Impact of Phase Stability
on the Corrosion Behavior of the Austenitic
Candidate Materials for NNWSI

Daniel B. Bullen
Gregory E. Gdowski
R. Daniel McCright

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IMPACT OF PHASE STABILITY ON THE CORROSION BEHAVIOR OF THE AUSTENITIC CANDIDATE MATERIALS FOR NNWSI.

DANIEL B. BULLEN*, GREGORY E. GDOWSKI* AND R. DANIEL McCRIGHT**
* Science & Engineering Associates, Inc., 5820 Stoneridge Mall Rd., Suite 100, Pleasanton, CA 94566
** Nuclear Waste Management Program, Lawrence Livermore National Laboratory, P.O. Box 808 L-369, Livermore, CA 94550.

ABSTRACT
The Nuclear Waste Management Program at Lawrence Livermore National Laboratory is responsible for the development of the waste package design to meet the Nuclear Regulatory Commission licensing requirements for the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. The metallic container component of the waste package is required to assist in providing substantially complete containment of the waste for a period of up to 1000 years. Long term phase stability of the austenitic candidate materials (304L and 316L stainless steels and alloy 825) over this time period at moderate temperatures (100-250°C) can impact the mechanical and corrosion behavior of the metal barrier.

A review of the technical literature with respect to phase stability of 304L, 316L and 825 is presented. The impact of martensitic transformations, carbide precipitation and intermediate (α, ξ, and η) phase formation on the mechanical properties and corrosion behavior of these alloys at repository relevant conditions is discussed. The effect of sensitization on intergranular stress corrosion cracking (IGSCC) of each alloy is also addressed. A summary of the impact of phase stability on the degradation of each alloy in the proposed repository environment is included.

INTRODUCTION
The Nuclear Waste Management Program (NWMP) at Lawrence Livermore National Laboratory is responsible for the development of the waste package design to meet the Nuclear Regulatory Commission licensing requirements for the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. The waste will include spent fuel from civilian nuclear power plants (PWR and BWR fuel assemblies), commercial high level waste (CHLW) in the form of borosilicate glass containing commercial spent fuel reprocessing wastes, and defense high level waste (DHLW). The waste package is being designed for emplacement in the Topopah Spring Member of Paintbrush Tuff at the Yucca Mountain site in Nevada. The reference horizon is located 350 meters below the ground surface and 200 meters above the static water table. As a result of the unsaturated setting, the repository conditions will be slightly oxidizing.

The Metal Barrier Selection and Testing Task is responsible for the selection of the materials to be employed in the waste package container. Six candidate materials (three austenitic materials and three copper-based alloys) are currently under consideration. The austenitic materials are 304L stainless steel, 316L stainless steel and alloy 825. The metallurgical phase stability of the container material is a factor in the selection of a material for advanced design work.

The design criteria for the metal barrier [1] require that the waste containers maintain mechanical integrity for a period of approximately 50 years after emplacement to permit retrieval of the nuclear waste during the preclosure phase of repository operation. The engineered barrier system is required to provide substantially complete containment of the waste for a period of 300 to 1000 years. During the containment period, the metal barrier will be exposed to a changing environment. For a representative spent fuel waste package [radioactive decay heat of 3.3 kW/package and 57 KW/acre] containing 10-year out-of-reactor fuel, the surface of the container will reach a maximum temperature of about 250°C a few years after emplacement. Temperature will decay to about 150°C at about 100 years after emplacement. This temperature will also include the highest gamma radiation field from the decay of the fission products, which have moderate half-lives. Waste packages containing borosilicate waste forms will develop lower peak temperatures on the container surface than spent fuel waste packages. The phase stability of the metal barrier material over the containment period will impact the mechanical and
corrosion properties. Changes in the microstructure can result in considerable reduction in the fracture strength of the material. Precipitation of carbides at grain boundaries can modify the local alloy composition resulting in conditions favorable to intergranular stress corrosion cracking (IGSCC).

AUSTENITIC CANDIDATE ALLOYS

The austenitic alloys 304L stainless steel, 316L stainless steel and alloy 825 are candidate materials for the metal barrier in the NNWSI Project due to their toughness and relatively good corrosion resistance. The typical composition of these alloys is presented in Table 1. General review articles on the constitution and structure of stainless steels and austenitic alloys have been identified in the technical literature [2-4]. A summary of these articles and a review of physical metallurgy relevant to repository conditions are provided here. The austenitic candidate materials are all derived from the ternary iron-chromium-nickel system. A review of the basic metallurgy of this system is an informative introduction to the aspects of phase stability that are critical to understanding the long-term performance of these alloys.

