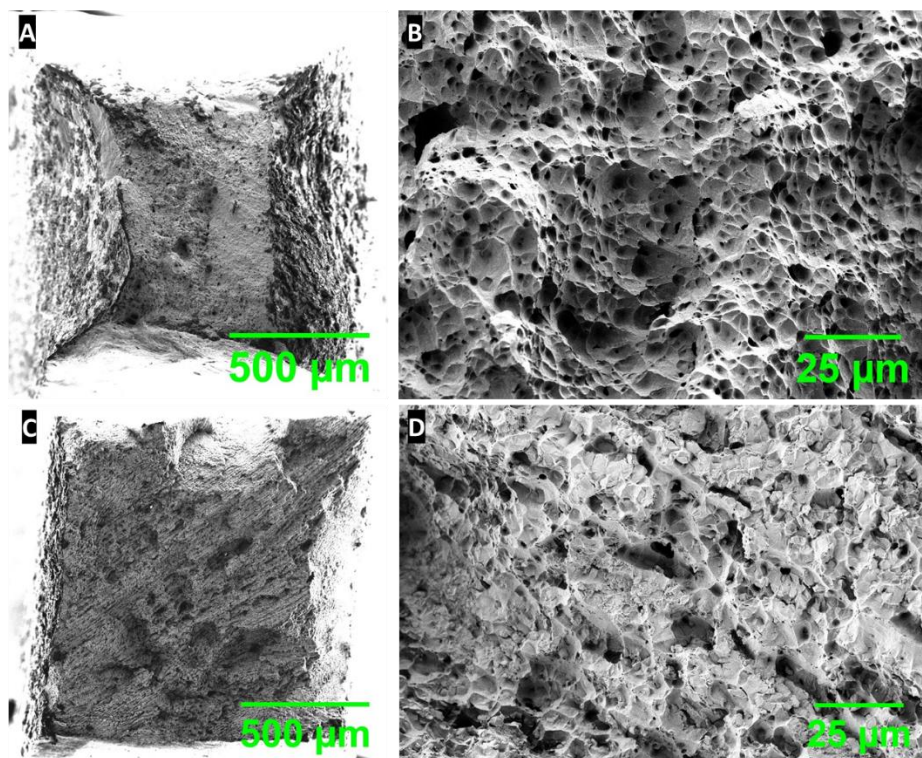


Figure 73 – Fracture surface images of welded 316H samples pulled in the unexposed (A,B) and 750°C aged (C,D) conditions. Loss of ductility after aging observed in lack of necking and shift to smaller dimples and micron-scale cleavage.

Exposure of welded 316H to either 550°C environment resulted in a very similar fracture surface. Samples of both exposures showed decreases in sample necking, with a decline in dimple size to 1-2µm. Similar to that of 316L, each of the exposed fracture surfaces for welded 316H (including 750°C aged) exhibited parallel lines in the direction of solidification during the weld. Given that these samples also fractured in the fusion zone, it can be assumed that the additional C content in 316H has not had the same suppressing effect on σ -phase precipitation in welded material as it did in base material. It is also likely that there was precipitation of small grain boundary carbides due to the elevated carbon content relative to 316L, but these carbides were not coarsened to the point at which they became ductility-limiting. The effect of

grain boundary carbides is supported by the pseudo-parallel striations which appeared to follow the solidification direction during welding. This effect is also more exaggerated after 750°C aging, which fits the kinetics of diffusion constituents and coarsening of carbides.

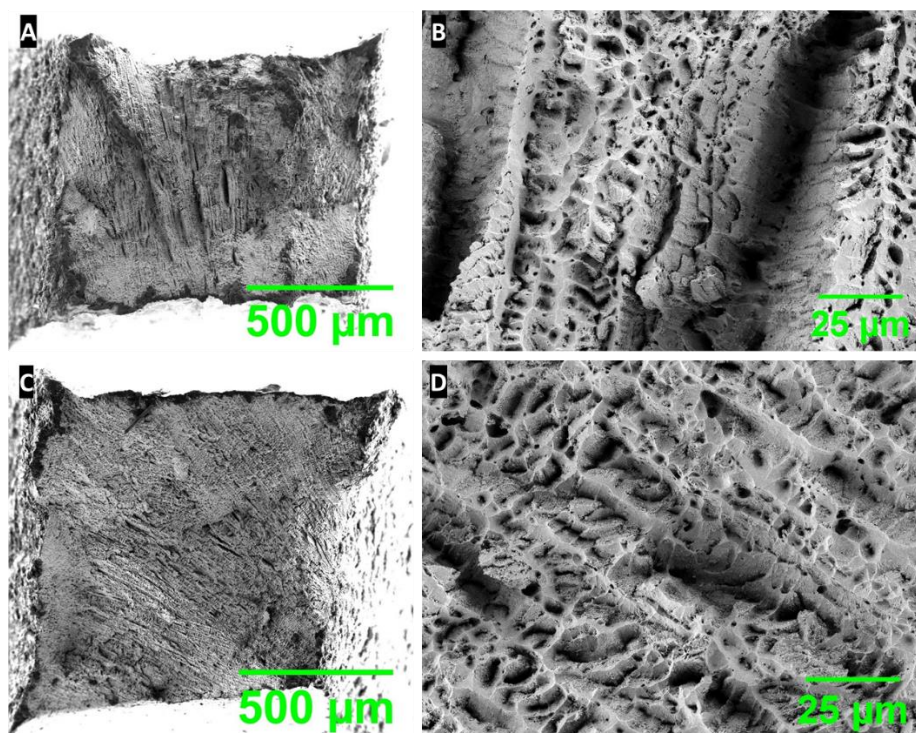


Figure 74 – Fracture surface SEM of welded 316H samples which were exposed to 550°C in Ar (A,B) or CO₂ (C,D) for 1,000 hours. Fracture surfaces show no discernable differences in fracture mode.

6.5. 316 Overall Summary

This experiment was designed to analyze the effect of carbon on the performance of the 316 alloy in the CO₂ environment. This not only involved long-term aging of base material – which has been completed before (see section 2.2.2) – but also the exposure to CO₂ at almost the upper temperature limit for 316 application in a CO₂ Brayton cycle. In addition, both 316L and 316H were welded using GTAW and analyzed in the same environments. In this way, the study covered the potential implications of sensitization and a higher alloy carbon on the performance of 316 in the CO₂ environment.

Analysis of both 316L and 316H after exposure at 550°C, 20MPa for 1,000 hours revealed very little corrosive attack. The majority of the 316 surface consisted of a Cr-rich oxide which was on the order of 100s of nanometers thick, with occasional nodules of Fe-rich, dual-phase oxide with a maximum observed thickness of 5µm. There was also no additional attack observed in the fusion zone or HAZ, either on the austenitic matrix or along grain boundaries. Further, there was no severe embrittlement in the HAZ for either variant of 316, as all welded samples fractured in the fusion zone. This is an interesting result, as the HAZ of 316H has been known to exhibit sensitization in the form of Cr-depletion along grain boundaries, leading to additional grain boundary corrosion. The lack of any observed preferential attack along grain boundaries in the 316H here indicates that the CO₂ environment at 550°C did not oxidize this alloy fast enough to locally deplete the Cr-content to the point that Fe got preferentially oxidized, even with the HAZ sensitization associated with 316H.

Additionally, analyzing 316L and 316H side-by-side allowed for direct understanding of how extra carbon in the alloy affects the thermal evolution of the alloy. In either variant, there is much greater alloying carbon in 316 than what is soluble in the matrix, so long term aging should result in precipitation of carbides – typically M₂₃C₆ – and higher temperature will allow for faster precipitation. For this purpose, aging at 750°C can be used as a good estimation of a much longer aging at 550°C. Results indicate that embrittlement has only started after 1,000 hours at 550°C, and it has delivered its first macroscopic effect only after 1,000 hours at 750°C.

Further, 316L exhibited σ-phase embrittlement, while the higher C-content of 316H encouraged carbide formation at the expense of intermetallics. This σ-phase precipitated in islands of δ-ferrite, which were located the rolling direction in base material and along the dendritic axes in the fusion zone. These precipitates were embrittling at room temperature, but have been shown not to be when above 150°C [44]. The embrittlement observed in 316H (with >2x the carbon content) was slightly more than that for 316L, but not severe. Unlike the σ-phase of 316L, this embrittlement – mainly due to the precipitation of

grain boundary carbides – will affect the ductility at higher temperatures as well. If 316H is taken to be an indicator of 316L performance after substantial carburization, then this level of carburization will not have severe detrimental effects for 316L. Additionally, with an understanding that oxidation needs to occur before carburization – thereby liberating carbon to diffuse into the alloy – 316 would need to oxidize much more than it has shown at 550°C. Given that the oxide formed in the first 1,000 hours has been shown to be very protective and thin, with parabolic oxide growth, it can be stated that 316 will not exhibit a loss of ductility within the 20 year lifespan of a CO₂ power plant, and likely until much later, when utilized at or below 550°C.

7. Grade 92 Ferritic-Martensitic Steel

Grade 92 F-M steel (from here on referred to as P92) is a dual phase steel used in industry because of its good strength and corrosion properties up to about 500°C. Based on the previous corrosion performance of the alloy (see section 2.1.3.3), it was estimated that the corrosion limit of P92 was near 450°C. Because of this, 450°C was chosen as an exposure temperature in RG CO₂ for this alloy. As an estimate of the projected performance beyond the possible time scale in this study, P92 was also exposed to RG CO₂ at 550°C. Further, because of the potential for self-diffusion of alloying elements, grain growth, and self-precipitation, P92 was exposed at 550°C in UHP Ar so as to isolate the effect of prolonged aging. In this way, the study was designed to discover the unique effects of CO₂ corrosion on the mechanical performance of P92.

7.1. Sample Procurement

Samples were acquired from Anderson Laboratories, and 9CRWV-TIG [83] filler was purchased from Euroweld Limited. Welding was performed on 1/8" plates according to the welding procedure detailed in Table 20. Samples of both base and welded material were produced through wire EDM processing, with a target thickness of 0.063", with all surface effects of welding removed. The number of tensile samples tested for each material in each condition are given in Table 9. Additional samples were exposed for the purpose of corrosion analysis and mass change statistics.

Table 12 – Total number of P92 tensile samples tested at each analysis condition

Type of Sample	Unexposed	450°C CO ₂	550°C CO ₂	550°C Ar
P92 Base	3	2	3	3
P92 Weld	6	3	3	1

7.2. Exposure Analysis

The oxide formed by P92 at both temperatures consists of a two-phase oxide: an outer magnetite layer (Fe_3O_4) and an inner Cr-rich spinel (mean stoichiometry likely similar to that of P91: $\text{Fe}_{2.3}\text{Cr}_{0.7}\text{O}_4$) [26], [27]. The oxidation in P92 was anticipated to be the most aggressive observed in this work, given previous studies addressed in section 2.1.3.3. No spallation was observed in this alloy after exposure to CO_2 for 1,000 hours at 20MPa at either 450°C or 550°C, so mass change was used as an estimate of total oxygen and carbon absorption by the alloy.

7.2.1. Mass Change

The change in mass demonstrated the expected corrosion increase from 550°C CO_2 exposure relative to that of 450°C. For base material, exposure to 550°C resulted in $4.950 \pm 0.007 \text{ mg/cm}^2$, and exposure to 450°C resulted in $1.429 \pm 0.031 \text{ mg/cm}^2$. For welded samples, 550°C exposure resulted in $4.508 \pm 0.675 \text{ mg/cm}^2$ while 450°C exposure resulted in $1.541 \pm 0.042 \text{ mg/cm}^2$. This shows that there was little difference between welded and base material samples at either temperature, so the welding process likely did not increase corrosion in any significant fashion. Also, the mass gain in samples exposed to CO_2 at 550°C was roughly three times that in those exposed at 450°C, indicating three times the oxidation and – likely – carburization. This needs to be confirmed in later analysis. Mass change was measured for the 1,000 hour, 550°C aging as a quality assurance technique, and found to be negligible: $-0.0079 \pm 0.0165 \text{ mg/cm}^2$ for base material and $-0.0429 \pm 0.0174 \text{ mg/cm}^2$ for welded samples. This indicates that the aging environment was essentially free of oxygen (and carbon, and other reactants).

7.2.2. Oxidation

Each exposure in CO_2 resulted in a duplex oxide formation with an outer magnetite and an inner Fe-Cr spinel. Analysis of the oxide of each exposure (see Figure 75) was performed, with no difference observed between the base material and the fusion zone after exposure at the same temperature and duration. However, exposure for 1,000 hours at 550°C and 450°C were found to have oxide thicknesses of

31.8±1.0µm and 11.1±0.7µm, respectively. This indicates that the oxidation in 550°C was roughly three times that in 450°C, mirroring the mass change results. In addition, the different sections of the oxide were measured. For 550°C exposure, magnetite accounted for 62±3% of the total oxide, while the Fe-Cr spinel accounted for the rest. This was matched in 450°C exposure, as magnetite and hematite accounted for 62±6% of the total oxide. The equal ratios of the two oxide thicknesses within the duplex structure, despite a three times difference in oxidation rate, supports that the oxidation process functions in the same fashion at both temperatures – hypothesized through the available space model.

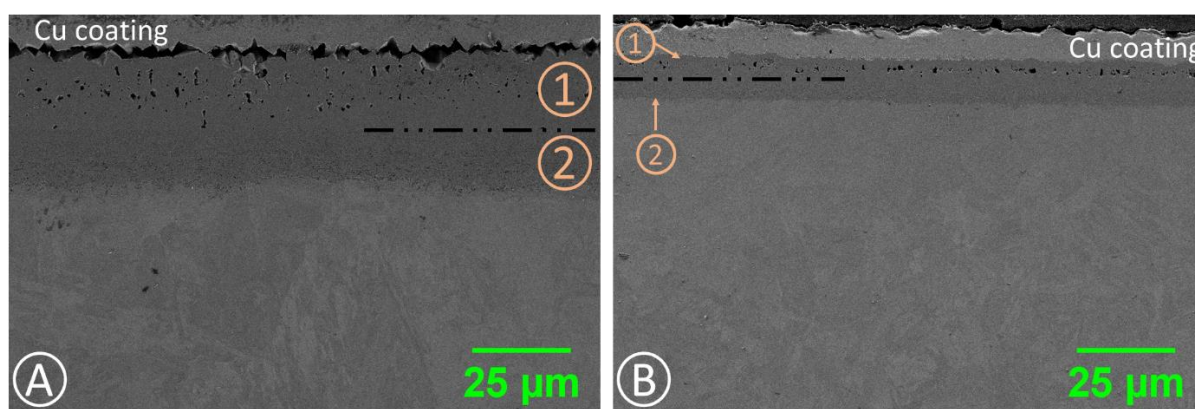


Figure 75 - Oxide of P92 exposed to 550°C (A) and 450°C (B) showing a duplex oxide formation of (1) an outer magnetite (Fe_3O_4) and (2) an inner Cr-rich spinel

The IOZ was also measured separately from the oxide. This region was only observed after exposure to CO_2 at 550°C, and can be observed in Figure 76. The IOZ thickness varied from 2.5-4.0µm, with an average thickness of 3.3±0.5µm. Directly above the IOZ was a region of similar thickness which was visually different from both the IOZ and Fe-Cr spinel. It is believed that this is indicative of the transition from an IOZ to being a part of the Fe-Cr spinel. As described in section 2.1.3.3, this region was likely undergoing Fe-oxidation of the Cr-depleted matrix surrounding the FeCr_2O_4 (chromite) islands. An EDS line scan was performed over the oxide, see Figure 77, which showed the IOZ, as well as both regions of the duplex oxide. This scan confirms the thickness of the IOZ measured with SEM, and indicates that the actively oxidizing region is not compositionally different from the Fe-Cr spinel.

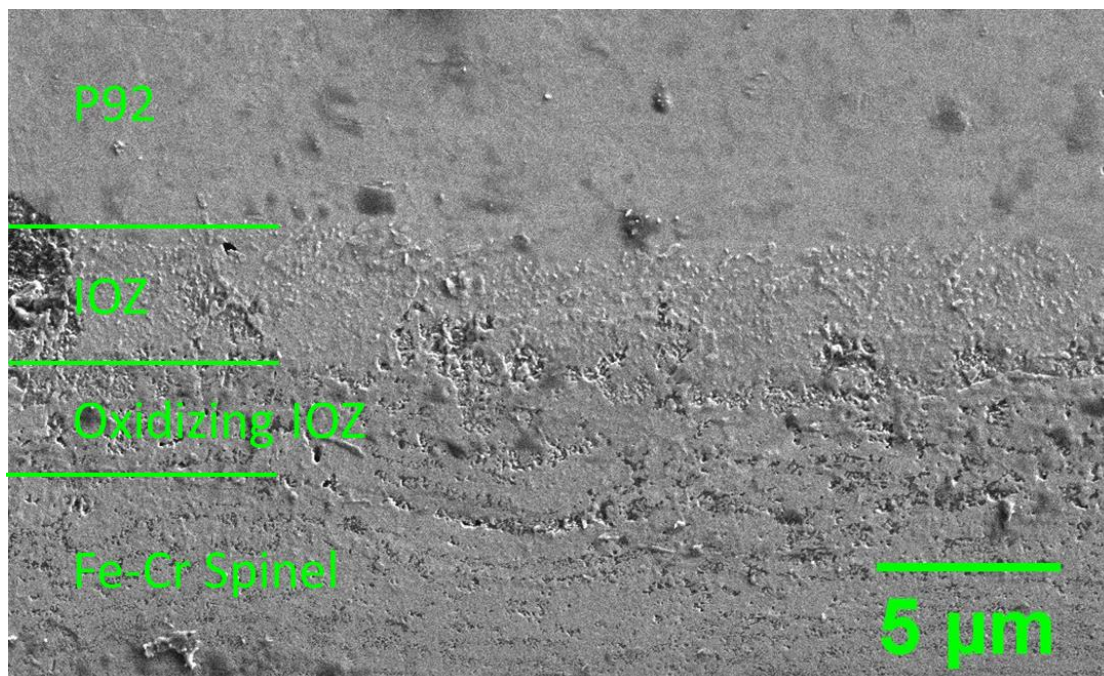


Figure 76 – Image of the oxide-metal interface of P92 which was exposed to CO₂ at 550°C, 20MPa for 1,000 hours. Shows the base alloy, IOZ, and Fe-Cr spinel, as well as the transition region from IOZ to Fe-Cr spinel.

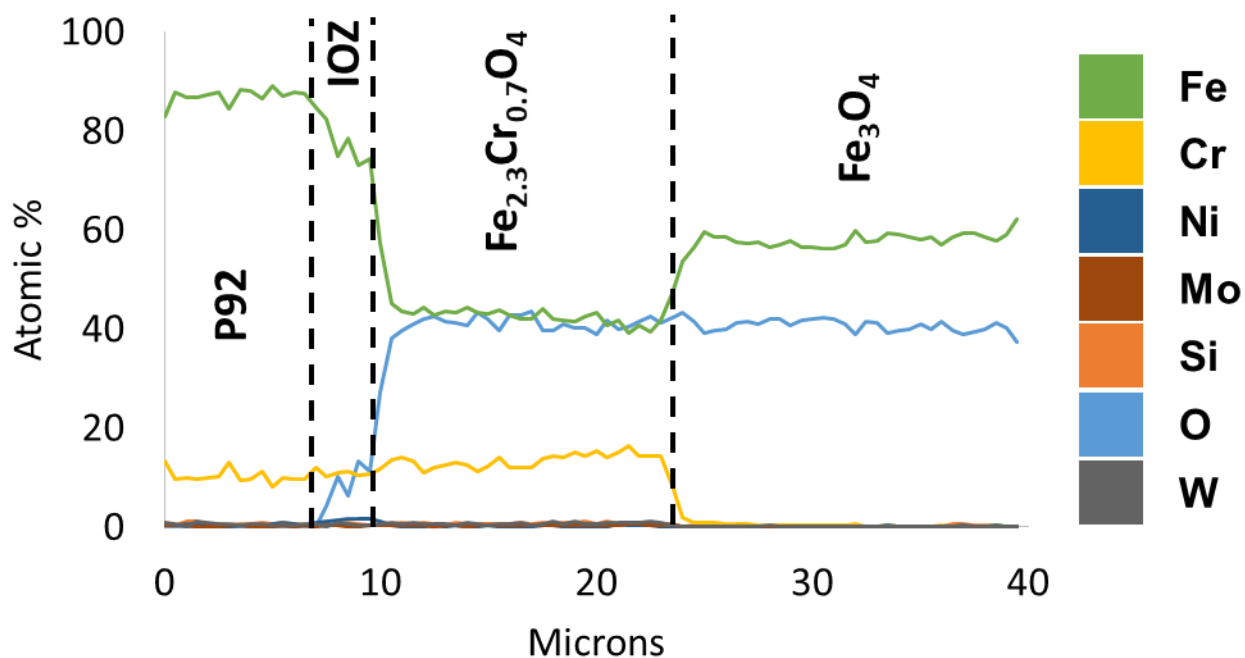


Figure 77 – EDS line scan from base material into the oxide of P92 after exposure to CO₂ at 550°C, 20MPa for 1,000 hours. Shows the IOZ region, which is roughly 3µm thick, along with the relative atomic % of each oxide.

While 450°C exposure did not yield an IOZ which was visible with SEM, it did exhibit an otherwise very typical oxide, shown in Figure 78. The duplex oxide formed with an inward, equiaxed Fe-Cr spinel, along with an outward, columnar magnetite, as observed in previous work [33]. External growth of equiaxed hematite (Fe_2O_3), preceding the development of magnetite, was observed in 450°C but not in 550°C samples. This was likely due to the fact that higher temperature encouraged Fe diffusion more quickly to the surface at 550°C, keeping the hematite layer very thin or non-existent. Additionally, there was large voiding in the Fe-oxide of P92 which was exposed at both 550°C and 450°C, and the calculated porosity was roughly 3-6% (from image processing).