The most basic phases encountered in this ternary system are dictated by the allotropic forms of iron. Between the melting point (1539°C) and about 1390°C, pure iron exists as a body-centered cubic (bcc) structure, delta (δ) ferrite. From about 1390°C to 910°C, iron has face-centered cubic (fcc) structure, austenite or the gamma phase (γ). Below 910°C, iron again becomes bcc with a structure identified as alpha (α) ferrite. There is no obvious microstructural difference between δ and α ferrite. This convention of nomenclature has been adopted to allow distinction between the conditions of formation. The addition of chromium (up to about 7 weight percent) to iron reduces the temperature of the bcc to fcc to bcc transformations. Above 7% chromium, the temperature range over which austenite exists is gradually reduced. Above 13% chromium, no α to γ transformation occurs and ferrite is stable at all temperatures. Hence, chromium is said to be a ferrite-forming element. Other elements commonly employed in stainless steels that behave similarly are molybdenum, silicon, aluminum, titanium and niobium.

Austenitic stainless steels all contain more than 16% chromium. It is obvious that a chromium content of this magnitude would produce an entirely ferritic material. The effect of chromium is counteracted by the addition of nickel. The austenite phase region is significantly increased by the addition of nickel to iron. Therefore, nickel is called an austenite-forming element. Manganese, copper and cobalt can also be employed as austenite-forming elements in certain alloy applications. The carbon and nitrogen content are also important in establishing the stability of the austenite phase. Even though these elements are present in small amounts, these elements are strong austenite stabilizers.

Table I. Composition of Austenitic Candidate Container Alloys for the NNWSI Project (Wt. %)

<table>
<thead>
<tr>
<th>Element</th>
<th>304 SS*</th>
<th>304L SS</th>
<th>316 SS*</th>
<th>316L SS</th>
<th>Alloy 825</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.08</td>
<td>0.03 Max.</td>
<td>0.08</td>
<td>0.03 Max.</td>
<td>0.05 Max.</td>
</tr>
<tr>
<td>Mn</td>
<td>2.00</td>
<td>2.00 Max.</td>
<td>2.00</td>
<td>2.00 Max.</td>
<td>1.0 Max.</td>
</tr>
<tr>
<td>Si</td>
<td>1.00</td>
<td>1.00 Max.</td>
<td>1.00</td>
<td>1.00 Max.</td>
<td>0.5 Max.</td>
</tr>
<tr>
<td>Cr</td>
<td>18-20</td>
<td>18-20</td>
<td>16-18</td>
<td>16-18</td>
<td>19.5-23.5</td>
</tr>
<tr>
<td>Ni</td>
<td>8-10.5</td>
<td>8-12</td>
<td>10-14</td>
<td>10-14</td>
<td>38-46</td>
</tr>
<tr>
<td>P</td>
<td>0.045</td>
<td>0.045 Max.</td>
<td>0.045</td>
<td>0.045 Max.</td>
<td>----</td>
</tr>
<tr>
<td>S</td>
<td>0.03</td>
<td>0.03 Max.</td>
<td>0.03</td>
<td>0.03 Max.</td>
<td>0.03 Max.</td>
</tr>
<tr>
<td>Cu</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>1.5-3.0</td>
</tr>
<tr>
<td>Ti</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>0.6-1.2</td>
</tr>
<tr>
<td>N</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>0.10</td>
<td>----</td>
</tr>
<tr>
<td>Mo</td>
<td>----</td>
<td>----</td>
<td>2-3</td>
<td>2-3</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* Compositions of the 304 SS and 316 SS are provided as a point of reference. These materials are not candidate container materials for the NNWSI Project.
Metastable Alloy Systems

The phase transformations discussed previously represent the equilibrium conditions for these alloy systems. It should be noted that many alloy applications employ thermomechanical treatments that can result in nonequilibrium states. The equilibrium phases may not form due to kinetic limitations during cooling. Hence, a metastable phase may be present at temperatures which are not conducive to equilibrium phase formation. This is the case for the 304L and 316L stainless steels. The compositions of these alloys suggest that the ferrite phase should be in equilibrium with the austenite phase at temperatures around 200°C. However, the diffusion processes that permit the precipitation of the ferrite phase are severely limited at this low temperature. This produces an alloy that has an austenitic microstructure that is stable for reasonable engineering lifetimes (10 to 40 years). The stability of these alloys over the considerably longer time periods of interest in the repository (up to 1000 years) will have significant impact on materials selection and performance.

To more fully comprehend the complex equilibrium phases present in these alloys, it is necessary to consider the ternary Fe-Cr-Ni system. The Fe-Cr-Ni ternary phase diagram at 650°C is shown in Figure 1 [4]. This diagram indicates compositions where α, σ and γ phases are thermodynamically stable. The stability of the austenite phase is dependent upon the thermomechanical history of the material. Figure 2 shows the regions of stability and metastability in the Fe-Cr-Ni ternary system as a function of the quench temperature. This figure does not represent the equilibrium conditions that would be expected for infinitely long cooling times. Figure 2a shows the stable and metastable phases present at room temperature after rapid cooling from the temperature of maximum austenite content [5]. Note the large region of metastable austenite (AM) and the regions of martensite and ferrite structure. The structure of alloys quenched from a temperature of 1100°C is shown in Figure 2b [6]. The stable austenite region is slightly reduced with an increase in the regions where austenite may transform to martensite upon cold working. The ranges of austenite stability presented in the two diagrams in Figure 2 differ due to compositional variation. Commercial alloys usually retain the austenitic microstructure at room temperature as indicated in Figure 2a. More recent work on alloys with lower carbon content and more detailed microchemical analysis reveals transformation of austenite at temperatures as low as room temperature as indicated in Figure 2b. Part of the variation in austenite stability is due to the effect of carbon content. Low temperature conversion

![Figure 1. Iron-Chromium-Nickel equilibrium phase diagram at 650°C [4]. Note the approximate compositions of the 304L, 316L and 825 candidate materials.](image-url)
Martenite Transformations

Transformation processes

The austenite to martensite transformation is a very important process in the field of materials science and engineering, particularly in the study of stainless steels. The transformation is characterized by a change in the crystal structure of the material, from a face-centered cubic (fcc) structure to a body-centered tetragonal (bct) or a body-centered monoclinic (bmc) structure. This transformation is driven by the need for a lower energy state and is often accompanied by a change in the magnetic properties of the material.

The transformation process is affected by various factors such as alloy composition, temperature, strain, and strain rate. The transformation temperature, known as the critical transformation temperature, is a key parameter that determines the stability of the austenite phase. Austenite stability maps are used to predict the transformation behavior of different alloys.

In the Fe-Cr-Ni system, the transformation behavior is particularly complex due to the presence of multiple phases and the influence of the alloy composition. The metastable phase diagram shown in Figure 2(a) provides a visual representation of the transformation behavior of different alloys.

The transformation process is accompanied by changes in the mechanical properties of the material. Martensitic transformations are associated with increased hardness, toughness, and strength, but they also introduce residual stresses and can lead to cracking and embrittlement. These effects are important considerations in the design and application of stainless steels in various industries.

The transformation behavior of different alloys is critical in understanding their performance under different conditions. The metastable phase diagram shown in Figure 2(a) provides a visual representation of the transformation behavior of different alloys.

Figure 2

(a) Phases after quenching from 1100°C (b) Metastable phase diagram for Fe-Cr-Ni system
Carbide Formation

The ubiquitous carbide in iron-based austenitic alloys is M$_{23}$C$_6$. This carbide is formed in the absence of any strong carbide forming elements. If strong carbide forming elements, such as titanium, are present, M$_{23}$C$_6$ is usually formed in equilibrium with these carbides. The low carbon alloy austenites proposed for use as container materials will be less susceptible to carbide precipitation than alloys with higher carbon content. However, the possibility for carbide precipitation still exists. This precipitation would initially occur at grain boundaries and could result in the depletion of chromium in the vicinity of the grain boundary. This reduction in Cr can lead to a breakdown in the passive oxide layer resulting in susceptibility to localized corrosion. This phenomena is known as sensitization. This can ultimately lead to intergranular stress corrosion cracking of the container.