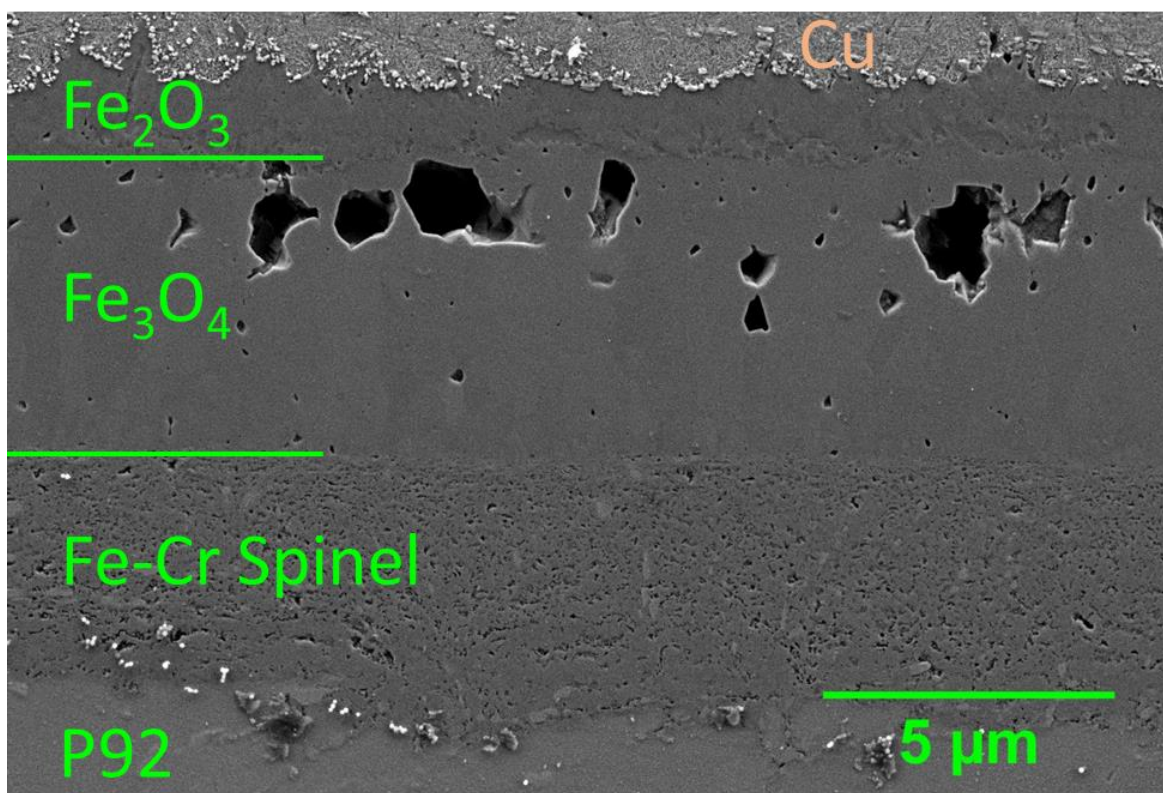


Figure 78 – Oxide from P92 exposed to CO_2 at 450°C, 20MPa for 1,000 hours. Shows outer Fe-oxide is comprised of both columnar (associated with magnetite) and equiaxed (hematite) grains. Fe-Cr spinel is rich with nano- and micro-voids.

7.2.3. Carburization and Thermal Aging

7.2.3.1. Microhardness

Carburization analysis was performed through several avenues. The first, microhardness, also monitored the impact of thermal aging, and consisted of analyzing the hardness of the matrix, both near the oxide and in the bulk. Bulk hardness measurements were made with averaging 25 measurements, while depth measurements, given in Figure 79, were made by averaging 2-4 measurements at equal depths from the oxide. Bulk measurements found CO₂ exposure at 550°C resulted in 241.2 ± 1.6 HV, while 450°C resulted in 252.8 ± 2.2 HV. In addition, the bulk of 550°C aged P92 was found to have a hardness of 239.2 ± 2.1 HV, essentially equivalent to that of CO₂-exposed. These match the hardness values reported in literature for post-heat treatment P92, which are in the range of 240-275 HV [48], [72], and indicate no effects of CO₂ in the bulk.

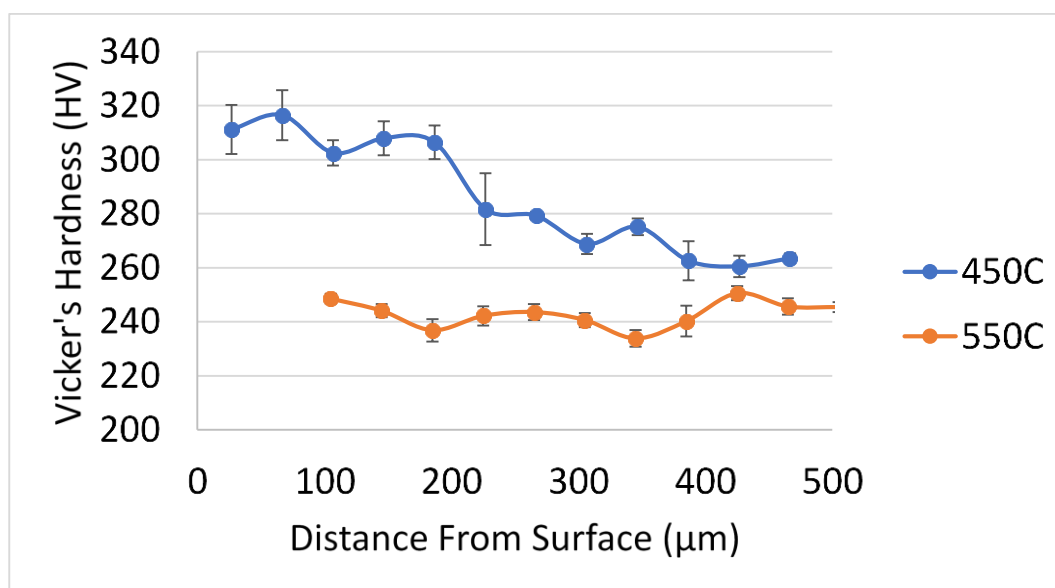


Figure 79 – Microhardness measurements of P92 moving away from the oxide after CO₂ exposure

Depth measurements indicated that after exposure to 450°C there was a decreasing hardness profile from the surface, and this has been shown to be representative of the amount and depth of carburization [30]. The 550°C exposure, however, did not share this profile; the hardness of each point matched the bulk hardness. As will be discussed below, this is likely because the measurements were begun near the end of the carburized zone.

7.2.3.2. Carburization Depth

GD-OES was used to analyze the depth profile of carbon from the surface for both CO₂ exposures, and this is seen in Figure 80. As has been shown in previous work [33], there is a large amount of carbon deposition from each exposure. Both exposures revealed little carbon in the outer magnetite, as observed previously [33], [84]. The carbon in the magnetite layer has also been shown to decrease with additional corrosion (carbon level indicated in 450°C may be an inherent effect of the measurement), and this was observed as no carbon was left in magnetite after exposure to 550°C. The carbon profile then reaches the maximum in the inner Fe-Cr spinel.

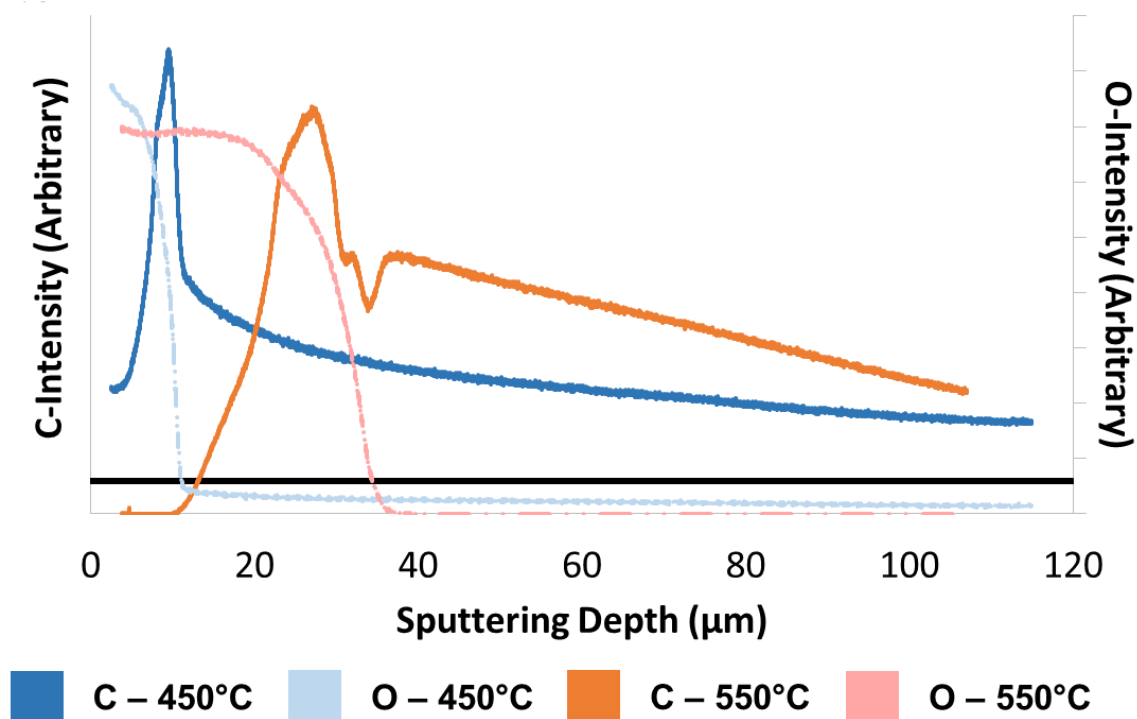


Figure 80 – GD-OES results for P92 samples which were exposed to CO₂ at 20MPa for 1,000h. Carbon plotted against left axis, oxygen plotted against the right. A black line indicates the measured carbon for an unexposed sample (base alloy carbon)

Beneath the Fe-Cr spinel, the different temperature exposures resulted in divergent carbon profiles. For 550°C, a small nadir occurred just as the alloy was reached, likely corresponding to the IOZ [26], [84]. As

depth increased in the alloy, carbon content decreased in a linear fashion (observed previously for P91 in [84]). Conversely, the profile for 450°C-exposed material decreased in a gradual exponential decay, approximating a concentration gradient typical for diffusion. A decrease in carbon after the oxide has been observed at 450°C [30], but it was likely too thin for the depth resolution of this analysis.

This shows that while the micro-hardness measurements which were taken on samples exposed at 450°C were representative of carburization, those taken on samples exposed at 550°C were not. This could be due grain growth at 550°C, though no evidence was found of grain growth. It is likely that the carbon ingress at 550°C resulted in a different density of carbides or interaction of carbon that at 450°C. When taken in context to the different carbon depth profiles from each exposure, it is likely that the interaction of carbon at each exposure was likely different, likely due to the temperature difference, but also possibly due to a difference in total carbon deposition.

While it is not possible with the current equipment to measure deeper than is seen here, a linear extrapolation was used to estimate the depth to which carburization occurred (the final 60µm of measurement was used to create a linear extrapolation for 450°C). In 450°C exposure, this depth of carburization projected to occur at 185µm – roughly equal to the depth at which the microhardness profile returned to lower values, though a slight underestimation (as expected, as the curve was not truly linear). In 550°C exposure it projected to occur at 150µm, which was significantly shallower than for 450°C. In addition, these projected carburization depth profiles were used to calculate an integrated total carburization. This found that exposure to CO₂ at 550°C carburized 15% more than at 450°C, despite resulting in three times the mass gain. This indicates that while carburization and oxidation are linked, the link seems not to carry a constant ratio of C to O across different oxidation rates or temperatures.

7.2.3.3. Chemical Etching

This projection for 550°C was found to match etching analysis. Figure 81 shows the etched cross-section of P92 after exposure to CO₂ at 550°C for 1,000 hours. This revealed a 3-6µm thick layer of heavy carbon deposition, corresponding to the peak of carbon at the end of the oxide, as well as a carburization depth below the oxide of 100-125µm (135-160µm below the surface). This depth matches the GD-OES data, and seems to indicate a difference in the carbon profile at 550°C compared to 450°C. The change in tensile properties between 450°C and 550°C is likely not a function of increased carbon deposition, but rather of the effect that the carbon has on the material at the respective temperatures.

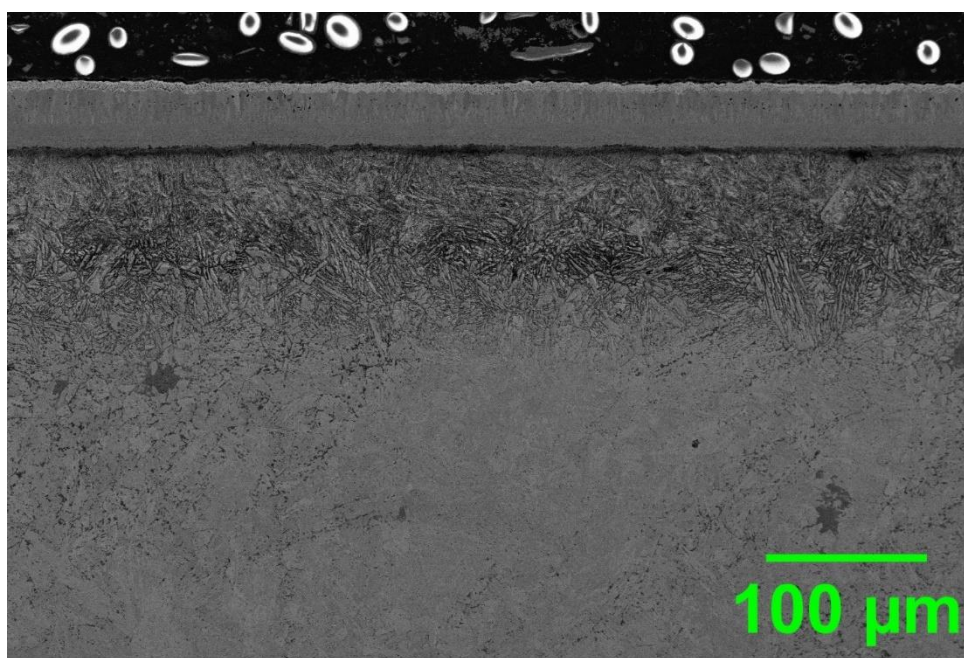


Figure 81 – Etched P92 base material after exposure to CO₂ at 550°C, 20MPa for 1,000h. Shows a carburization depth of 100-125µm below a ~35µm thick oxide.

As can be noted from Figure 80, the amount of deposited carbon in the first 70-80µm below the oxide was significantly higher in 550°C-exposed samples than in 450°C. Further, while the carbon profile from 450°C could be interpreted as exponential decrease corresponding to a diffusion profile, the carbon profile from 550°C was linear. This can be understood by assuming that a large portion of the carbon deposited in P92 at 450°C moved through the material without forming embrittling carbides. Meanwhile, the carbon deposited at 550°C, being at higher temperature, was more likely to form carbides and become

solidly entrenched, unable to continue to diffuse into the bulk of the alloy. For various alloys and conditions, the low reported temperature for Cr-rich, $M_{23}C_6$ carbide precipitation is near 500°C, so it would follow that there would be substantially more carbides formed at 550°C than 450°C [18]. This could explain the limited diffusion distance at 550°C relative to 450°C, and would project that there will be additional embrittlement at the higher temperature relative to the lower. Additionally, as was discussed earlier, carbon has been observed primarily in carbide form after CO₂ exposure at 550°C. While carbon appears not to have saturated the gauge of tensile samples used in this work, the embrittlement from Cr-carbides at a depth of 125µm (the estimated carburization distance from the magnetite-spinel interface which defines the original surface) would compromise roughly 30% of the gauge cross-section.

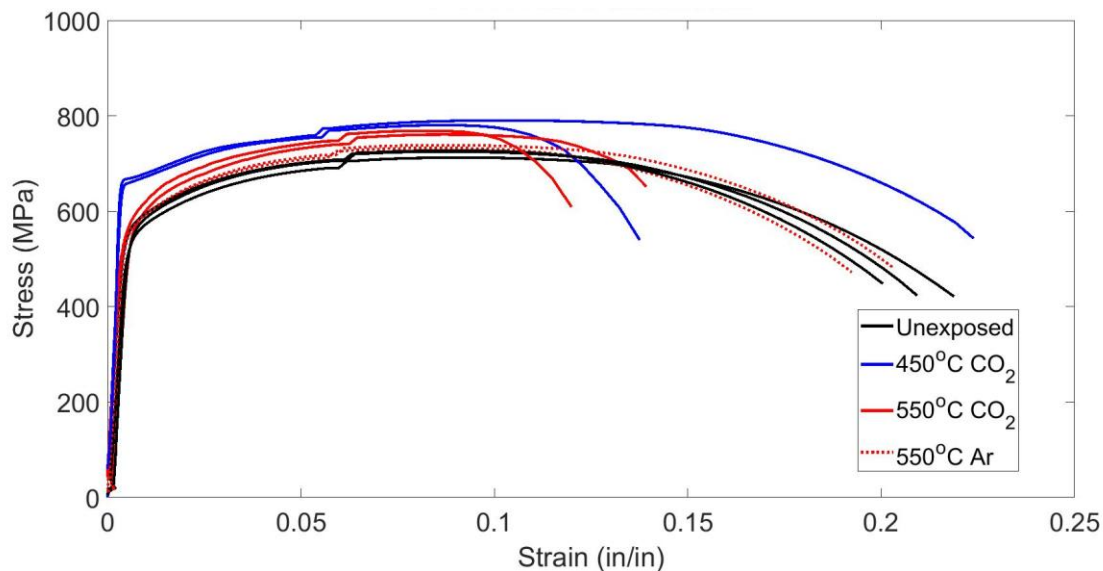
7.3. Mechanical Analysis

7.3.1. Tensile Results

Tensile results, given in Table 13, indicate that strengthening occurs after both CO₂ exposures, for both welded and base material. For base material, the 450°C resulted in a 20% increase in yield strength (YS) and a 10% increase in ultimate tensile strength (UTS). The measured elongation decreased by 12%, but the large variance of results indicated no statistically significant drop in elongation (Figure 82 shows that only one sample exhibited decreased elongation). Meanwhile, the samples exposed to CO₂ at 550°C experienced moderate increases in YS and UTS – 5% and 7%, respectively – with a 32% loss in elongation relative to unexposed. In contrast to this, there was no observed mechanical effects of the neutral environment heat treatment at 550°C, an effect which has been seen before [49], and indicated that laves phase precipitates did not grow to a mechanically detrimental level [55]. The differences in performance from different exposure conditions can be most accurately observed in the stress-strain curves, given in Figure 82.

Table 13 – Tensile results for P92 samples after the given exposure.

	UTS (MPa)	0.2% YS (MPa)	Elongation (%)	Failure Location
Base: Unexposed	722 ± 4	562 ± 5	20.7 ± 0.5	N/A
Base: 450°C CO₂	785 ± 5	664 ± 4	18.1 ± 4.3	N/A
Base: 550°C CO₂	766 ± 2	577 ± 3	13.4 ± 0.6	N/A
Base: 550°C Aging	735 ± 2	560 ± 1	19.9 ± 0.3	N/A
Welded: Unexposed	669 ± 1	509 ± 10	15.7 ± 0.2	FG-HAZ
Welded: 450°C CO₂	709 ± 3	593 ± 10	14.6 ± 0.2	FG-HAZ
Welded: 550°C CO₂	711 ± 3	518 ± 7	11.2 ± 0.6	FG-HAZ
Welded: 550°C Aging	674	496	15.1	FG-HAZ

Figure 82 – Stress-strain curves for P92 base and welded samples. Shows main differences being increased yield for 450°C CO₂ exposure, and decreased elongation for 550°C CO₂ exposure.

Welded samples exhibited similar results. 450°C exposure in CO₂ resulted in a 16% increase in YS and a 6% increase in UTS, with only a 7% drop in elongation relative to unexposed. Exposure to CO₂ at 550°C resulted in a negligible effect on YS and a 6% increase in UTS, with a drop in ductility of 29%. This is a very similar effect to that of base material: while CO₂ exposure at 450°C increased strength with little or no cost in ductility, exposure at 550°C began to have a negative effect on mechanical properties. In another similar result to that of base material, neutral aging at 550°C resulted in no meaningful change in tensile properties. These effects can easily be seen in the stress-strain curves shown in Figure 83. Regardless of

exposure, all samples appeared to fail in the HAZ, likely in the fine-grained HAZ (FG-HAZ), which has previously been identified as a weak point in P92 welds [69].

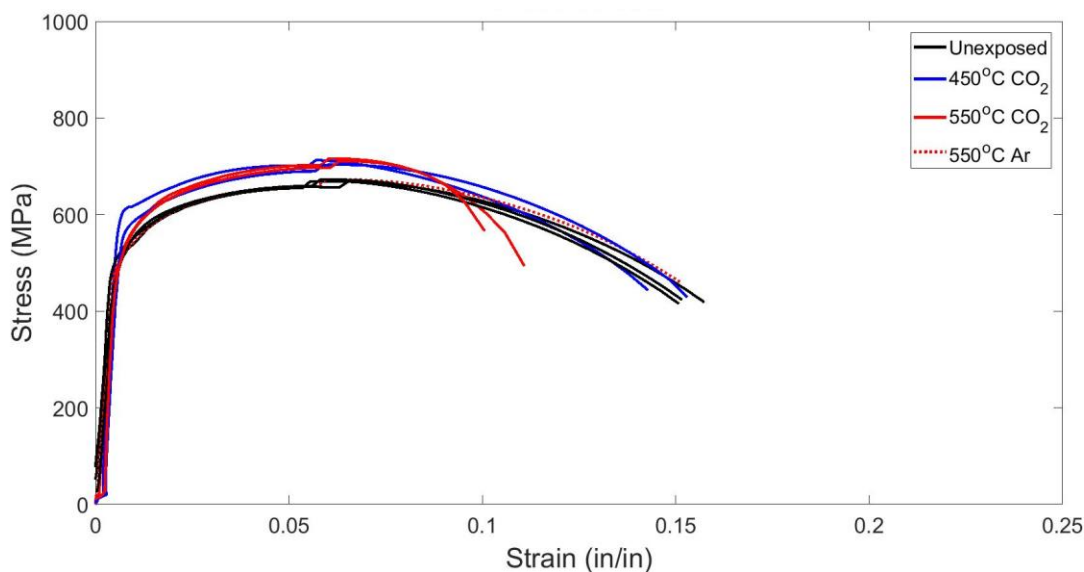


Figure 83 – Stress-strain curves for several of the welded P92 samples.

The tensile results showed that welded samples were consistently weaker and less ductile than the base material. However, both welded and base samples exhibited the same response to exposure relative to the unexposed condition. This shows that welding did not impact the mechanical response to either heat treatment or the s-CO₂ environment for P92. It also mirrored the results of mass change and both oxidation and carburization analyses, so it can be determined that the effect of the s-CO₂ environment is the same on base and welded samples. Therefore, the differences between base and welded samples will not be commented on in the following section, as the analysis would be redundant.

Additionally, after exposure to CO₂ at 550°C, 20MPa for 1,000 hours, base material lost 29% of its ductility, while welded samples lost 35%. These values are very close to the 30% of the cross-section that corresponds to the internally oxidized and carburized regions discussed in sections 7.2.2 and 7.2.3. While there may not be such a linear relationship between ductility and corroded volume, the scale of the effects

is similar enough to indicate a trend worth following. The precise failure mode will be analyzed in more detail in the following section.

7.3.2. Fracture Surface Analysis

The fracture surfaces of pulled base material samples were examined for differences in rupture mechanism. As can be seen in Figure 84 A, unexposed P92 exhibited necking of the gauge, corresponding to the ductility observed after peak stress in the stress-strain curves (this region can be seen in Figure 82 and Figure 83). Figure 84 B shows that the fracture surface was composed of a majority of MVC with micron-scale dimples as well as some brittle cleavage, each corresponding to the microstructural phases, soft ferrite and hard martensite. The prolonged aging at 550°C for 1,000 hours did not change this fracture mode, as shown in Figure 84 C and D. The exposure of base material to 450°C for 1,000 hours resulted in a similar fracture surface. Figure 84 E and F show slightly less necking (image taken from the less ductile of the two samples), but with the same mixture of micron-scale dimples and cleavage. The shared mode of fracture between unexposed, 550°C aged, and 450°C CO₂-exposed samples indicates that the ductility of the material did not change significantly from either exposure. For 450°C CO₂, this means that the more ductile of the two tested samples was likely to be more representative of what would typically occur, and the lower ductility of the other could be due to a manufacturing impurity that was magnified by the small dimensions of the samples used in this study.

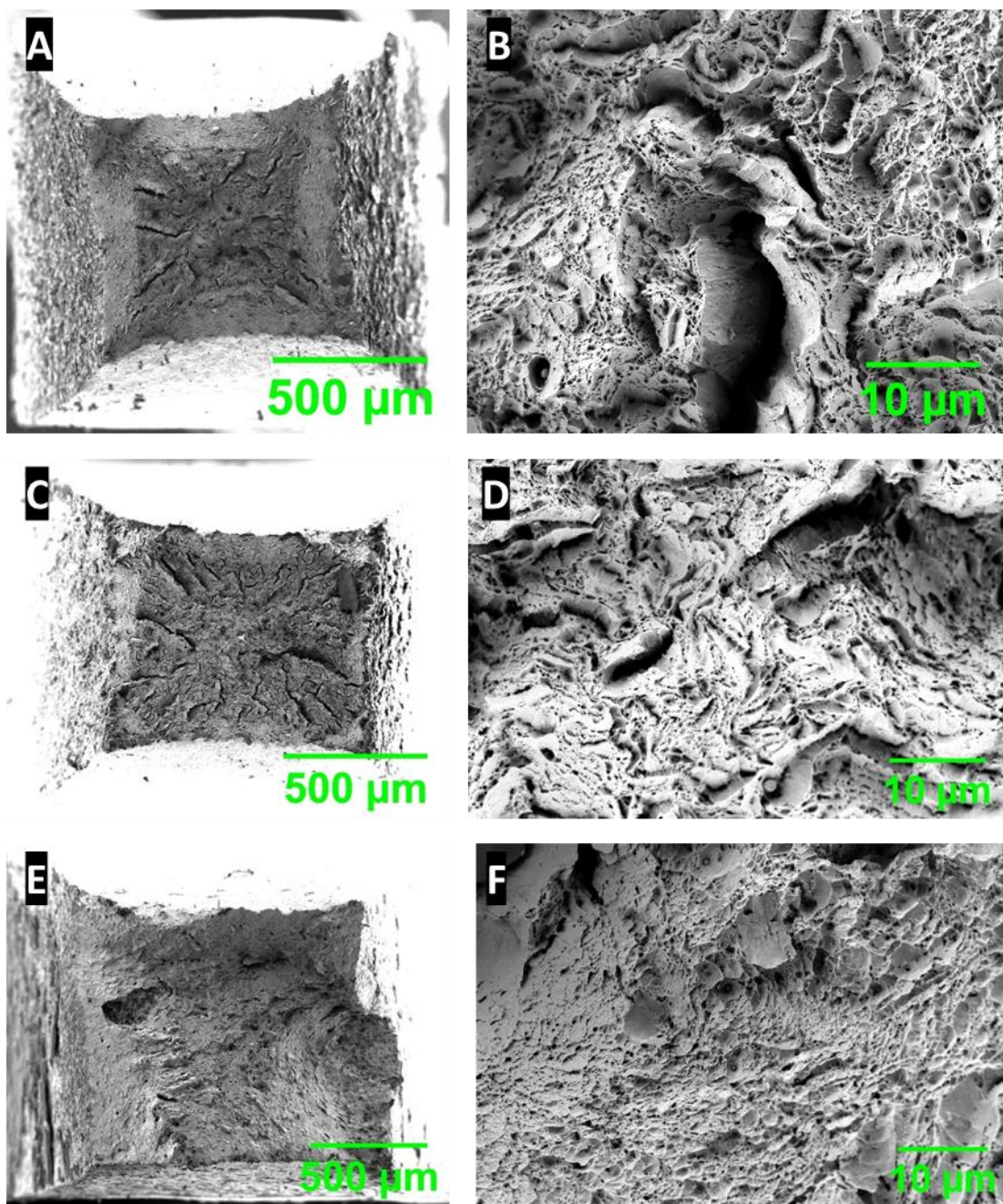


Figure 84 – Fracture surface images for P92 base material ruptured unexposed (A,B) and after neutral aging at 550°C (C,D) show a mixture of micron-sized dimples (MVC) and cleavage, combined with overall sample necking. Fracture surface images for CO₂ exposed at 450°C (E,F) show a similar mixture of MVC and cleavage, with decreased sample necking corresponding to lowered elongation observed in this sample.

As seen in Figure 85, analysis of the samples exposed to CO₂ at 550°C showed an altered fracture surface.

There was little-to-no localized necking observed, corresponding to the lowered elongation in the tensile

results. In addition, while there was still a mixture of MVC and cleavage, the sample cross-section was divided into roughly equal regions in which MVC dominated (Figure 85 B) and cleavage dominated (Figure 85 C). These regions were not depth-dependent, though they could be the product of outer carbide embrittlement. Coarsened carbides could have initiated cracks which propagated through grain boundaries into the depths of the material, producing the fracture surface imaged here. Whatever the cause of the location of the two different failure regions, there is an effect of coarsening of carbides which has caused embrittlement [55], [56], [59].

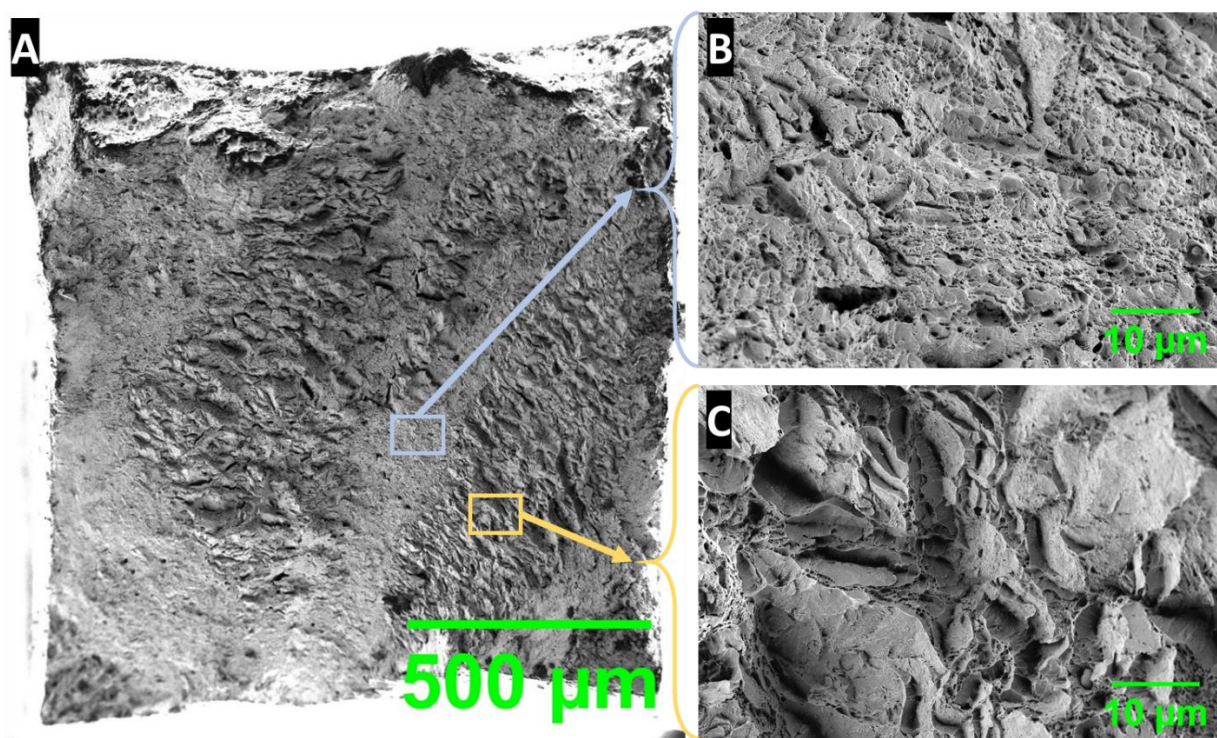


Figure 85 – Fracture surface images for CO₂-exposed base material at 550°C. Characterized by very little necking, as well as regions dominated by a roughly even split of regions dominated by MVC (B) and cleavage (C).

7.4. P92 Overall Summary

Exposures of P92 in CO₂ at 20MPa for 1,000 hours were completed at temperatures of 450°C and 550°C, and a comparative aging study was completed in Ar at 550°C, 0.02MPa for 1,000 hours. Similar values for mass gain and oxide thickness, as well as similar mechanical property responses to exposure, allow for

the conclusion that there was no observed difference between welded and base P92. After noting the lowered strength and ductility of welded (and post-weld heat treated) P92 relative to base material, it can be assumed that they will corrode and age equivalently.

Tensile testing showed that P92 exposed to CO₂ at 450°C resulted in increased YS and UTS without any loss in ductility. Conversely, when P92 was exposed to CO₂ at 550°C it exhibited a small increase in strength with a large drop in elongation. These effects were due to the impact of CO₂ corrosion, as the neutral aging at 550°C did not change tensile properties relative to unexposed.

P92 exposed to CO₂ at 550°C produced both a mass gain and oxide thickness of roughly three times that of 450°C exposure. However, GD-OES and etching showed that carbon deposition did not follow this trend, with only an estimated 15% increase of the deposited carbon at 550°C exposure over that at 450°C. The difference in mechanical properties was, therefore, a result of how this carbon interacted with P92 at the different temperatures. It is hypothesized that Cr-carbides form more slowly at 450°C than the rate at which carbon is deposited (through oxidation and diffusion), while the opposite is true at 550°C: carbides form at a rate comparable to carbon availability. This provides an explanation for the similar presence of carbon within P92 at both temperatures, but only an embrittling effect of carbides at 550°C.

There was only a moderate increase in carburization at 550°C, but this does not wholly disprove the hypothesis that oxidation and carburization are linked for corrosion of 9Cr steels in pure CO₂. This simply disproves that the ratio of carbon-to-oxygen deposition is equivalent at every condition. It also proves that the use of higher temperature exposure to definitively project long-term exposure at lower temperatures is not applicable with these temperatures. While significantly longer exposure of 450°C may result in Cr-carbide formation that embrittles the material, the depth of carburization and the distribution of carbides will be different than those in an equivalently embrittled specimen exposed at 550°C.

Carbide growth dominated the mechanical response of P92 to prolonged exposure. 1,000 hours of exposure to CO₂ at 450°C did not develop carbides beyond the critical size where embrittlement occurred. Conversely, the 550°C CO₂ exposure experienced carburization which affected the ductility severely; as seen from the embrittled fracture surface, the carbides negated all localized necking observed in all other sample conditions. This carburization produced a high density of carbon within 100-125µm of the oxide which indicated significant carbide growth. Additionally, the oxidation and carburization profiles matched the established theory of P92 corrosion in CO₂: the available space model along with preferential internal oxidation of Cr, creating an internal oxidation zone beneath the Fe-Cr spinel.

The performance of P92 in these environments is, therefore, dependent on two variables: the availability of carbon, and the temperature. With a lot of deposited carbon at 450°C, there was no observed embrittlement, likely due to only moderate carbide precipitation and coarsening after 1,000 hours. With a moderately increased carbon availability at 550°C, there was significant embrittlement, likely from the temperature being in the range of rapid Cr-carbide formation. However, throughout thermal aging – with no carbon deposition – the temperature was high enough to encourage Cr-carbide precipitation and coarsening, and no embrittlement was observed. Without the presence of excess carbon, temperature, and enough time to precipitate and coarsen carbides, there will be no embrittlement of P92 in this high temperature environment.

8. Dissimilar Welds:

The transitions between high temperature and medium or low temperature sections of a cycle often require the joining of dissimilar alloys. Dissimilar welding is typically a more difficult process than similar welding, as the filler metal cannot be optimized for one microstructure – it must find a compromise between two alloys that can often be extremely different. Therefore, a complete characterization of candidate alloys is made through analysis of the dissimilar welds to those candidate alloys in different temperature regimes. For this purpose, the high temperature alloys analyzed here (740H and 282) were welded to each of the medium temperature alloys (316L and P92). These welds were performed by and according to procedures researched by the manufacturers of the superior alloys, with filler metals recommended for these specific dissimilar welds. They were then be placed in the same environments as the medium temperature alloys, corresponding to the theoretical location of these welds in an operational power cycle.

8.1. Dissimilar Welding of 740H

8.1.1. Sample Procurement

740H was welded to both 316L and P92. INCONEL filler metal 82 (FM82) was used as filler because – based on conversations with Brian Baker and Ronald Gollihue at Special Metals – it had produced the best results in terms of mechanical strength between the alloys. For consistency, P92 and 316L were provided from the same heat as the material analyzed in previous chapters.

8.1.2. Initial Weldment Analysis

Initial welds were performed with the following procedure: flat, butt weld with no root gap; 10.5V arc voltage; 9.5 in/min travel speed; 20 in/min wire speed; and 150A current. Weldments were received in the form of 1/8” thick plate. Weldments were then milled to roughly 0.063” thickness to remove surface

defects, just as the similar welds were in previous chapters. A sample of each weld was then analyzed for weld quality control. It was then discovered that, similar to the first similar weld of 740H, the weld procedure resulted in incomplete fusion. Figure 86 shows etched optical images of each dissimilar weld after machining to 0.063" thickness, and they confirm that incomplete fusion occurred in both cases.

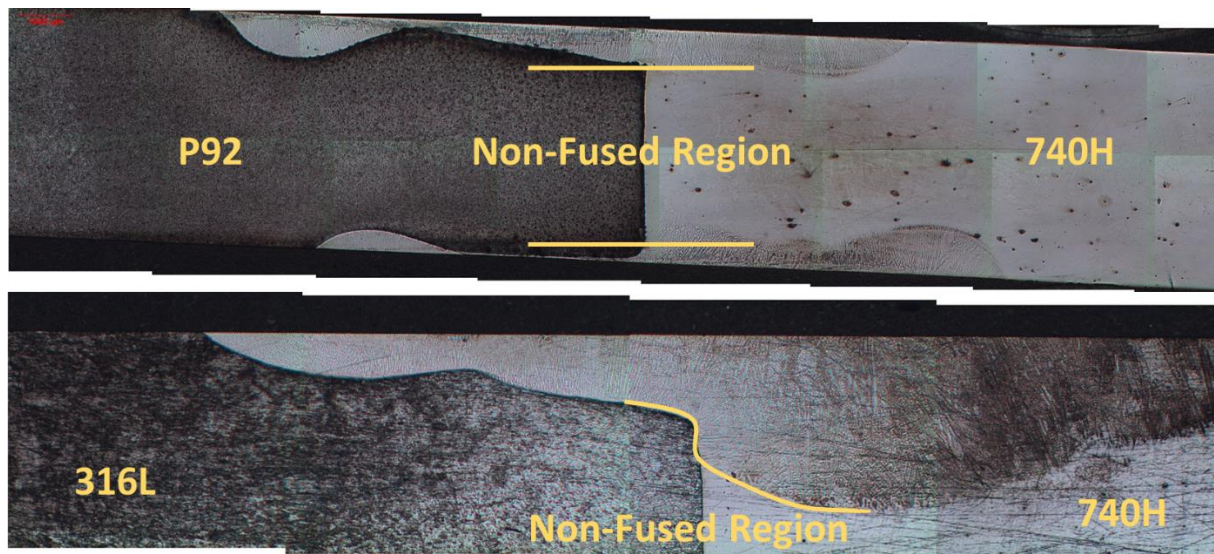


Figure 86 – Optical images of etched as-received weldments of dissimilar welds with 740H. Welding was performed with a root and cap pass, but did not achieve full penetration in either weld.

Tensile results confirmed that these welds were not of representative quality, with premature failure occurring in nearly each trial, see Table 14. Further, all samples failed at the interface between the two plates, supporting the conclusion of incomplete fusion.

Table 14 – Tensile results from the initial dissimilar welds of 740H

Sample	UTS (MPa)	YS (MPa)	Elongation (%)	Failure Location
740H-P92 #1	230	---	0.08	P92/740H Interface
740H-P92 #2	472	---	0.25	
740H-316L #1	600	303	47.7	316L/740H Interface
740H-316L #2	567	307	47.1	
740H-316L #3	498	317	14.3	
740H-316L #7	524	329	18.3	
740H-316L #8	532	335	18.3	
740H-316L #9	559	319	26.5	

8.1.3. Weldment Analysis – New Procedure

Because of the above analysis, the alloys were re-welded with a revised procedure matching that in Table 20, the most important addition being a wide root gap to ensure complete melting within the fusion zone. Complete penetration was confirmed by Special Metals prior to analysis at UW-Madison. However, subsequent tensile analysis of welded samples revealed properties still lagging behind those reported by Special Metals. As can be seen in Table 15, tensile results were inconsistent in a manner which had nothing to do with exposure. Dissimilar welds to 316L actually exhibited worse performance with the new weld condition.

Table 15 – Tensile results from the new procedure for dissimilar welds of 740H

Sample	UTS (MPa)	YS (MPa)	Elongation (%)	Failure Location
740H-P92 #2 (550°C CO ₂)	738	460	16.5	Fusion Zone
740H-P92 #3 (550°C CO ₂)	741	493	13.1	
740H-P92 #4 (550°C CO ₂)	599	537	4.0	
740H-P92 #6 (450°C CO ₂)	699	503	12.4	
740H-P92 #10 (Unexposed)	484	458	5.8	
740H-316L #2 (550°C CO ₂)	316	236	6.7	Fusion Zone
740H-316L #3 (550°C CO ₂)	324	202	5.5	
740H-316L #4 (550°C CO ₂)	195	166	3.6	
740H-316L #5 (550°C CO ₂)	519	331	17.0	
740H-316L #7 (Unexposed)	360	249	7.3	

Because the fusion zone was the failure location in all samples, the weld was analyzed for possible cracking. Figure 87 shows that cracks were indeed observed within the fusion zones of both dissimilar welds. The differences in performance between the P92 welds – in which some samples performed well and others didn't – and 316L welds – which all performed below expectations – was then hypothesized. The cracking in P92 might have originated at the weldment surface and propagated inward. This would lead to inconsistent effects on welded samples, given that the surface of weldments were removed through machining. The cracks in 316L, on the other hand, appeared to have originated in the bulk of the

fusion zone during cooling, possibly due to a gradient in composition or another factor such as cooling rate or oxide formation.

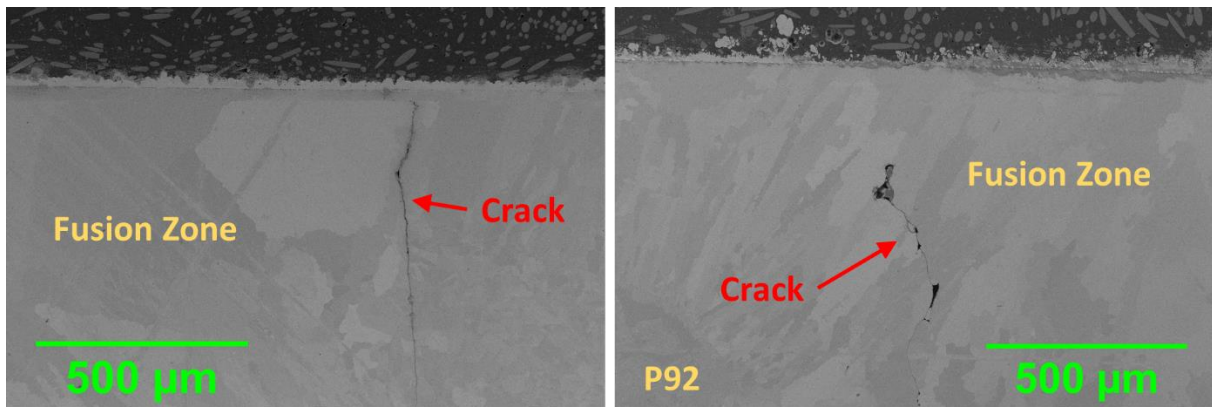


Figure 87 – SEM images of dissimilar welds between 740H and 316L (left) and P92 (right). Show cracking within the weld zone for both cases.

8.1.4. Corrosion Performance of 740H Dissimilar Welds

Despite the presence of cracking in the welds, the corrosion performance of the weld was still analyzed. This was done to understand the performance of the corrosion in each alloy in close proximity to a dissimilar material. Mass change, given in Figure 88, shows that the samples which were dissimilar welded to P92 showed decreased oxidation compared to base P92. Corrosion samples were typically comprised of 60-80% inferior alloy, so this makes sense for P92 samples. Dissimilar welds to 316L, however, exhibited equivalent mass gain. This is likely due to the high performance of 316L at 550°C, which is very similar to that of the INCONELs.

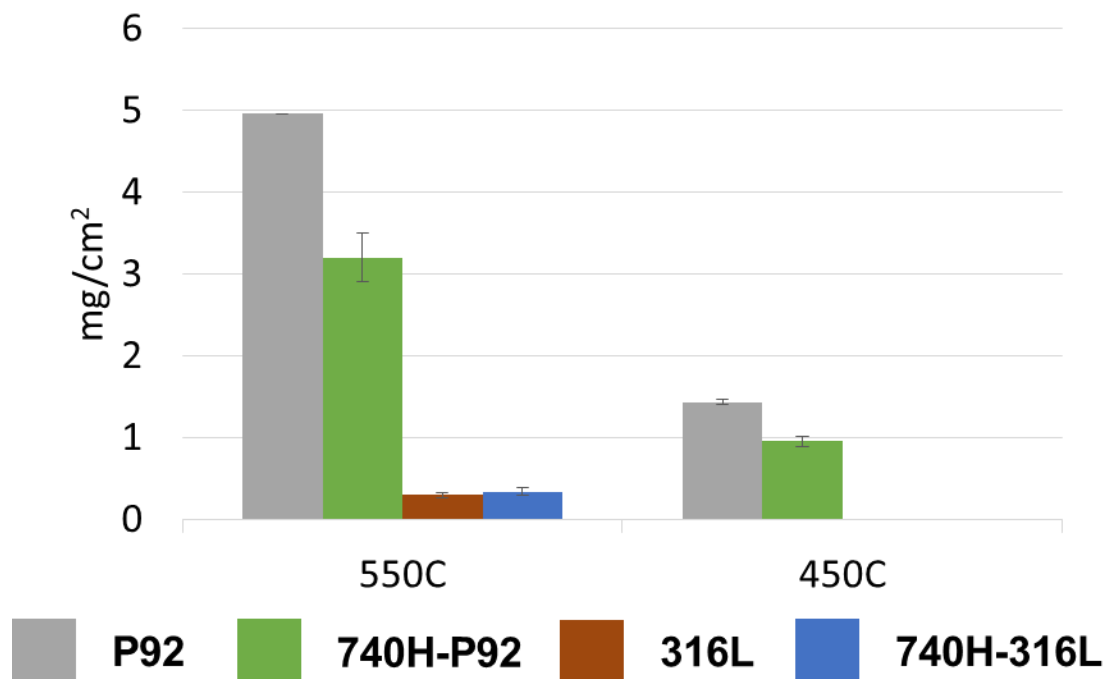


Figure 88 – Mass change for 740H dissimilar welds compared to the inferior alloy base material

As can be seen in Figure 89, oxidation remained constant within the P92 HAZ, and then decreased immediately when P92 gave way to the fusion zone and FM82. This indicates that there was no observed galvanic corrosion at the interface between the dissimilar metals. The high Cr and Ni content of FM82 provided good corrosion resistance – on the order of 740H – growing a very thin chromia oxide layer. The carburization region on P92 was seen to have extended into the alloy, but did not penetrate the fusion zone. The interface of the dissimilar weld to 316L was also analyzed, but no obvious corrosion differences between the two materials were observed, as both exhibited very thin, protective chromia scales.

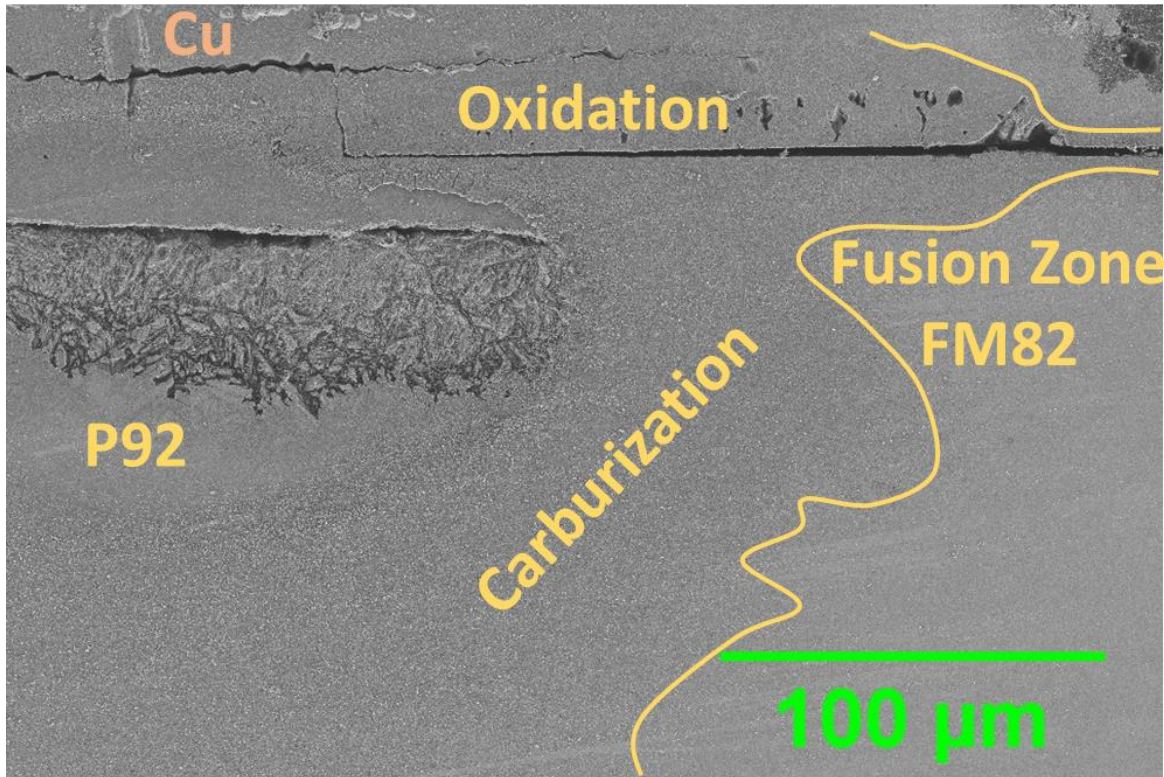


Figure 89 – HAZ/fusion interface for 740H-P92 weld exposed to CO₂ at 550°C, 20MPa for 1,000 hours.

8.1.5. 740H Dissimilar Welding Summary

Welds were performed by the welding research lab of Special Metals, the manufacturer of 740H. While previous work had been performed to create a dissimilar welding procedure to the two alloys analyzed here, P92 and 316L, this procedure proved insufficient to create a weldment of good mechanical strength with repeatability. Because of this, no accurate analysis of mechanical performance after exposure to CO₂ was possible for these dissimilar welds. Work was then done to analyze the specific failings of this procedure. The first issue – incomplete penetration – was solved by changing a few parameters of weld speed and power along with introducing a root gap between the plates. The second issue – cracking within the fusion zone – will need to be solved in future work. This indicates that with 740H, which was seen to be difficult to weld to itself in section 4, it is generally difficult to achieve consistent results from

welding. Therefore, each type of weld that involves 740H in an industrial application should first be developed to have a specific procedure for good, repeatable quality.

Corrosion analysis of the weld indicated no ill effects associated with galvanic corrosion. Mass change indicated that there was no corrosion increase due to the dissimilar joining, showing reduced or similar corrosion relative to base material of the inferior alloy. In addition, FM82 exhibited good corrosion resistance up to 550°C. With dissimilar welding to P92, there was no carburization found within the fusion zone. All observed carburization appeared to remain contained within P92.

8.2. Dissimilar Welding of 282

8.2.1. Sample Procurement

282 was welded to both 316L and P92 according to the procedure given in Table 20. Welding was performed by Jeremy Caron of the Research and Technology Group of Haynes International. Similar to 740H dissimilar welds, P92 and 316L were provided from the same heat as the material analyzed in previous chapters to ensure consistency in analysis between similar and dissimilar welds.

8.2.2. Weldment Analysis

The weldment was analyzed for full penetration and cracking. Figure 90 shows that the root and cap pass were sufficient to achieve full penetration for both welds. In addition, no cracking was observed in the HAZ or the fusion zone of either weld. This indicates that the welds were of good quality and would perform well mechanically. As is seen below, this was the case.

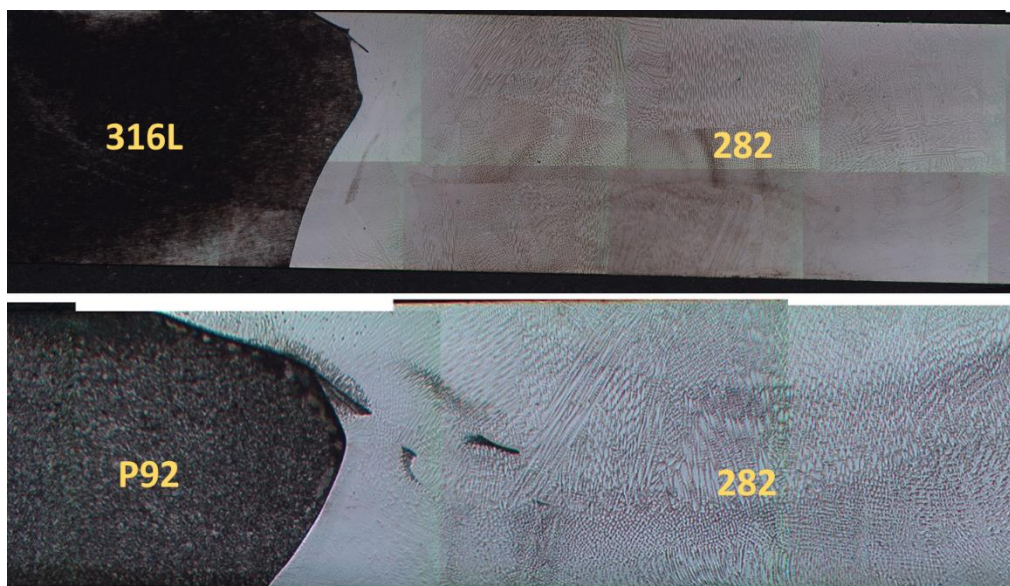


Figure 90 – Optical images of etched as-received weldments of dissimilar welds with 740H. Welding was performed with a root and cap pass and achieved full penetration.

8.2.3. Corrosion Performance of 282 Dissimilar Welds

As the 282 dissimilar welds were found to be of good quality, samples of each weldment were exposed to CO₂. 316L welds were exposed to 550°C in both CO₂ and Ar, while P92 welds were exposed to CO₂ at both 450°C and 550°C and aged in Ar at 550°C, all for 1,000 hours. The corrosion performance of these dissimilar welds was analyzed below.

8.2.3.1. Mass Change

Similar to that of 740H, all dissimilar welds performed as expected in terms of corrosion. All mass data, given in Figure 91, showed that mass change for the dissimilar welds was roughly 60-70% that of the inferior base alloy. Samples contained 60-80% of the Fe-based alloy, so this was consistent corrosion performance with what was anticipated relative to the base inferior alloy. In addition, mass change measurements were performed for 550°C neutral aging for quality assurance, and were found to be negligible. While mass change showed that there was no catastrophic damage to the corrosion resistance

due to joining these alloys, the oxide must be analyzed to give a more detailed understanding of localized phenomena.

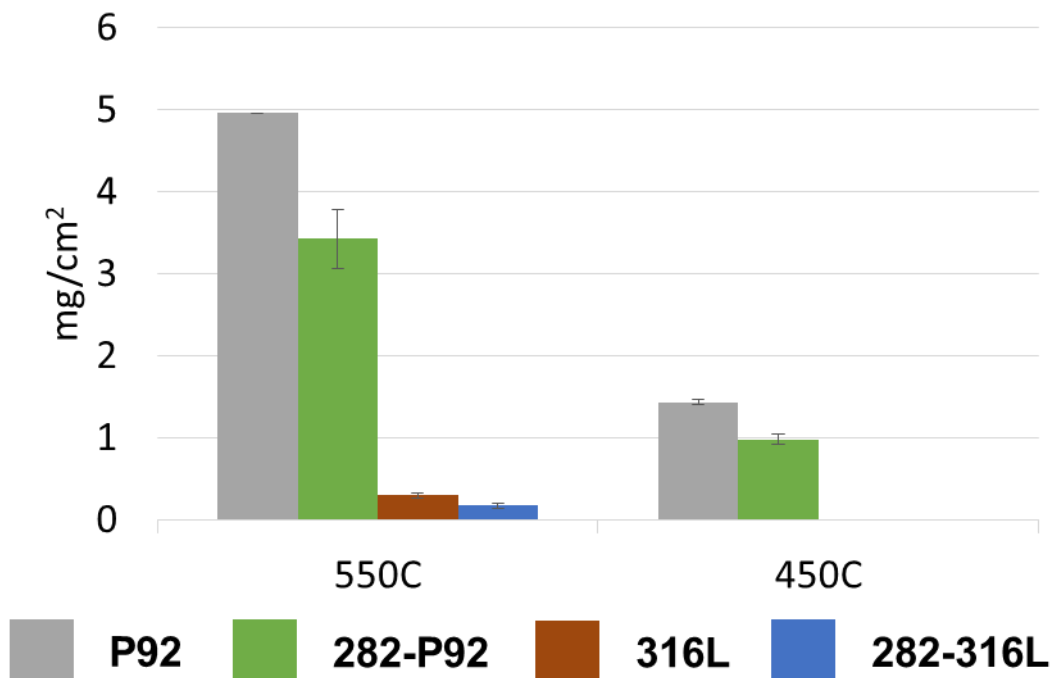


Figure 91 – Mass change for 1,000 hours of exposure for 282 dissimilar welds compared to the inferior alloy base material.

8.2.3.2. Oxide Analysis

Oxidation was observed to be very consistent in P92, similar with what was seen above for the base and similar welded material. However, at the interface with 282 there was an increase in oxide thickness in both 450°C and 550°C. As is shown in Figure 92, the oxide increased in thickness from ~11-12µm to ~17µm in 450°C and from ~35µm to ~44µm in 550°C. As was discussed above in section 7, this phenomenon was not observed along grain boundaries. It is believed, therefore, that the interface with the fusion line functions as a diffusion pathway for both Fe and O to increase local oxidation.

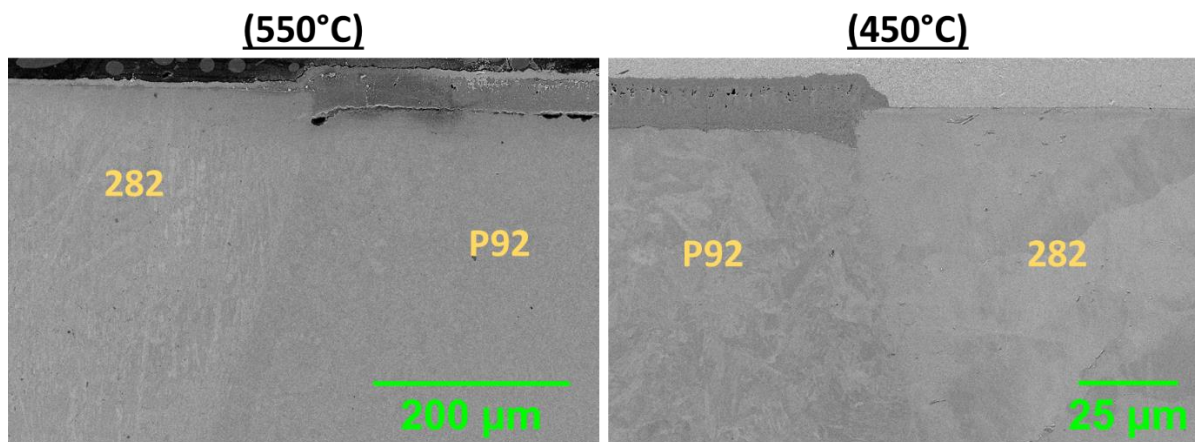


Figure 92 – Cross-sectional images of the interface between P92 and the fusion zone, comprised of 282 filler, after exposure to CO₂ at either 550°C (left) or 450°C (right). Shows that there was increased corrosion within a few microns of the interface during both exposures.

8.2.3.3. Surface Analysis

Figure 93 shows surface SEM of this interface for 282-P92 welds after exposures to 550°C and 450°C in CO₂ for 1,000 hours. Both temperatures reveal different performance from each alloy. In 450°C, 282 exhibited a primarily Cr₂O₃ scale, but such little oxidation occurred that the polishing lines from the original sample preparation was still visible. After 550°C exposure, a more developed Cr₂O₃ oxide was present, along with nodules of thicker oxide. EDS line scans, shown in Figure 94, identified these nodules as primarily TiO₂, and that they were also present in 450°C, just not visible in image in Figure 93.

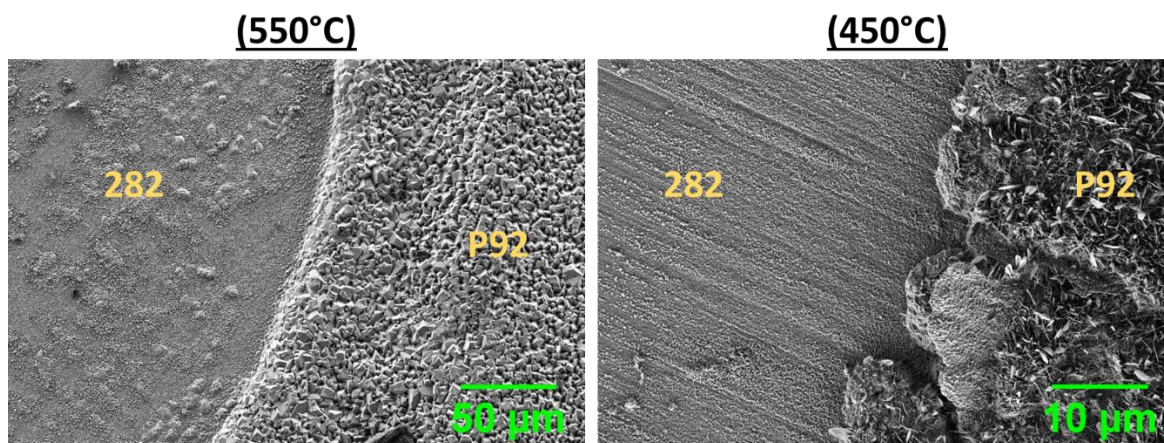


Figure 93 – Surface SEM of the interface of 282-P92 after exposure at 550°C (left) or 450°C (right). External surface shows columnar magnetite at 550°C and whisker hematite at 450°C.

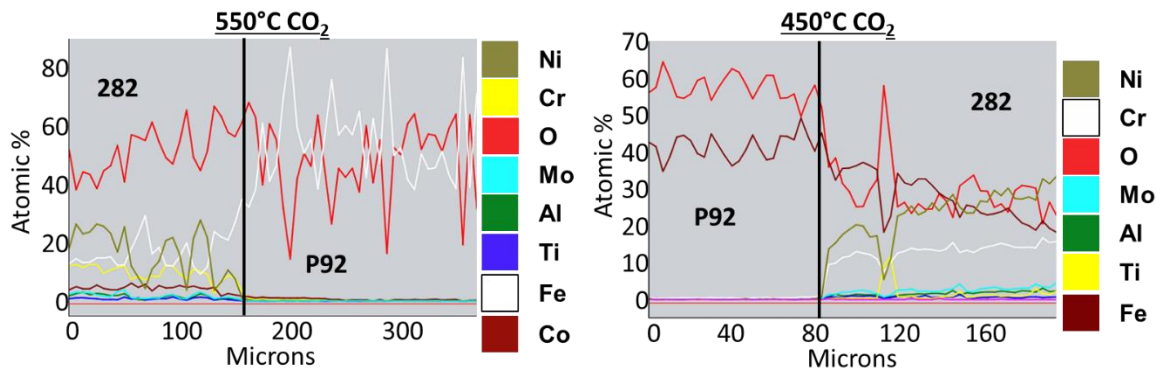


Figure 94 – Surface EDS line scans across the interface of the fusion zone (282) and the P92 HAZ after exposure to CO₂ at 550°C (left) or 450°C (right).

Also shown in Figure 93 is that P92 has different growth of oxide on the surface at each temperature. As discussed in section 7, P92 exhibits hematite on the surface after exposure to CO₂ at 450°C. Figure 95 shows an SEM image of this surface layer, with the main surface feature covering P92 in the right image of Figure 93 being the needles or whiskers of hematite growth. This layer was not present after exposure at 550°C, as was seen in section 7.

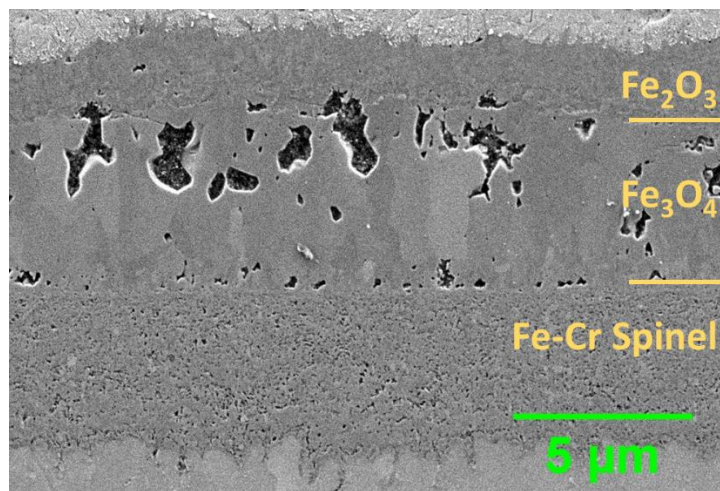


Figure 95 – SEM images of the oxide grown after exposure of P92 to CO₂ at 450°C, 20MPa for 1,000 hours. Both oxides are identical to what was seen in base or similar welded material.

As was discussed in section 8.2.3.2, there was not much corrosion which occurred in the 282-316L. Figure 96 shows an EDS map of the interface between the materials. As can be seen, there was very little oxide formation on either material. In fact, at the location analyzed here, there appears to be a stronger O

signal coming from the 282 than from the Fe-based 316L. This is an example of how little oxidation there was seen on both of these materials, even near the interface of one another.

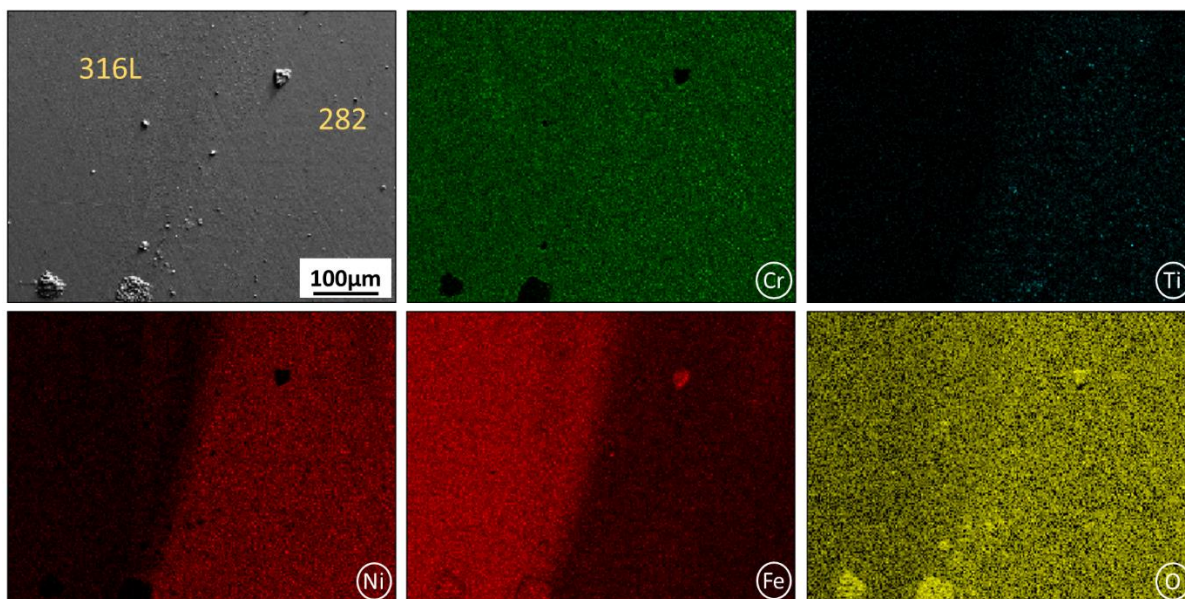


Figure 96 – EDS of interface between 282 and 316L after exposure to CO₂ at 550°C, 20MPa for 1,000 hours.

Overall, the samples appeared to corrode equivalently to the base metals. A small increase in oxide depth within a few microns of the interface of P92 with 282 was seen as the only corrosive impact of the dissimilar welding. This increase is believed to occur due to the mismatch of the ferritic-martensitic microstructure of P92 and the austenitic microstructure of 282. It allowed for an accelerated pathway for diffusion of Fe ions outward and O ions inward to enhance oxidation. Samples are anticipated to respond mechanically to exposure very similarly to that of the base material of the inferior alloy.

8.2.4. Mechanical Performance of 282 Dissimilar Welds

8.2.4.1. Tensile Results

Tensile samples were pulled in the as-welded (and PWHT, in the case of P92) condition, as well as after every exposure. The tensile results, along with the number of tensile samples, for each condition are provided in Table 16. 282-P92 samples responded to exposure in a very similar manner to that of similarly

welded P92. UTS increases were similar in both CO₂ exposures, and while YS increased as well, a more dramatic increase was observed in samples exposed at 450°C. Also, elongation actually improved after 450°C exposure – likely a figment of a small sample size – and decreased significantly after 550°C exposure. While the numbers in Table 16 appear to indicate that 550°C aging had an effect on UTS and YS, this is the result of being removed from a separate segment of the weld which was of higher quality. The two unexposed samples tested from this section of weld produced very similar results to those after thermal aging. Therefore, no mechanical change is ascribed to thermal aging.

Table 16 – Tensile results for 282 dissimilar welds before and after high temperature exposure

	UTS (MPa)	0.2% YS (MPa)	Elongation (%)	Failure Location	Samples Tested
282-P92: Unexposed	662 ± 6	509 ± 4	14.6 ± 0.3	P92 FG-HAZ	8
282-P92: 450°C CO₂	750 ± 4	616 ± 3	15.6 ± 0.1	P92 FG-HAZ	2
282-P92: 550°C CO₂	752 ± 4	561 ± 6	9.4 ± 0.1	P92 FG-HAZ	2
282-P92: 550°C Aging	694 ± 3	533 ± 10	12.3 ± 0.5	P92 FG-HAZ	3
282-316L: Unexposed	536 ± 29	273 ± 15	52.5 ± 2.2	316L HAZ	3
282-316L: 550°C CO₂	575 ± 16	294 ± 9	52.2 ± 1.9	316L HAZ	4
282-316L: 550°C Aging	613 ± 3	353 ± 12	41.0 ± 3.8	316L HAZ	3

The 282-316L dissimilar welds also responded like the similar welds of the inferior alloy. Due to small sample sizes, there was no statistically significant difference between the values before and after exposure to CO₂ at 550°C. The average values were very similar to those of similarly welded 316L, but it appeared that the quality of each weld was variable enough that the errors overlapped. Finally, in a similar fashion to the 282-P92 welds, a different plate was used for the 550°C aging test than was used for the other testing. There appeared to be high variance between different sections of the same weldments for all of the dissimilar welds studied here, which was likely the culprit behind the enhanced strength and lowered elongation observed in the 282-316L 550°C aged samples.

8.2.4.2. Fracture Surface Analysis

In addition to the tensile results, the fracture mode of the dissimilar welds mirrored that of the similar welds of the inferior alloys. Figure 97 A and B show the fracture surface of a 282-P92 weld which had

been exposed to CO₂ at 450°C, 20MPa for 1,000 hours. This surface was effectively identical to that of unexposed, as well as that of P92 similar welds: localized necking along with a combination of MVC with micron-scaled dimples and brittle cleavage. Additionally, Figure 97 C, D, and E show that the fracture surface of 282-P92 which was exposed to CO₂ at 550°C also had the same appearance as similar welded P92 in the same conditions: little-to-no necking and two distinct regions of fracture in which cleavage dominated (shown in Figure 97 D) or MVC dominated (Figure 97 E). It should be noted that while the fracture surfaces of unexposed and 550°C aged samples are not shown here, they appeared identical to those of P92 similar welds tested at the same conditions

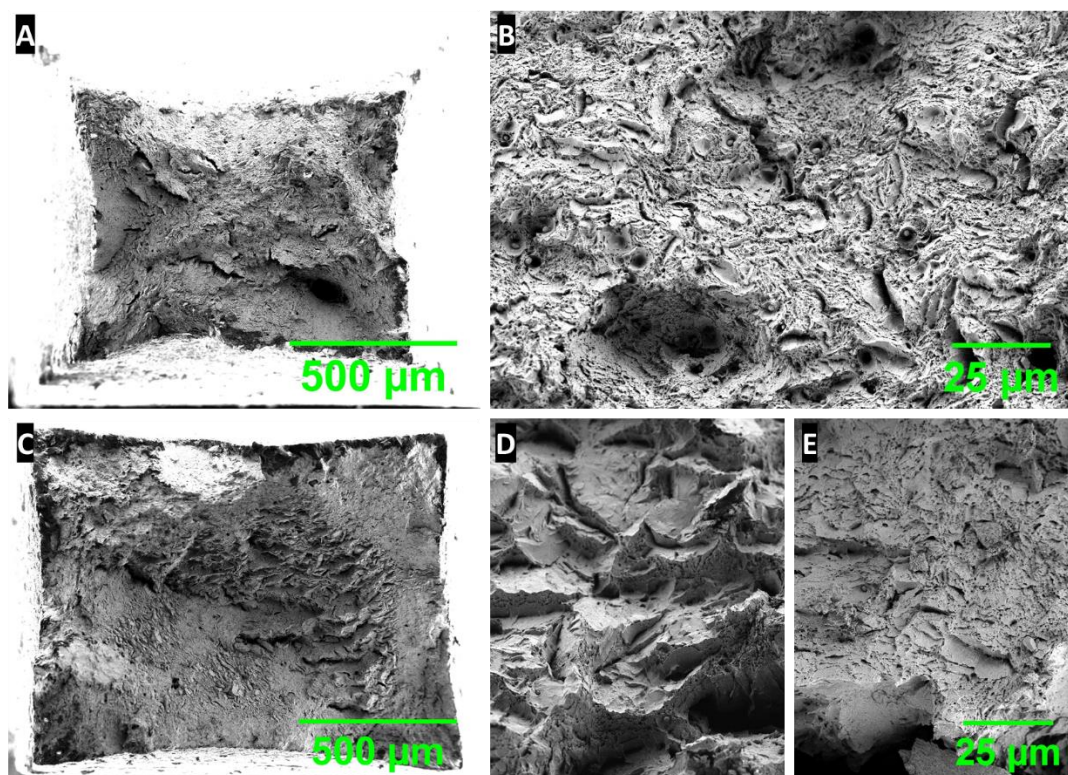


Figure 97 – Fracture surface images of 282-P92 dissimilar welded samples after exposure to CO₂ at 450°C (A,B) or 550°C (C-E). Fracture surfaces appear very similar to those of similar welds.

The fracture surface of a 282-316L sample after exposure to CO₂ at 550°C, 20MPa for 1,000 hours is shown in Figure 98. As can be recalled from section 6, the fracture surface observed here looks almost exactly like that of base 316L which was exposed in either CO₂ or Ar at 550°C. As the failure for this dissimilar

weld sample occurred inside the HAZ, it can be understood that σ -phase precipitation and growth were effectively identical in both base material and the HAZ. Finally, the fracture surfaces of unexposed and 550°C aged samples are not shown here, as they also appeared identical to those of 316L base material in the same conditions.

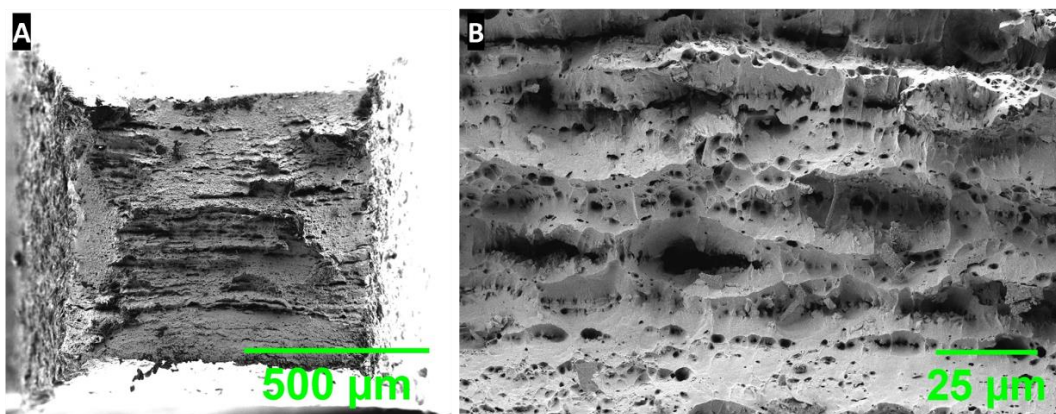


Figure 98 – fracture surface of a 282-316L sample after exposure to CO₂ at 550°C. Fracture surface identical to that of base 316L exposed in the same conditions.

8.2.5. 282 Dissimilar Welding Summary

282 dissimilar welds were performed by Haynes International and confirmed to be of good quality, with full penetration and no observed cracking. Overall corrosion was very similar to that of the base material of the inferior alloy. Oxide thickness was observed to be very consistent, with the one exception of the oxide of P92 on the interface with 282. This interface is believed to have acted as a diffusion pathway for Fe and O ions, and resulted in a local increase in oxide thickness of 5-10µm. Mechanical analysis identified that the dissimilar welds responded to the high temperature environments in nearly identical fashion to that of the similar welds of the lesser Fe-based alloys. This is a promising result for the potential application of these alloys in an s-CO₂ Brayton cycle.

9. Improving Corrosion Resistance

9.1. Corrosion in CO₂

9.1.1. Alloy Corrosion

The work presented thus far has covered candidate alloys for use for piping, valves, and other components at medium and high temperature within an s-CO₂ Brayton cycle. Results indicate that Ni-based alloys, such as 740H and 282, were relatively unaffected by corrosion in the s-CO₂ environment up to 750°C and are suitable as construction materials. Similarly, austenitic stainless steels with at least 16% Cr – such as 316L and 316H – performed very well in CO₂ at temperatures up to 550°C. These alloys have each been shown to primarily form a Cr₂O₃ scale which was very thin (1-4µm for 740H and 282 in 750°C, 100s of nm for 316 in 550°C), protective, and both adherent and coherent. The presence of this scale corresponds to no measurable embrittlement due to carburization. This resistance to carbon deposition is due primarily to limiting oxidation, required for the liberation of carbon from CO₂ and CO [84].

These alloys, therefore, perform admirably in CO₂ at the corresponding temperatures and are preferred because of their corrosion performance and high temperature strength. However, they – especially the Ni-based superalloys – come with a hefty price tag, and are often difficult and expensive to machine and weld. This can increase the price of a power cycle components substantially, even to the point of effectively prohibiting the commercial development of the technology. It is very important, therefore, to explore methods of reducing material costs. This chapter explores this possibility of capitalizing on the benefits of the above high-performing alloys by exploring realistic protective coatings that can help to minimize corrosion of lower Ni/Cr alloy metals.

For all of these alloys, the development of a contiguous, protective chromia scale curbs oxygen transport through to the alloy, which in turn reduces carburization. It has been seen in P92 steel – which has been

used in low temperature steam power conversion cycles – that the absence of this protective oxide layer resulted in continual oxidation at a much higher rate than chromia-forming alloys. This alloy, tested in CO₂ at both 450°C and 550°C, oxidizes to form a duplex oxide of an outer magnetite (Fe₃O₄) and an inner Fe-Cr spinel (Fe_{2.3}Cr_{0.7}O₄). This duplex oxide is protective in the short term: it produces oxidation rates which follow parabolic kinetics. However, in the long-term this grade of Fe-based alloy is susceptible to carburization and carbide formation, resulting in embrittlement and potentially breakaway oxidation. This is because, while the Fe-Cr spinel is somewhat protective, it does not inhibit the diffusion of carbon or oxygen as efficiently as the contiguous Cr₂O₃ scales produced in more corrosion-resistant alloys. The development of the duplex oxide should, therefore, not be considered “protective.” Instead, it allows for a higher corrosion rate which lowers the maximum temperature at which the alloy can be used in CO₂. The formation of a more fully protective scale – such as Cr₂O₃ or Al₂O₃ – is desirable for the long-term viability of a material for use in an s-CO₂ Brayton cycle. Therefore, a method which limits corrosion of alloys which form a non-protective scale – like Fe-alloys P92 at or above 450°C and 316 above roughly 600°C – would allow for a precipitous reduction in the overall cycle cost.

9.1.2. Methods of Alloy Protection

Creating an environment which is non-reactive is typically difficult for alloys, as there are often many alloying components with variable reactions with the working fluid. For example, to make Cr non-oxidizing at 750°C, it is necessary to reduce the pO₂ below roughly 10⁻³⁰atm, which is often extremely difficult and still only solves one type of reaction for one alloying element. Therefore, reducing corrosion in alloys typically means either forming a protective, self-healing scale or else slowing the kinetics of oxidation via another means. The former was observed above in the performance of 740H and 282 at 750°C, which typically brings a relatively high alloy cost, as well as 316 at 550°C. The latter is an avenue for creating a high-performing material with minimal increase in cost, and will be explored in this chapter.

Coatings are often used to limit environmental reactions to structural materials. In the CO₂ environment, a coating would be designed primarily to limit carburization – which diffuses deep into the material and mechanically embrittles – and secondarily to curb oxidation. This could be done through many different avenues: coating of a thin Cr or Al layer on the surface, possibly including pre-exposure oxidation; oxide spray coating directly onto the surface; shot-pinning or other surface preparation technique, etc. However, coating is difficult to engineer, and often an issue with Cr and Al is that their oxides have drastically different coefficients of thermal expansion compared with the substrate and spall off during thermal cycling [85].

One avenue which was analyzed in conjunction with this work is the application of a Cu coating which could directly act as a barrier to oxygen and carbon diffusion. A diffusion barrier could slow the oxidation and corrosion process to a point at which alloy lifetimes increase substantially, and it could also encourage the formation of a protective coating by keeping the pO₂ at the surface of the substrate below that needed for Fe-oxidation. The benefits of Cu as a diffusion barrier coating include: it is very ductile; it is very conductive (so coating to a conductive substrate is very simple); it is very adhesive and cohesive; and its thermal expansion (17.1×10^{-6} m/mK) [86] is near that of main-alloying constituents like Ni (15.4×10^{-6} m/mK) and stainless steels like 316 (16.0×10^{-6} m/mK) [85]. This provides a distinct advantage over ceramic coatings, such as Cr₂O₃, in an application which may experience thermal cycling. As will be explained in the following sections, the application of Cu coating as a diffusion barrier coating could drastically reduce CO₂ corrosion and allow the use of lesser alloys at higher temperatures than would otherwise be possible.

Other potential coatings include: Ni, Cr, Cr₂O₃, Al₂O₃, and others. The ceramics are not preferred because cracking would be likely under any conditions of thermal cycling. Additionally, Ni has been shown to oxidize and carburize readily in CO₂ at 750°C [17] and, as will be seen below, it is relatively difficult to ensure it is non-reactive in CO₂. Cr may be an option worth exploring as well. However, the aptitude of

Cr to form Cr-carbides may be problematic for either carburizing from the environment [17] or removing carbides from the underlying material and weakening the substrate.

9.2. Diffusion in Copper

For corrosion to occur beneath a coating, diffusion through the coating must occur. A Cu coating can be applied through several techniques, including thermal spray, electroplating or electroless plating. It is assumed for this work that a technique will be optimized for each material to minimize the voiding within the coating. Diffusion of corroding elements through the coating will, therefore, be dominated by solid-state diffusion. The diffusion rate of C through Cu has been predicted to follow equation (16) [87], while the diffusion of O through Cu is given by equation (2) [88] for 700-1300°C. Estimation of the diffusion coefficients based on these equations at a temperature of 750°C are $6.16 \times 10^{-12} \text{ m}^2/\text{s}$ for C and $4.25 \times 10^{-10} \text{ m}^2/\text{s}$ for O.

$$D_C = 2.35 \times 10^{-11} \exp\left(\frac{Q}{kT}\right) = \left[\frac{cm^2}{s}\right], \quad Q = -0.93 \text{ [eV]} \quad (16)$$

$$D_O = 1.16 \times 10^{-2} \exp\left(\frac{Q}{RT}\right) = \left[\frac{cm^2}{s}\right], \quad Q = -67.3 \text{ [kJ]} \quad (2)$$

This indicates that diffusion of both C and O will be slow through Cu – supported by [89] – but O diffuses roughly two orders of magnitude faster. Therefore, if oxidation can be limited – either through a thick coating or through forming a protective oxide – carbon deposition will necessarily be limited as well. And since this coating is designed primarily to inhibit carbon ingress, it is possible that a very thin coating may be able to effectively eliminate carburization. Further, even the diffusion oxygen appears very small, over 3 orders of magnitude slower than observed with NiO [90], indicating that Cu is a promising diffusion barrier coating relative to other alloys.

In the case of Fe-based alloys, the minimum goal might be to limit the flow of oxygen so that the surface of the underlying alloy experiences only a very low pO_2 . At very low pO_2 (at 750°C, roughly 10^{-21} atm $> pO_2 > 10^{-30}$ atm), Cr will oxidize preferentially over Fe [9]. If the pO_2 can be maintained in this range for a sufficient amount of time to form a protective Cr_2O_3 oxide, the underlying material should not experience carburization. Further, it should exhibit corrosion performance on the order of chromia-forming alloys such as Ni-based superalloys which would persist even if the Cu coating is removed. However, even if a fully-protective oxide is not formed, carbon diffusion should be sufficiently slowed to significantly delay any embrittling effects from carburization and carbide formation. This theory could be utilized to increase the applicable temperature of Fe-based alloys like P92 and 316 up to where the allowable stress is the design-limiting factor, not corrosion performance.

9.3. Thermodynamics of Cu in CO₂

It is important that the coating can survive the environment that it is designed for. Cu is a good barrier for C diffusion, but if it is removed through corrosion from the environment any benefits are removed as well. Figure 99 shows that CO₂ contains a pO_2 which is high enough to oxidize Cu into Cu₂O up to 750°C and above [9]. Cu₂O is not considered a protective scale, and is typically removed from the Cu surface after oxidation, so this high pO_2 condition renders Cu unusable in pure CO₂. However, with the addition of roughly 10ppm CO into CO₂, the pO_2 is lowered and the reaction becomes de-oxidizing at or below 750°C. This means that Cu can be rendered noble in the CO₂ environment with only a very small CO impurity. As 10ppm is a relatively low value – on the order of typical impurity levels in industrial grade CO₂ – the cycle would not need to be re-designed to incorporate different working fluid properties in order to achieve this state in a theoretical Brayton cycle. It is actually likely that this amount of CO will be present in an s-CO₂ Brayton cycle without intentional addition, as the oxidation process causes a CO build-up in the environment [17].

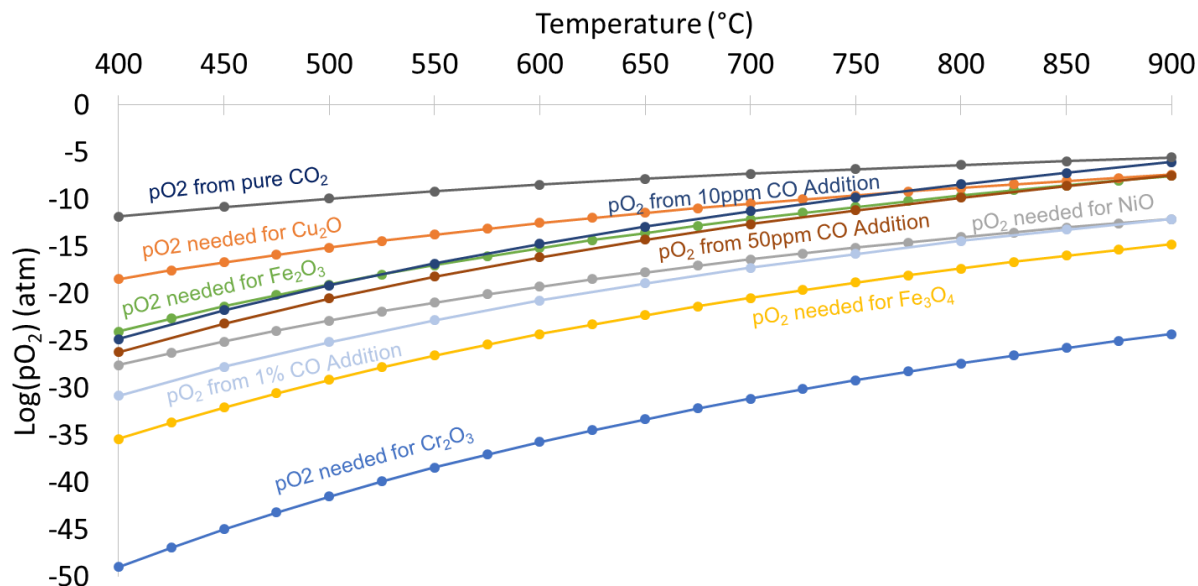


Figure 99 – Thermodynamic calculations for the pO_2 for CO_2 with different CO impurities as a function of temperature, plotted along with equilibrium pO_2 for the labelled oxidation reactions [9].

Through the increase of CO content of CO_2 , it appears possible to manipulate the pO_2 to create non-oxidizing environments for different elements. Figure 99 shows that the addition of 50ppm CO eliminates the formation of not only Cu_2O , but hematite (Fe_2O_3) as well (below about 800°C). Further, the addition of 1% CO renders Ni non-reactive below about 850°C, and further CO addition would eliminate all oxidation of Fe. In addition, small additions of CO have been shown to eliminate excessive oxidation of graphite, which is very useful for nuclear applications [91], [92]. However, CO and CO_2 have significantly different fluid properties [93], so adding significant fractions of CO affects the fluid properties and may require cycle components to be re-designed. This difference in necessary impurities to eliminate oxidation is another advantage to Cu, as well as why it has been pursued as a diffusion barrier to both O and C.

Additionally, the formation of any intermetallics with the substrate is a concern, as it could remove material from the alloy, create diffusion pathways for gas influx, and/or create a eutectic which results in melting. Therefore, the melting point of Cu (1083°C [94]) and its eutectics should be well above any

application temperature. Previous analysis of the Cu-Fe-Cr-Ni systems indicate that there are likely no eutectics with low liquidus temperatures, and that Cu has a very low miscibility with these elements in the solid phase [95], [96]. This indicates good thermodynamic compatibility with steels and other structural alloys, and that Cu is additionally preferable to different potential coatings, such as Ni or Cr.

9.4. Initial Results – Cu Coating

9.4.1. Tensile Results

Preliminary Cu exposures have been performed at UW-Madison as proof-of-concept studies to evaluate the effectiveness of copper coating on the reduction of carburization and oxidation on different alloys at a variety of temperatures. As stated in section 2.1.3.2, 316 has produced poor corrosion resistance above about 600°C, producing a duplex oxide which can spall off. Because of this – and the similar coefficient of thermal expansion with Cu – 316L was considered a good candidate to prove the viability of the coating. In-house electroplating was performed to crudely coat Cu onto samples of 316L. Both coated and bare samples were then exposed for 1,000 hours in RG CO₂ with and without 50ppm CO at 750°C, 20MPa. While these studies were not quantitative in terms of coating thickness against benefit, they were indicative of the accuracy of the thermodynamic calculations from section 9.3. In all conditions except coated and exposed with added CO, 316L exhibited a duplex oxide – similar to P92 from section 7 – and significant carburization. Tensile results – see Table 17 – revealed that, as expected, this carburization caused embrittlement. Given the time and temperature of the exposure, the deposited carbon likely formed carbides, beginning on the edge of the sample and working inwards. However, 316L which was Cu-coated and exposed in a 50ppm CO-doped CO₂ environment performed very similarly to 316L which was aged in a non-corrosive environment, as explored in section 6.

Table 17 – Tensile results for 316L after exposure to CO₂ at 750°C in two environments, as well as with and without Cu coating

	UTS (MPa)	YS (MPa)	Elongation (%)	Samples Tested
Unexposed	624 ± 7	302 ± 2	76.1 ± 0.7	2
Bare, 750°C CO₂	598 ± 11	220 ± 1	26.6 ± 3.3	2
Cu, 750°C CO₂	590 ± 13	233 ± 8	29.1 ± 7.8	2
Bare, 750°C CO₂ + 50ppm CO	498 ± 8	291 ± 20	7.5 ± 1	3
Cu, 750°C CO₂ + 50ppm CO	641 ± 2	263 ± 2	68.7 ± 2.4	3
316L Base 750°C Aging	630 ± 12	244 ± 4	60.9 ± 0.9	2

It should be noted that samples were tested in the unexposed condition with and without Cu-coating. It was found that the coating contributed to added yield strength, but fractured well before UTS was reached. This effect was not observed after exposure, as the Cu appeared to have annealed to the point of being very weak, so it was not assumed to have a large impact on these results.

9.4.2. Fracture Surface Analysis

Fracture surfaces analysis can provide some support for the above conclusions. The images in Figure 100 show the fracture surface from 316L with no copper coating after exposure to CO₂ with 50ppm CO at 750°C, 20MPa for 1,000 hours. In comparison to unexposed material, seen in section 6, there has been a shift from transgranular to intergranular fracture. Further, there was an observable increase in embrittlement near the sample surface, with near-oxide grains exhibiting the highly brittle full-face cleavage (Figure 100 D). Conversely, grains in the interior of the sample (Figure 100 B) show a mixture of micron-scale cleavage and dimples, a significant embrittlement relative to the as-received condition and even 750°C aged 316H from section 6, but much more ductile than the near-oxide region. This was due to the depth-dependent density of grain boundary carbides, primarily M₂₃C₆ [41]. It should be noted that the apparent coatings observed in Figure 100 A and C were actually the two layers of a duplex oxide, similar to those seen in P92 (see section 7).

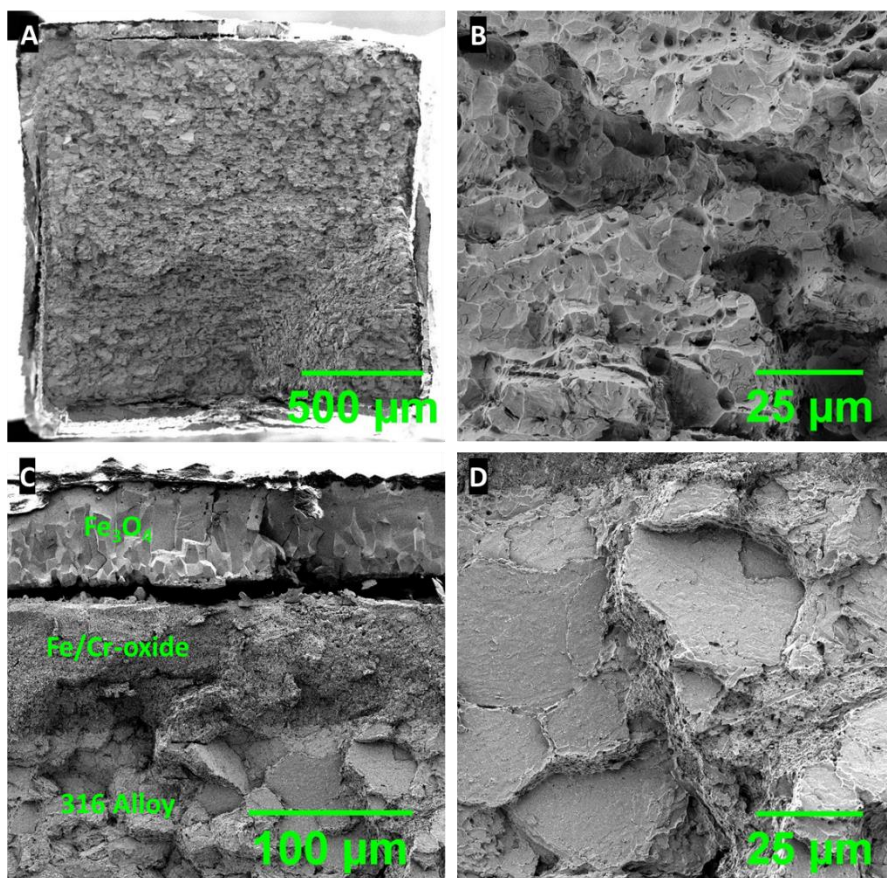


Figure 100 – Fracture surface of 316L exposed to CO₂ + 50ppm CO at 750°C, 20MPa for 1,000 hours. Fracture surface shows increasing embrittlement along grain boundaries near the sample surface.

Meanwhile, exposure to CO-doped CO₂ of Cu-coated 316L, shown in Figure 101, exhibited transgranular fracture akin to that after heat treatment, observed in aged 316L in Figure 67, complete with probable σ -phase embrittlement. This confirmed the hypothesis that the elimination of carburization could be achieved through a Cu coating.

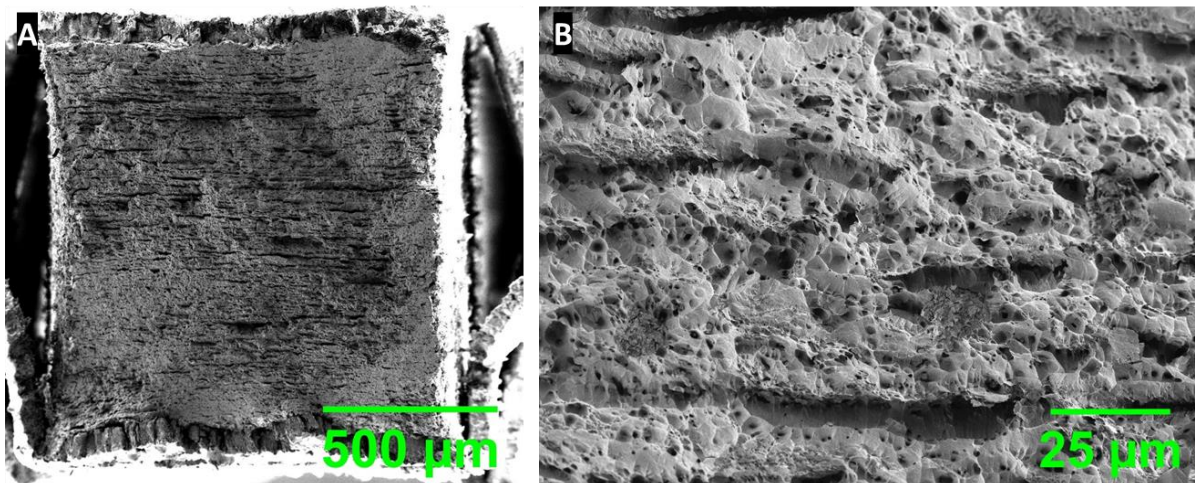


Figure 101 – Fracture surface of Cu-coated 316L after exposure to CO_2 + 50ppm CO at 750°C , 20MPa for 1,000 hours. Fracture surface mirrors that of 316L which was aged at 750°C for 1,000 hours.

9.4.3. Copper Thickness Variation

A follow-up test to the above tensile analysis was performed, analyzing the effect of different thickness of Cu coating on the performance in the s- CO_2 environment at 750°C , 20MPa over the course of 200 hours. In preparation for this experiment, Cu coatings of three target thicknesses were applied to 316L and 316H: $5\mu\text{m}$, $50\mu\text{m}$, and $100\mu\text{m}$ (samples will be referred to by their target thicknesses). Industry-standard techniques were used for these coatings in order to achieve the highest quality coating, as well as to assess the most accurate scenario of implementation. The two thicker coatings were applied through electrolytic plating, while the thinner coating was applied with an electroless technique which is common in the microchip industry. This electroless technique is an exciting technology because it has the potential to internally coat large L/D flow geometries, though it is limited with respect to deposition thickness [97], [98].

Samples were polished to 800-grit prior to coating, and mass measurements were taken before and after coating in order to estimate the coating thickness of each sample. Two samples of each coating thickness were then made into cross-sections and the coating thickness was checked with SEM to verify whether the calculation from mass change were accurate. Samples were measured at the center to find the

minimum thickness of the electroplated samples, and this was used as the measurement of the effective thickness. Cu-coating thicknesses were found to correspond to the mass change from Cu-deposition for electroplated samples, $\pm 10\%$. Additionally, the thickness variation relative to the edge was measured, with Figure 102 showing a variation of roughly 40% from the center to the edge at each thickness.

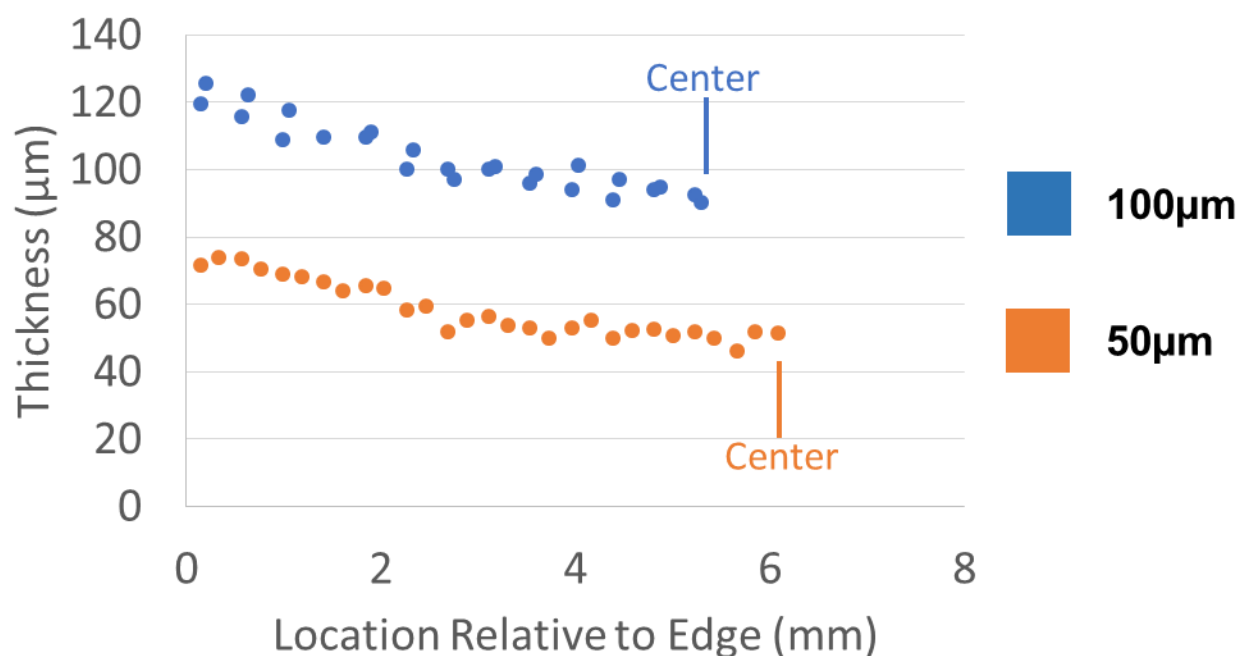


Figure 102 – Depth variation of Cu coating thickness on samples which were electroplated, with measurements taken along the diagonal from the corner to the center.

Surface preparation for the electroless coating process involved roughening the surface of samples. This caused a loss of mass which was unaccounted for by the before and after mass measurements. However, after measuring the coating thickness, the scoring of the sample surfaces appeared to have removed a consistent amount of material relative to the sample surface area. This allowed sample thicknesses to again be predicted within $\pm 10\%$, given the mass difference and an estimated substrate mass loss. The electroless process is not electrically driven, so the 5μm samples were found to have no variation of coating thickness based on location. Thickness measurements were, therefore, taken from several locations to achieve an estimation of average coating thickness.

Samples were then exposed for 200 hours continually to an average of 108ppm CO in RG CO₂ at 750°C, 20MPa. Figure 103 shows the calculated Cu-thickness of each sample plotted against its mass change. As can be seen, thickness varied between samples, and mass change performance varied accordingly. An exponential regression was performed on the two variables and they were shown to be related by the correlation shown in (3), with t_{Cu} being the Cu coating thickness. This correlation is very representative of the 200 hour data, as $r^2 = 0.983$. Uncoated samples experienced high levels of oxidation and spalled freely, so uncoated corrosion, while significantly greater than any Cu coated sample – was not measurable through mass change.

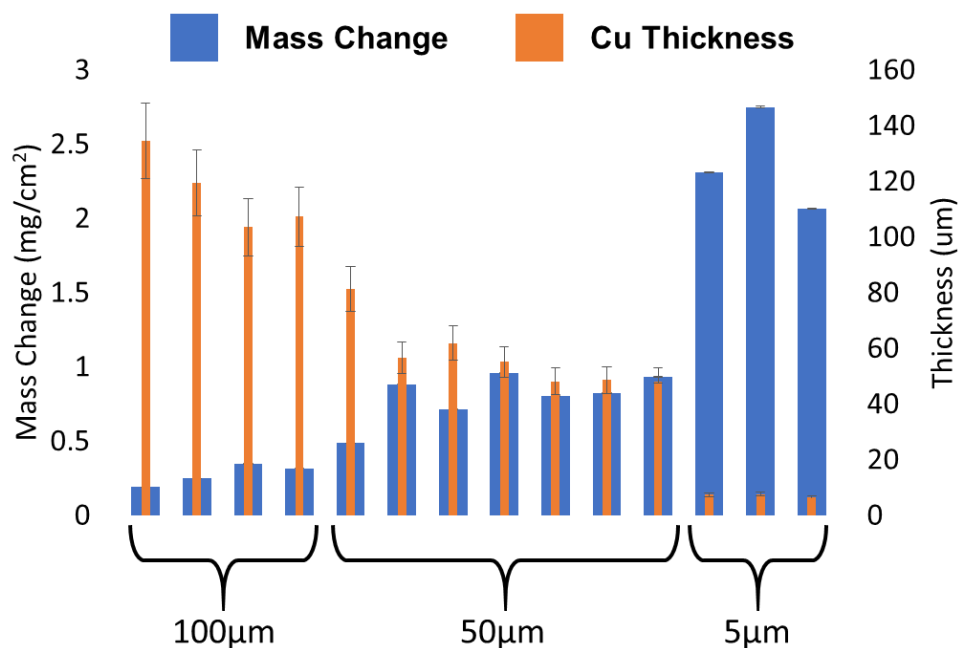


Figure 103 – Mass change and Cu coating thickness for each sample. Lower mass change is very well correlated to greater thickness of Cu coating.

$$\Delta m = 0.0248e^{-0.0195t_{Cu}} \quad (3)$$

9.5. Cu Coating Summary

Cu was proven to be an effective barrier to both oxidation and carburization in the CO₂ environment. After 1,000 hours of exposure to a CO-doped CO₂ environment, coated samples exhibited mechanical

properties which were nearly identical to those that were thermally aged in a neutral environment. Additionally, a coating as thin as 5-7 μm protected samples from severe attack, while coatings of 100 μm limited oxidation to that seen in 750°C CO₂ by Ni-based superalloys. Coating thickness was observed to have an exponential relationship to mass gain in the environment, with a high correlation of determination. Further work will need to be done to understand the breadth of this effect on both oxidation and carburization. The goal should be to identify a coating thickness which can encourage the formation of a continuous and protective chromia scale, so that any wear of the coating – possible with low strength Cu at temperature – will not be disastrous to the alloy. In addition, a better understanding the coating performance will assist with uses of other types of high temperature materials which were previously thought unusable in an oxidizing or carburizing environment, such as ceramic-metal composites [89].

10. Conclusions

Welding is a very important variable to analyze in the manufacture of components and piping for the s-CO₂ Brayton cycle, and it should be considered during alloy design and selection for pressure vessel components. While no increase of corrosion was observed in any of the weld joints studied in this work, the understanding of these welds has led to some interesting and relevant observations in several areas. First, it was discovered that there was not an appropriate procedure for welding of thin plates of 740H. Through this work, a new procedure was developed for 1/8" thick plate which was fully penetrating and crack-free. Also in 740H, the fusion zone exhibited a reduction in mechanical properties, likely due to the inconsistent grain boundary carbide growth and the inhomogeneous development of strengthening precipitates. In addition, 740H was shown to have no precipitate-free zone after stress-free exposure at 750°C for 1,000 hours. Further, 740H requires additional welding research to produce good quality weldments of varying sizes and geometries, for both similar and dissimilar welds. Conversely, 282 was shown to have a weak precipitate-free zone along grain boundaries wherever carbides were present, and the fusion zone had carbides present along all grain boundaries, creating a continuous layer of weak γ matrix. Fe-base alloys were found to have no exaggerated mechanical or corrosion effects in the weld from the high temperature CO₂ environment. Finally, dissimilar welding appeared to have no observable ill-effects on either corrosion or mechanical performance. There was no galvanic corrosion observed, and mechanical properties were similar to the lower strength alloy after similar welding.

All similar welds failed in the fusion zone, with the exception of P92 which failed in the fine-grained HAZ. Both 282 dissimilar welds failed in the HAZ of the inferior alloy. These results were not affected by exposure to CO₂. Therefore, there was no evolution within these welds which embrittled another region preferentially to the point where it became ductility or strength-limiting. This conclusion, confirmed with cross-sectional analysis, shows that the evolution of mechanical properties was not enhanced in specific

regions due to CO₂ corrosion, and the corrosion response of the fusion zone and HAZ was similar to that of base material. Welded corrosion response for these alloys should, therefore, be similar to that of base material

The analysis of mechanical performance in this work was performed at room temperature. High temperature properties were estimated through use of previous studies and analysis of microstructural evolution of the materials. This showed that some results were indicative of high temperature performance, while others were restricted to affecting room temperature properties. An example of this is 316: 316L and 316H were both embrittled after aging at 750°C, but only 316H projected to be embrittled at high temperature. This was because 316H nucleated grain boundary carbides – embrittling at all temperatures – while 316L precipitated σ -phase – which only embrittles below roughly 150°C.

As shown in previous works, the oxidation rate in CO₂ is somewhat less than that in H₂O at comparable temperatures [17], [22], however, the s-CO₂ environment introduces the potential for carburization. This carburization could lead to embrittlement of the structural materials, with the possibility of premature failure or breakaway oxidation. Fortunately, it was found that the formation of a protective, continuous Cr₂O₃ scale minimizes the effects of carburization, suggesting that this is not an issue with alloys that form protective oxides. Alloys which formed this scale experienced only thermal aging beyond a depth of a few microns from the surface. This qualifies them as having good, protective corrosion resistance up to and including the temperatures at which this scale has been shown to form: 750°C for Ni-based precipitation-hardened alloys 282 and 740H, and 550°C for austenitic stainless steel 316.

The heat treatment of these alloys had varying effects. The Ni-based precipitation alloys were thermally aged within the temperature range which precipitates and grows grain boundary carbides and the strengthening phase, γ' . This led to embrittlement in all cases, and an increase in yield strength in most. The weld of 740H, in particular, was identified as mechanically weakened by the aging process. 316,

meanwhile, experienced small effects from thermal aging, but elemental and fracture analysis indicated the alloy's susceptibility to carbon embrittlement. 316H, the higher carbon variant, exhibited grain boundary failure corresponding to carbide formation, while 316L, with lower carbon, showed no embrittling carbides but was instead embrittled due to the development of σ -phase intermetallics along ferrite inclusions.

Conversely, P92 was observed to form a less protective duplex oxide at both 450°C and 550°C in CO₂. This duplex oxide was formed by preferentially oxidizing Cr in isolated islands beneath the oxide-metal interface, leaving the rest of the matrix Cr-poor. As the oxide moved through these islands, Fe was preferably oxidized, creating diffusion pathways for oxygen past the chromite islands and encouraging further oxidation. This oxide was observed to correspond to carburization, likely due to the Boudouard reaction which liberated carbon from the recombination of CO into CO₂ [84]. The carbon depth profile indicated that the carbon deposition likely occurred in the internally grown Fe-Cr spinel, and then diffused into the alloy. A similar amount of carbon deposition was observed in both exposures, but only the 550°C exposure resulted in measurable embrittlement. This indicates that embrittlement from carburization may be reliant on the formation of carbides, and exposure at 450°C for 1,000 hours was not sufficient to develop carbides past a critical size or density to embrittle the material. However, this oxide does not appear to be classically protective, as previous work has not confirmed a parabolic oxidation rate at either temperature [30], [31]. This alloy may produce a more linear oxidation trend, develop spallation, and even experience breakaway oxidation over a 20-year life cycle of a power cycle. Therefore, for 9-12%Cr steels – such as P92, which has relatively high creep strength up to about 600°C [23], [51] – to be suitable for operation in sCO₂ at or above 450°C, an additional protective coating technology may need to be developed.

Thermodynamic and diffusion analysis allowed for the development and implementation of one such coating technology: Cu combined with CO additions in CO₂. Cu is easily to apply, noble in CO-doped CO₂,

and an effective diffusion barrier to both oxygen and carbon. Work was completed which proved the effectiveness of the coating to inhibit carburization in samples of 316L. These coated samples performed nearly identically to thermally aged samples in an inert environment. In addition, a completed 200 hour exposure showed the limiting effect of Cu on oxidation of 316L, with an observed decrease in mass change with increased Cu coating thickness.

11. Future Work

The goal of this work was to better understand the effect of CO₂ on the performance of structural alloys, and in this way to increase the viability of the s-CO₂ Brayton cycle. The alloys analyzed here were selected to be exposed at specific temperatures based on previous corrosion studies in CO₂. Several factors of long-term exposure to the CO₂ environment which could affect long-term viability of structural materials were identified, with the most important factor being carburization. As was seen with P92 – as well as with 316L at 750°C – Fe-based alloys are susceptible to severe embrittlement from carbide formation.

This work was completed using room temperature testing. The impact of these phenomena at high temperature, however, can only be estimated, so future mechanical analysis at high temperatures is advised in order to get quantified data. Further, the analysis of dissimilar welds revealed difficulty with consistency and cracking. The persistence of this inconsistency indicates that fusion welding may not be preferred for these or other dissimilar welds, so other types of joints – such as explosion welding or friction welding – should be explored.

The difference in performance of 316 in CO₂ at 550°C versus 750°C indicates that there is a critical temperature or temperature range where corrosion performance changes from protective to unprotective. It is believed that this occurs somewhere between 550°C and 650°C, but this range should be reduced through future corrosion studies. This is especially important in relation to iron oxidation and spallation.

Additionally, it was demonstrated that the manipulation of the partial pressure of oxygen allows for a simple Cu coating to protect a substrate from this embrittling carburization. Now that this advantage from Cu coating has been identified, the technology should be developed. Many questions remain to be answered: will a protective Cr₂O₃ layer develop on Fe-Cr alloys which would otherwise form duplex oxides;

what is the effect of thermal cycling on the coating; what is the impact of a small scratch in the coating on the underlying material; does the coating need to be reapplied and, if so, how often; and so on. One of two goals could be pursued in order to consider Cu an effective coating: it encourages the formation of a continuous and protective chromia scale so long-term wear of the coating is not disastrous; or an initial thickness and maintenance schedule is identified which can effectively eliminate oxidation and/or carburization. If the latter can be developed, it opens up structural material selection to include materials which cannot survive in oxidizing environments. In addition to developing this theoretical understanding, coating techniques must be developed for each individual application. This involves coating to individual design conditions, such as conductivity of the substrate and the L/D of channel geometry, in order to achieve a high-performance coating.

Additionally, it might be possible to eliminate carburization through selective oxidation. Alloys such as P92 experience the majority of negative effects from the CO₂ environment through carburization. It may be possible to inject small amounts of impurities of O₂ or H₂O into CO₂ so that these alloys preferentially oxidize from non-carbon containing molecules. This technique would necessarily increase the pO₂ in the environment, increasing oxidation to some extent, but previous work in supercritical water has shown oxidation on a similar order as that in s-CO₂ [32], [99]. Therefore, it may be possible to limit carburization without increasing oxidation too drastically.

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Appendix

12.1. Alloy Compositions

	740H (Base Samples)	740H (Weld Samples)	740H (Filler Metal)	IN82 Filler Metal	282 (Nominal)	282 (heat #: 5-8370)	282 (heat #: 2-8384)
Cr	24.57	24.56	24.62	21.17	20	19.47	19.43
Co	20.09	20.02	20.19	---	10	10.13	10.42
Al	1.33	1.37	1.34	---	1.5	1.48	1.50
Ti	1.33	1.47	1.36	0.30	2.1	2.25	2.16
Nb	1.46	1.52	1.52	2.43*		<0.1	<0.1
Fe	0.1491	0.2	0.24	0.58	1.5	0.79	0.68
C	0.023	0.036	0.043	0.027	0.06	0.065	0.064
Mn	0.245	0.3	0.25	2.92	0.3	0.08	0.05
Mo	0.35	0.503	0.007	---	8.5	8.58	8.55
Si	0.17	0.15	0.14	0.16	0.15	<0.05	<0.05
Cu	0.015	0.016	0.032	0.04	---	<0.01	<0.01
P	0.0023	0.004	0.007	0.004	---	0.002	0.002
S	0.003	<0.001	0.001	0.001	---	<0.002	<0.002
B	0.0013	0.002	0.002	---	0.005	0.005	0.005
Ni	50.04	49.79	50.12	72.23	57	Bal (57.1)	Bal (57.1)
Ta	0.004	0.011	0.008	---	---	<0.01	<0.01
N	0.0038	0.003	---				
V	0.012	0.01	0.01				
W	0.022	0.046	0.044			0.03	0.01
Zr	0.021	---	0.023			0.002	<0.002
UTS (aged) UTS (annealed) UTS (at 926°C)	1,151 MPa					1,158 MPa* 855 MPa	
YS (aged) YS (annealed) YS (at 926°C)	737 MPa					724 MPa* 396 MPa	
El (%): aged El (%): annealed El (%): at 926°C	35.57%					33%* 62%	
R of A (%)	37.98%						

Table 18 - Alloy Compositions I (Wt %) *Nb + Ta

	P92	P92 (used in this work)	9CRWV-TIG (Filler)	316L	316L Filler	316H	ER316H (Filler)
--	-----	-------------------------	--------------------	------	-------------	------	-----------------

	Min	Max						
Cr	8.500	9.500	8.94	9.04	16.73		16.07	18.0-20.0
Co	---	---	---	0.045	---		---	---
Al	---	0.040	0.02	0.007	---		---	---
Ti	---	---	---	<0.001	---		---	---
Nb	0.040	0.090	---	0.062	---		---	---
Fe	85.784	89.109	Bal (88.0)	Bal (87.0)	69.43		Bal (70.3)	Bal (59-68)
C	0.070	0.130	0.11	0.092	0.019		0.0523	0.04-0.06
Mn	0.300	0.600	---	0.68	1.22		0.840	1.0-2.5
Mo	0.300	0.600	0.5	0.41	2.07		2.09	2.0-3.0
Si	---	0.500	0.1	0.22	0.39		0.504	0.30-0.65
Cu	---	---	---	0.03	---		---	Max 0.75
P	---	0.020	---	0.009	0.030		0.0272	Max 0.03
S	---	0.010	---	0.008	0.0036		0	Max 0.03
B	0.001	0.006	---	0.003	---		---	---
Ni	---	0.400	0.21	0.49	10.07		10.08	11.0-14.0
Ta	---	---	---	---	---		---	---
N	---	0.030	---	0.058	0.030		---	---
V	0.150	0.250	0.2	0.17	---		---	---
W	1.500	2.000	1.91	1.65	---		---	---
Zr	---	---		---	---		---	---
Sn	---	---		0.003	---	---	---	---
Sb	---	---		0.001	---	---	---	---
As	---	---		0.004	---	---	---	---

Table 19 - Alloy Compositions II (Wt %)

12.2. Welding Procedures

Base Material 1	316H	316L	P92 F-M Steel	282 (heat #: 2-8370)	282 (heat #: 2-8370)	282 (heat #: 2-8370)	740H	740H	740H
Base Material 2	316H	316L	P92 F-M Steel	282 (heat #: 2-8370)	316SS	P92 F-M Steel	740H	316SS	P92 F-M Steel
Filler Metal	ER316H	316L	9CRWV-TIG	282 (heat #: 5-8384)	282 (heat #: 5-8384)	282 (heat #: 5-8384)	740H (heat #: HT2127JY)	INCONEL 82 (heat #: NX8730DR)	INCONEL 82 (heat #: NX8730DR)
Filler Metal Wire Diameter (in)	1/8	3/32	3/32	1/16	1/16	1/16	0.045	0.045	0.045
Filler Wire Speed (in/min)	Manual	Manual	Manual	Manual	Manual	Manual	15	25	25
Shielding Gas*	100% Ar	100% Ar	100% Ar	100% Ar	100% Ar	100% Ar	75% Ar 25% He	75% Ar 25% He	75% Ar 25% He
Shielding Gas Flow Rate				20 cfh	20 cfh	20 cfh			
Backing Gas	N/A	N/A	N/A	100% Ar	100% Ar	100% Ar	N/A	N/A	N/A
Backing Gas Flow Rate	N/A	N/A	N/A	10 cfh	10 cfh	10 cfh	N/A	N/A	N/A

Power Source	DC Negative	DC Negative	DC Negative	DC Negative	DC Negative	DC Negative	DC Negative	DC Negative	DC Negative
# of Passes		1	1	2	2	2	2	2	2
Weld Current (A)	141	125	Plate 1: 135 Plate 2: 144	Root: 70 Cover: 90	Root: 90 Cover: 115	Root: 70 Cover: 90	150	150	150
Weld Voltage (V)				Root: 11.5 Cover: 14.0	Root: 11.5 Cover: 14.0	Root: 11.5 Cover: 14.0	14.5	15	15
Travel Speed (in/min)	2-3	2-3	2	4-6	4-6	4-6	9.5	8	8
Root Gap (in)	1/8	~0.15	0.15	3/32	3/32	3/32	3/32	3/32	3/32
Type of Joint	Flat butt	Flat butt	Flat butt	Flat butt	Flat butt	Flat butt	Single V butt	Single V butt	Single V butt
Preheating	None	None	200-250°C	None	None	None	None	None	None
Post-weld Heat Treatment	None	None	765°C/2.5h/FC	800°C/4h/FC	None	760°C/30min/AC	800°C/4h/AC	None	760°C/30min/AC

Table 20 - Welding parameters for welds analyzed in this work (* = gas compositions ignoring trace impurities)

12.3. Strain Image Correlation

Strain analysis was performed using the following procedure to take high quality pictures during the test.

The resulting pictures were then analyzed after testing using the below MATLAB script for image processing, with distance calibration relative to tab marking locations.

12.3.1. Strain Measurement Procedure

- Mark sample on side of each tab multiple times. In this work, this was performed by first coloring one edge of the tab with a black marker. The sample was then leveled in a vice and a mill made thin markings at discrete, known locations – four on the larger tab, three on the smaller.
- Mark the sample on the gauge in multiple places. This was done in this work by first coloring one edge with a black marker, then using a shiny silver marker to put discrete dots over the black. The location of the dots does not matter, as long as they are on the gauge. Four dots were typically used in this work.
- Tensile grips were used which could accommodate the small gauge length of this work. Also, scrap metal of similar thickness to the samples was used as backing for the grips so there was no pinching and subsequent slippage during testing.
- Care was taken when installing sample in the grips that no deflection or torsion occurred which would alter tensile results.
- Camera was mounted on a tripod and levelled on two axes to ensure sample was pulled along the horizontal plane of the camera (to achieve a wider view). Camera was positioned as close as possible to the sample while remaining in focus and able to capture the total movement of the sample tab markings until rupture.

- External lighting was used to enhance differences in brightness from the markings and the rest of the sample.
- Pre-test images were taken and analyzed with the image processing code to ensure quality was sufficient for an accurate measurement. If image quality was insufficient, lighting or camera settings were adjusted, or else sample would be removed and markings re-made.
- The camera hardware was as follows:
 - Camera: Nikon D7000
 - Lens: Nikon Micro-NIKKOR 105mm f/2.8
- The camera was set to the following settings:
 - Frame Rate: 1,250 or 1,000Hz
 - Aperture: F32
 - ISO: 400
- Interval timer shooting was used, with the following settings:
 - 1 second interval
 - 950 intervals with 1 image per interval (1 shot every second for 950 seconds)
 - Pictures were manually stopped when test was complete
- Test was performed by starting the interval timer and waiting for 15 pictures to be taken. Test was then begun at the moment of the 16th picture. Any inconsistencies with this procedure were noted and accounted for.
 - These images were used to calibrate the starting point of the test (zero strain).
- Once the test was complete, each part of the sample was delicately removed and isolated so that the fracture surfaces would not touch anything abrasive and be altered.

12.3.2. Image Processing Script – MATLAB

```
%Start Image Processor
tic;
clc;
clear all;
close all;
disp('Image Processor...');
workspace;

tic

%Set folder to .m folder
if(~isdeployed)
    cd(fileparts(which(mfilename)));
end

%% Input Data
%Set root directory
rootdirectory = 'C:\Users\Andrew\Box Sync\Tensile Testing\Pictures - Tensile Tests\H282-P92 #21\DSC_';

%Inputs specific to each test
calibration_pics=16;
total_picture_number=425+calibration_pics;
picture_number_test=total_picture_number-calibration_pics;
multiplier=1;

start_point=9785;

start_point_test=start_point+calibration_pics;
threshold_value1=80;
threshold_value1a=30;

pic_threshold_change1=5550;

threshold_value_silver1=20;
threshold_value_silver1a=7;

threshold_value_silver1b=5;

%Number of pictures taken before test started.
%Number of pictures in test (including the calibration pictures)
%Number of pictures in tensile test
%Equal to 1 when analyzing test, put at a higher number to check binary
threshold
%The number which proceeds the number of the first picture of the test
(for accessing pictures off of the computer)

%Sets initial threshold for a mark on the tab
%Sets new threshold for a mark on the tab (optional - only after number
of pictures defined in pic_threshold_change1)
%Sets number of picture (not counting calibration pics) which switches
the threshold value used for the tab from threshold_value1 to
threshold_value1a (if not using, set to greater than
picture_number_test)
%Sets initial threshold for a mark on the gauge
%Sets new threshold for a mark on the gauge (optional - only after
number of pictures defined in pic_threshold_change_silver1)
%Sets new threshold for a mark on the gauge (optional - only after
number of pictures defined in pic_threshold_change_silver2)
```



```

file_number_dark=strcat('Dark #',file_number-start_point);           %sets dark title
file_number_light=strcat('Light #',file_number-start_point);         %sets light title
file_name = strcat(file_number,'.jpg');
img_loc = strcat(rootdirectory,file_name); %concatenates the two strings to form one complete directory.
originalImage = imread(img_loc);
iptsetpref('ImshowAxesVisible','on');

%If first run through, select the size of the window
if i==1
    gray_image=rgb2gray(originalImage);           %Sets array file for image in grey-scale
    crop_image= imcrop(gray_image,[xstart ystart deltax deltay]); %imcrop is [(x start) (y start) (delta x) (delta y)]
    crop_image_silver= imcrop(gray_image,[xstart_silver ystart_silver deltax_silver deltay_silver]); %imcrop is [(x start) (y start) (delta x) (delta y)]

    figure()
    imshow(originalImage)
    dims_image=size(crop_image);                  %finds the dimensions of this array
    middle=uint16(dims_image(1)/2);
    for u=center_start_initial:center_end_initial %eliminates any gauge influence on the matrix which will be used to measure
                                                the tab mark locations
        for uu=1:deltay+1
            crop_image(uu,u)=0;
        end
    end
end

if i~=1
    gray_image=rgb2gray(originalImage);           %Sets array file for image in grey-scale
    crop_image= imcrop(gray_image,[xstart ystart deltax deltay]); %imcrop is [(x start) (y start) (delta x) (delta y)]
    crop_image_silver= imcrop(gray_image,[xstart_silver ystart_silver deltax_silver deltay_silver]); %imcrop is [(x start) (y start) (delta x) (delta y)]

    middle=uint16(dims_image(1)/2);
    dims_image=size(crop_image);                  %finds the dimensions of this array
    center_start_continual=round(horiz_loc_silver_cal(i-1,1)-center_define_offset);
    center_end_continual=round(horiz_loc_silver_cal(i-1,number_peaks_silver)+center_define_offset);
    for u=center_start_continual:center_end_continual
        for uu=1:deltay+1
            crop_image(uu,u)=0;
        end
    end
end

%Binary Image via Threshold
binaryImage1 = crop_image > threshold_value1;
binaryImage1 = imfill(binaryImage1, 'holes');
binaryImage_silver1 = crop_image_silver > threshold_value_silver1;

%Binary Image via Threshold Shaft
binaryImage2=crop_image < threshold_value1;
binaryImage_silver2 = crop_image_silver < threshold_value_silver1;

% THE FOLLOWING IS OPTIONAL: ONLY USED WHEN DEBUGGING
%% %% figure()
%% %% imshow(binaryImage2)
%% %% figure()
%% %% imshow(binaryImage_silver2)

%run the centroid function on the tab and gauge binary matrices
centroid = regionprops(binaryImage1,{'Centroid','EquivDiameter','Eccentricity','Perimeter','Area'}); %tab centroid
centroid_silver = regionprops(binaryImage_silver1,{'Centroid','EquivDiameter','Eccentricity','Perimeter','Area'}); %gauge centroid

const=1; %Initiates step variable
struct_size=length(centroid); %Finds struct size (centroid)
for j=1:struct_size %Searches struct for the points of interest
    %if the centroid area is within the range defined for a tab marking, it remembers its location
    if centroid(j).Area(1)>minimum_centroid_mark && centroid(j).Area(1)<maximum_centroid_mark
        horiz_loc_cal(i,const)=centroid(j).Centroid(1);
        vert_loc_cal(i,const)=centroid(j).Centroid(2);
        const=const+1;
    end
end

const=1; %Initiates step variable
struct_size=length(centroid_silver); %Finds struct size (centroid)
for j=1:struct_size %Searches struct for the points of interest
    %if the centroid area is within the range defined for a gauge marking, it remembers its location
    if centroid_silver(j).Area(1)>minimum_centroid_mark_silver && centroid_silver(j).Area(1)<maximum_centroid_mark_silver
        horiz_loc_silver_cal(i,const)=centroid_silver(j).Centroid(1)+xstart_silver-xstart;
        vert_loc_silver_cal(i,const)=centroid_silver(j).Centroid(2);
        const=const+1;
    end
end

if i==1 %shows the first image, complete with measured marking locations
    figure(), imshow(binaryImage_silver2), title('Gauge');
    hold on
    plot(horiz_loc_silver_cal-(xstart_silver-xstart),vert_loc_silver_cal,'o')
    hold off
    figure, imshow(binaryImage2), title('Tabs');
    hold on
    plot(horiz_loc_silver_cal,vert_loc_silver_cal,'o',horiz_loc_cal,vert_loc_cal,'x')
    hold off
end

end

%% Finding Calibration between pixels and mm

```

```

horiz_loc_avg_mean=mean(horiz_loc_cal);           %establishes average (mean) original postion of peaks (averaged over calibration
                                                    pics)
horiz_loc_avg_median=median(horiz_loc_cal);        %establishes average (median) original postion of peaks (averaged over
                                                    calibration pics)'
horiz_loc_silver_mean=mean(horiz_loc_silver_cal);
horiz_loc_silver_median=median(horiz_loc_silver_cal);

% Initiating matrices and arrays
cal_pixels_mark_dist_tab_mean=zeros(3,number_peaks);
cal_pixels_mark_dist_tab_median=zeros(3,number_peaks);
mark_dist_new_tab=zeros(3,number_peaks_silver);
silver_cal_differences_mean=zeros(3,number_peaks_silver);
silver_cal_differences_median=zeros(3,number_peaks_silver);
xstart_silver_continual=zeros(picture_number_test,1);
horiz_loc=zeros(picture_number_test,number_peaks);
vert_loc=zeros(picture_number_test,number_peaks);
horiz_loc_silver=zeros(picture_number_test,number_peaks_silver);
vert_loc_silver=zeros(picture_number_test,number_peaks_silver);
distances_mean=zeros(picture_number_test,21);
distances_median=zeros(picture_number_test,21);
x=zeros(picture_number_test);

for pix_cal_x=1:number_peaks-1      %This loop finds the differences between all the marks in each picture for mean and median
    for pix_cal_y=pix_cal_x:number_peaks
        if (pix_cal_x==1 || pix_cal_x==2 || pix_cal_x==3) && pix_cal_y>=4
            cal_pixels_mark_dist_tab_mean(pix_cal_x,pix_cal_y)=horiz_loc_avg_mean(pix_cal_y)-horiz_loc_avg_mean(pix_cal_x);
            cal_pixels_mark_dist_tab_median(pix_cal_x,pix_cal_y)=horiz_loc_avg_median(pix_cal_y)-horiz_loc_avg_median(pix_cal_x);
            mark_dist_new_tab(pix_cal_x,pix_cal_y)=mark_dist(pix_cal_x,pix_cal_y);
        end
    end
end

cal_pixels_per_mm_mean=cal_pixels_mark_dist_tab_mean./mark_dist_new_tab;           %Finds pixels in each mm from each averaged
                                                    (mean) difference between peaks
cal_pixels_per_mm_mean_no_zeros=cal_pixels_per_mm_mean(cal_pixels_per_mm_mean>=0); %Removes zeros, creates an 1x array
cal_pixels_per_mm_median=cal_pixels_mark_dist_tab_median./mark_dist_new_tab;        %Finds pixels in each mm from each averaged
                                                    (median) difference between peaks
cal_pixels_per_mm_median_no_zeros=cal_pixels_per_mm_median(cal_pixels_per_mm_median>=0); %Removes zeros, creates an 1x array

cal_avg_pixels_per_mm_mean=mean(cal_pixels_per_mm_mean_no_zeros);                 %Finds mean pixels in each mm
mark_dist_measured_mm_mean=cal_pixels_mark_dist_tab_mean/cal_avg_pixels_per_mm_mean; %mm between peaks (mean)
mark_dist_measured_in_mean=mark_dist_measured_mm_mean*0.0393701;                  %in between peaks (mean)
cal_avg_pixels_per_mm_median=mean(cal_pixels_per_mm_median_no_zeros);              %Finds mean pixels in each mm
mark_dist_measured_mm_median=cal_pixels_mark_dist_tab_median/cal_avg_pixels_per_mm_median; %mm between peaks (median)
mark_dist_measured_in_median=mark_dist_measured_mm_median*0.0393701;              %in between peaks (median)
mark_diff_mean=mark_dist_new_tab-mark_dist_measured_mm_mean;                     %Difference (mm) between input differences and
                                                    measured differences (mean)
mark_diff_median=mark_dist_new_tab-mark_dist_measured_mm_median;                  %Difference (mm) between input differences and
                                                    measured differences (median)
mark_diff_mean_no_zeros=mark_diff_mean(mark_diff_mean~=0);                       %Removes zeros
mark_diff_median_no_zeros=mark_diff_median(mark_diff_median~=0);                   %Removes zeros
mark_diff_mean_stddev=std(mark_diff_mean_no_zeros);                               %Finds standard deviation of mean values (to
                                                    determine accuracy between mean/median)
mark_diff_mean_std_error=mark_diff_mean_stddev/sqrt(calibration_pics);
mark_diff_median_stddev=std(mark_diff_median_no_zeros);                           %Finds standard deviation of median values (to
                                                    determine accuracy between mean/median)
mark_diff_median_std_error=mark_diff_median_stddev/sqrt(calibration_pics);
mark_diff_mean_avg_from_zero=mean(abs(mark_diff_mean_no_zeros));                  %Finds average distance from zero of mean values (to
                                                    determine accuracy between mean/median)
mark_diff_median_avg_from_zero=mean(abs(mark_diff_median_no_zeros));               %Finds average distance from zero of median values
                                                    (to determine accuracy between mean/median)

cal_pixels_mark_dist_mean_no_zeros=cal_pixels_mark_dist_tab_mean(cal_pixels_mark_dist_tab_mean~=0); %Removes zeros from the tab
                                                    distance matrix (mean)
cal_pixels_mark_dist_median_no_zeros=cal_pixels_mark_dist_tab_median(cal_pixels_mark_dist_tab_median~=0); %Removes zeros from the
                                                    tab distance matrix (median)

cal_mark_diff_median=cal_pixels_mark_dist_median_no_zeros;                        %Switches to a variable name which is more convenient
cal_mark_diff_mean=cal_pixels_mark_dist_mean_no_zeros;                           %Switches to a variable name which is more convenient

%% Finding Error in Measurement of Gauge Mark Locations

for pix_x=1:number_peaks_silver-1      %This loop finds the differences between all the marks in each picture for mean and median
    for pix_y=pix_x:number_peaks_silver
        silver_cal_differences_mean(pix_x,pix_y)=horiz_loc_silver_mean(pix_y)-horiz_loc_silver_mean(pix_x);
        silver_cal_differences_median(pix_x,pix_y)=horiz_loc_silver_median(pix_y)-horiz_loc_silver_median(pix_x);
    end
end

silver_cal_differences_mean_no_zeros=silver_cal_differences_mean(silver_cal_differences_mean~=0); %Removes zeros from the
                                                    matrix - creates a 1x array
silver_cal_differences_median_no_zeros=silver_cal_differences_median(silver_cal_differences_median~=0); %Removes zeros from the
                                                    matrix - creates a 1x array
silver_cal_distances_mean=silver_cal_differences_mean_no_zeros;                    %Saves the array into a matrix
silver_cal_distances_median=silver_cal_differences_median_no_zeros;                 %Saves the array into a matrix

qqq_silver=1;
for q_silver=[3,4]                      %This loop selects out the distances which will factor into elongation (between
                                        different tabs) - in order: 1 to 4, 1 to 5, 1 to 6, 2 to 4, etc.
    silver_cal_elongation_mean(qqq_silver)=silver_cal_distances_mean(q_silver);
    silver_cal_elongation_median(qqq_silver)=silver_cal_distances_median(q_silver);
    qqq_silver=qqq_silver+1;
end

silver_cal_differences_wide_vector=horiz_loc_silver_cal(:,4)-horiz_loc_silver_cal(:,1);
silver_cal_differences_thin_vector=horiz_loc_silver_cal(:,3)-horiz_loc_silver_cal(:,2);

```

```

silver_marks_wide_std_dev_pixels=std(silver_cal_differences_wide_vector); %Finds standard deviation of median values (to
silver_marks_wide_std_error_pixels=silver_marks_wide_std_dev_pixels/sqrt(calibration_pics); %determine accuracy between mean/median)
silver_marks_thin_std_dev_pixels=std(silver_cal_differences_thin_vector); %Finds standard deviation of median values (to
silver_marks_thin_std_error_pixels=silver_marks_thin_std_dev_pixels/sqrt(calibration_pics); %determine accuracy between mean/median)
silver_marks_wide_std_error_percent=silver_marks_wide_std_error_pixels/silver_cal_elongation_median(2)*100;
silver_marks_thin_std_error_percent=silver_marks_thin_std_error_pixels/silver_cal_elongation_median(1)*100;
silver_marks_wide_std_error_test_pics_percent=silver_marks_wide_std_dev_pixels/silver_cal_elongation_median(2)*100;
silver_marks_thin_std_error_test_pics_percent=silver_marks_thin_std_dev_pixels/silver_cal_elongation_median(1)*100;

h=waitbar(calibration_pics/total_picture_number,'Analyzing Test Pictures...'); %Brings up a status bar which monitors completion
status of the test

jack_threshold_value2=0;
%% Analyzing Test Pictures
for i=1:picture_number_test
    %Establishing the correct file number to select (according to camera file save settings
    if i==pic_threshold_change1
        jack_threshold_value2=1;
        threshold_value1=threshold_value1a;
    end
    if i==pic_threshold_change_silver1
        threshold_value_silver1=threshold_value_silver1a;
    end
    if i==pic_threshold_change_silver2
        threshold_value_silver1=threshold_value_silver1b;
    end
    if start_point_test+i*multiplier>=10000
        start_point_test=start_point_test-9999;
    end
    if start_point_test+i*multiplier<10
        file_number=strcat('000',num2str(start_point_test+i*multiplier));
    end
    if start_point_test+i*multiplier<100 && start_point_test+i*multiplier>=10
        file_number=strcat('00',num2str(start_point_test+i*multiplier));
    end
    if start_point_test+i*multiplier<1000 && start_point_test+i*multiplier>=100
        file_number=strcat('0',num2str(start_point_test+i*multiplier));
    end
    if start_point_test+i*multiplier>=1000 && start_point_test+i*multiplier<=9999
        file_number=num2str(start_point_test+i*multiplier);
    end

    file_number_dark=strcat('Dark #',file_number-start_point); %sets dark title
    file_number_light=strcat('Light #',file_number-start_point); %sets light title
    file_name = strcat(file_number,'.jpg');
    img_loc = strcat(rootdirectory,file_name); %concatenates the two strings to form one complete directory.
    originalImage = imread(img_loc);
    iptsetpref('ImshowAxesVisible','on');

    %If first run through, select the size of the gauge window
    if i==1
        gray_image=rgb2gray(originalImage); %Sets array file for image in grey-scale
        crop_image= imcrop(gray_image,[xstart ystart deltax deltay]); %imcrop is [(x start) (y start) (delta x) (delta y)]
        crop_image_silver= imcrop(gray_image,[xstart_silver ystart_silver deltax_silver deltay_silver]); %imcrop is [(x start) (y
start) (delta x) (delta y)]

        dims_image=size(crop_image); %finds the dimensions of this array
        middle=uint16(dims_image(1)/2);
        xstart_silver_continual_scalar=xstart_silver;
        for u=center_start_initial:center_end_initial
            for uu=1:deltay+1
                crop_image(uu,u)=0;
            end
        end
    end
end

%If not first run through, select gauge window based off previous gauge locations and center_define_offset variable
if i~=1
    gray_image=rgb2gray(originalImage); %Sets array file for image in grey-scale
    crop_image= imcrop(gray_image,[xstart ystart deltax deltay]); %imcrop is [(x start) (y start) (delta x) (delta y)]
    if i<pic_threshold_silver_finished
        xstart_silver_continual(i)=round(horiz_loc_silver(i-1,1)-center_define_offset);
        xstart_silver_continual_scalar=xstart_silver_continual(i);
        deltax_silver=round(horiz_loc_silver(i-1,number_peaks_silver)+center_define_offset-xstart_silver_continual_scalar);
        %imcrop is [(x start) (y start) (delta x) (delta y)]
        crop_image_silver= imcrop(gray_image,[xstart_silver_continual_scalar ystart_silver deltax_silver deltay_silver]);
        dims_image=size(crop_image); %finds the dimensions of this array
        middle=uint16(dims_image(1)/2);
        center_start_continual=xstart_silver_continual;
        center_end_continual=round(horiz_loc_silver(i-1,number_peaks_silver)+center_define_offset);
    end
    if i>=pic_threshold_silver_finished
        xstart_silver_continual_scalar=round(horiz_loc(i-1,3)+center_define_offset);
        center_end_continual=round(horiz_loc(i-1,4)-center_define_offset);
        deltax_silver=round(horiz_loc(i-1,4)-center_define_offset-xstart_silver_continual_scalar);
    end
    for u=xstart_silver_continual_scalar:xstart_silver_continual_scalar+deltax_silver
        for uu=1:deltay+1
            crop_image(uu,u)=0;
        end
    end
end

%Binary Image via Threshold
binaryImage1 = crop_image > threshold_value1;

```

```

binaryImage1 = imfill(binaryImage1, 'holes');
binaryImage_silver1 = crop_image_silver > threshold_value_silver1;

%Binary Image via Threshold Shaft
binaryImage2=crop_image < threshold_value1;
binaryImage_silver2 = crop_image_silver < threshold_value_silver1;

centroid = regionprops(binaryImage1,{'Centroid','EquivDiameter','Eccentricity','Perimeter','Area'});

const=1; %Initiates step variable
struct_size=length(centroid); %Finds struct size (centroid)
for j=1:struct_size %Searches struct for the points of interest
    if centroid(j).Area(1)>minimum_centroid_mark && centroid(j).Area(1)<maximum_centroid_mark
        horiz_loc(i,const)=centroid(j).Centroid(1);
        vert_loc(i,const)=centroid(j).Centroid(2);
        const=const+1;
    end
end
const=1; %Initiates step variable
for pix_x=1:number_peaks-1 %This loop finds the differences between all the marks in each picture for mean and median
    for pix_y=pix_x:number_peaks
        pixels_mark_dist_mean(pix_x,pix_y)=horiz_loc(i,pix_y)-horiz_loc(i,pix_x);
        pixels_mark_dist_median(pix_x,pix_y)=horiz_loc(i,pix_y)-horiz_loc(i,pix_x);
    end
end
if i<pic_threshold_silver_finished
    centroid_silver = regionprops(binaryImage_silver1,{'Centroid','EquivDiameter','Eccentricity','Perimeter','Area'});
    struct_size=length(centroid_silver); %Finds struct size (centroid)
    for j=1:struct_size %Searches struct for the points of interest
        if centroid_silver(j).Area(1)>minimum_centroid_mark_silver && centroid_silver(j).Area(1)<maximum_centroid_mark_silver
            horiz_loc_silver(i,const)=centroid_silver(j).Centroid(1)+xstart_silver_continual_scalar-xstart;
            vert_loc_silver(i,const)=centroid_silver(j).Centroid(2);
            const=const+1;
        end
    end
    %This loop finds the differences between all the marks in each picture for mean and median
    for pix_x=1:number_peaks_silver-1
        for pix_y=pix_x:number_peaks_silver
            silver_differences_mean(pix_x,pix_y)=horiz_loc_silver(i,pix_y)-horiz_loc_silver(i,pix_x);
            silver_differences_median(pix_x,pix_y)=horiz_loc_silver(i,pix_y)-horiz_loc_silver(i,pix_x);
        end
    end
    silver_differences_mean_no_zeros=silver_differences_mean(silver_differences_mean~=0);
    silver_differences_median_no_zeros=silver_differences_median(silver_differences_median~=0);
    distances_silver_mean(i,:)=silver_differences_mean_no_zeros;
    distances_silver_median(i,:)=silver_differences_median_no_zeros;
    x_silver(i)=i;
end

pixels_mark_dist_mean_no_zeros=pixels_mark_dist_mean(pixels_mark_dist_mean~=0); %Removes zeros from the matrix - creates a 1x array
pixels_mark_dist_median_no_zeros=pixels_mark_dist_median(pixels_mark_dist_median~=0); %Removes zeros from the matrix - creates a 1x array

size_no_zeros=length(pixels_mark_dist_mean_no_zeros); %Finds size of the just created 1x array (not used right now)
distances_mean(i,:)=pixels_mark_dist_mean_no_zeros; %Saves the array into a matrix
distances_median(i,:)=pixels_mark_dist_median_no_zeros; %Saves the array into a matrix
x(i)=i;

waitbar((calibration_pics+i)/total_picture_number); %Updates the status bar with current status
s=mod(i-1,pictures_to_show);
%plots the binary image with marking locations for every "pictures_to_show" number of pictures analyzed (status update)
if s==0
    figure()
    imshow(binaryImage2)
    title(file_number_light)
    hold on
    plot(horiz_loc(i,:),middle,'x')
    if i<pic_threshold_silver_finished
        plot(horiz_loc_silver(i,:),middle,'o') %Plots an x on the horizontal location that mark is at
        hold off
        figure()
        imshow(binaryImage_silver2)
        hold on
        plot(horiz_loc_silver(i,:)-(xstart_silver_continual_scalar-xstart),middle,'o') %Plots an x on the horizontal location that mark is at
    end
    hold off
end
end
close(h) %Closes waitbar

%% Finding Strain Values - Silver
qqq_silver=1;
for q_silver=[3,4] %This loop selects out the distances which will factor into elongation (between different tabs) - in order: 1 to 4, 1 to 5, 1 to 6, 2 to 4, etc.
    new_mark_diff_mean_silver(:,qqq_silver)=distances_silver_mean(:,q_silver);
    new_mark_diff_median_silver(:,qqq_silver)=distances_silver_median(:,q_silver);
    qqq_silver=qqq_silver+1;
end
if pic_threshold_silver_finished>picture_number_test
    pic_threshold_silver_finished=picture_number_test+1;
end
for i_elong=1:pic_threshold_silver_finished-1
    for i_elongation=1:2

```

```

    elongation_pixels_diff_mean(i_elong,i_elongation)=new_mark_diff_mean_silver(i_elong,i_elongation)-
        silver_cal_elongation_median(i_elongation); %Finds the individual elongation measurements based on each applicable
        peak difference (mean) (elongation_reference is elongation measurement to reference as the zero point)
    elongation_pixels_diff_median(i_elong,i_elongation)=new_mark_diff_median_silver(i_elong,i_elongation)-
        silver_cal_elongation_median(i_elongation); %Finds the individual elongation measurements based on each applicable
        peak difference (median)

engineering_strain_silver_mean(i_elong,i_elongation)=elongation_pixels_diff_mean(i_elong,i_elongation)/silver_cal_elongation_medi
    an(i_elongation);

engineering_strain_silver_median(i_elong,i_elongation)=elongation_pixels_diff_median(i_elong,i_elongation)/silver_cal_elongation_
    median(i_elongation);

end
engineering_strain_silver_mean_avg(i_elong,1)=mean(engineering_strain_silver_mean(i_elong,:));
engineering_strain_silver_median_avg(i_elong,1)=mean(engineering_strain_silver_median(i_elong,:));
elongation_average_pixels_mean(i_elong,1)=mean(elongation_pixels_diff_mean(i_elong,:)); %Finds the average elongation of
    each picture based on the applicable differences between peaks (mean)
elongation_average_pixels_median(i_elong,1)=mean(elongation_pixels_diff_median(i_elong,:)); %Finds the average elongation of
    each picture based on the applicable differences between peaks (median)

end

%% Finding Strain Values - Tab
qqq=1;
for q=[4:9,11:13,16:18] %This loop selects out the distances which will factor into elongation
    % (between different tabs) - in order: 1 to 4, 1 to 5, 1 to 6, 2 to 4, etc.

    new_mark_diff_mean(:,qqq)=distances_mean(:,q);
    new_mark_diff_median(:,qqq)=distances_median(:,q);
    qqq=qqq+1;
end

for i_elong=1:picture_number_test
    for i_elongation=1:mark_comparisons
        if mark_diff_mean_std_error>mark_diff_median_std_error
            elongation_pixels_diff_mean(i_elong,i_elongation)=new_mark_diff_mean(i_elong,i_elongation)-
                cal_mark_diff_median(i_elongation); %Finds the individual elongation measurements based on each applicable
                peak difference (mean) (elongation_reference is elongation measurement to reference as the zero point)
            elongation_pixels_diff_median(i_elong,i_elongation)=new_mark_diff_median(i_elong,i_elongation)-
                cal_mark_diff_median(i_elongation); %Finds the individual elongation measurements based on each applicable peak
                difference (median)
            calibration_checker=0;
        end
        if mark_diff_mean_std_error<=mark_diff_median_std_error
            elongation_pixels_diff_mean(i_elong,i_elongation)=new_mark_diff_mean(i_elong,i_elongation)-
                cal_mark_diff_mean(i_elongation); %Finds the individual elongation measurements based on each applicable
                peak difference (mean) (elongation_reference is elongation measurement to reference as the zero point)
            elongation_pixels_diff_median(i_elong,i_elongation)=new_mark_diff_median(i_elong,i_elongation)-
                cal_mark_diff_mean(i_elongation); %Finds the individual elongation measurements based on each applicable peak
                difference (median)
            calibration_checker=1;
        end
    end
    elongation_average_pixels_mean(i_elong,1)=mean(elongation_pixels_diff_mean(i_elong,:)); %Finds the average elongation of
        each picture based on the applicable differences between peaks (mean)
    elongation_average_pixels_median(i_elong,1)=mean(elongation_pixels_diff_median(i_elong,:)); %Finds the average elongation of
        each picture based on the applicable differences between peaks (median)

end

if calibration_checker==0 %If the median error value is lower than the mean, displays the message
    calibration_mean_or_median='Median Was Better (and was used)';
end
if calibration_checker==1 %If the median error value is higher than the mean, displays the message
    calibration_mean_or_median='Mean Was Better (and was used)';
end
elongation_average_mm_mean=elongation_average_pixels_mean/cal_avg_pixels_per_mm_median; %Finds the elongation (mm) of each
    picture (mean) - using median pixels/mm because more precise
elongation_average_mm_median=elongation_average_pixels_median/cal_avg_pixels_per_mm_median; %Finds the elongation (mm) of each
    picture (median)

strain_engineering_mm_mean=(elongation_average_mm_mean)/l_start_mm; %Engineering strain (mean)
strain_engineering_mm_median=(elongation_average_mm_median)/l_start_mm; %Engineering strain (median)
strain_true_mm_mean=log((elongation_average_mm_mean+l_start_mm)/l_start_mm); %True engineering strain (mean)
strain_true_mm_median=log((elongation_average_mm_median+l_start_mm)/l_start_mm); %True engineering strain (median)

toc %Finds the total time the code ran for (along with a "tic" from earlier in the code)

%% Graph Results
figure()
imshow(binaryImage2)
title(file_number_light)
hold on
plot(horiz_loc(i,:),middle,'x',horiz_loc_silver(i,:),middle,'o') %Plots an x on the horizontal location
    at which the mark is (on the tab)

hold off

figure()
imshow(binaryImage_silver2)
hold on
plot(horiz_loc_silver(i,:)-(xstart_silver_continual_scalar-xstart),middle,'o') %Plots an x on the horizontal location
    at which the mark is (on the gauge)

hold off

figure() %Plots the elongation (mean & median) against picture number
plot(x,elongation_average_mm_mean,'b',x,elongation_average_mm_median,'r')
xlabel('Picture #')
ylabel('Strain (in/in)')
title('Elongation vs. Picture # of Test (cal)')
axis([0 picture_number_test 0 max(elongation_average_mm_mean)])

```

```

figure()
plot(x_silver,engineering_strain_silver_mean_avg,'b',x,strain_engineering_mm_mean,'r')
xlabel('Picture #')
ylabel('Strain (in/in)')
title('Strain vs. Picture # of Test')
legend('Gauge Strain','Tab Strain')
axis([0 picture_number_test 0 max(engineering_strain_silver_mean_avg)])

```

12.4. Operation of Autoclaves

Autoclave systems were operated with care to ensure safe and accurate testing conditions. Prior to sample exposures, autoclaves were passivated with high temperature exposure to CO₂ to avoid any potential differences in gas composition. The autoclave, along with everything which was put into it (with the exception of previously exposed samples), was cleaned with ethanol and deionized water and then dried prior to testing. The autoclave was heated with bulk heating from tape resistance heaters which were applied directly to the outside of the autoclave. Additionally, the ends of the autoclave were resistance-heated by Ni-Cr wire.

By UW-Madison convention, tests were deemed to have “started” when the heaters were turned on, and “ended” when the heaters were turned off. Heating occurred over 1-6 hours (depending on autoclave size and exposure temperature), and cooling to 100°C occurred over 8-15 hours. Tests were started after removing excess air by filling to CO₂ bottle pressure (~5.75MPa) and venting down to near atmospheric before filling again. After starting to heat, pressure was allowed to climb with heating until the expansion due to heating was matched by the exit line flow rate. Once this occurred, the pump was turned on and test pressure (20MPa) was achieved within minutes.