A significant body of data exists in the literature on the nucleation and growth of carbide precipitates in austenitic alloys [15-19]. Cihal [15] and Stickler and Vinckier [16] completed studies on the precipitation of M$_{23}$C$_6$ carbides in 304 and 304L stainless steel. These studies utilized optical microscopy and intergranular corrosion detected by H$_2$SO$_4$-Cu$_2$SO$_4$ tests. Cihal observed the precipitation of M$_{23}$C$_6$ carbides as a function of temperature and location of formation. The results of Stickler and Vinckier indicate initial M$_{23}$C$_6$ carbide precipitation at austenite-ferrite interfaces. Carbides next form on grain boundaries followed by precipitation on noncoherent and coherent twin boundaries, respectively. The data from these two studies do not agree exactly. This is to be expected since the data were derived from x-ray and electron microscopy analysis on two alloys that were not identical. The precipitation of M$_{23}$C$_6$ carbides in 316 stainless steels is similar to the results presented. The only difference is that the times for precipitation are slightly shorter [17]. This shorter precipitation time appears contrary to the observation of sensitization in 304 SS prior to 316 SS. However, due to the presence of Mo, which is a strong carbide former, in 316 SS, observation of M$_{23}$C$_6$ carbide precipitation is not necessarily indicative of the onset of sensitization. The depletion of chromium is offset by the presence of molybdenum.

Carbide precipitation at grain boundaries can lead to local depletion of chromium (sensitization) resulting in increased susceptibility to intergranular corrosion. Cihal [15] and Stickler and Vinckier [16] measured the onset of intergranular corrosion as a function of precipitation time and temperature. The results of these tests are summarized in Figure 3. Both Cihal (Figure 3a) and Stickler and Vinckier (Figure 3b) observed the onset of intergranular corrosion at a temperature of about 650°C. The observation of intergranular corrosion lags behind the initiation of precipitation. This is most likely due to the fact that corrosion resistance is not significantly diminished until a significant depletion in chromium at the grain boundary has been attained.

![Figure 3. Effect of M$_{23}$C$_6$ carbide precipitation on intergranular corrosion of 304 stainless steels. (a) Alloy containing 0.05% C originally quenched from 1250°C [15]. (b) Alloy containing 0.038% C originally quenched from 1260°C [16].](image-url)
Precipitation studies have also been completed on 316 and 316L stainless steels. Weiss and Stickler [17] determined the effect of annealing temperature on the precipitation kinetics of 316L. This study indicated that at the higher annealing temperature (1260°C vs. 1090°C) the precipitation of M23C6 carbides began at shorter times and persisted at lower temperature over long time periods. A comparison was made of the precipitation kinetics of M23C6 carbides in 316 and 316L. The reduction in carbon content delays the onset of carbide precipitation. This allows for short term high temperature excursions, such as welding, with no carbide precipitation. At lower temperatures and longer time periods there is virtually no difference between the precipitation kinetics of 316 and 316L. This behavior may prove to be a significant factor in the degradation of the mechanical and corrosion properties of 316L in a repository environment.

If enough carbide precipitation occurs, the depletion of chromium and carbon in the matrix may result in transformation of the previously stable austenite to another phase. This phenomenon was noted by Weiss and Stickler for 304 stainless steel [18]. Significant M23C6 carbide precipitation resulted in the transformation of the stable austenite to martensite upon cooling to 77 K. This occurred only after relatively long time periods at elevated temperatures. However, it is informative to note that the possibility of this phenomenon exists and may be possible in the long time periods (1000 yrs) required for containment in the repository environment.

The long term, lower temperature precipitation of M23C6 carbides in the 304L and 316L stainless steels may significantly impact the mechanical and corrosion properties of these materials. The data discussed previously indicate the onset of grain boundary precipitation of M23C6 carbides at lower temperatures as time increases (t > 1500 hr). This precipitation is also greatly affected by the formation of intermediate phases as outlined in the following section.

Intermediate Phases

Alloy systems based on the transition metals iron and nickel, which also contain titanium, vanadium or chromium, can form a number of intermetallic phases. The austenitic stainless steels can form sigma (σ), chi (χ), and Laves (γ) phases that are thermodynamically stable. The compositions of these phases can adhere strictly to the prescribed stoichiometric ratios or the phases can exist over a range of composition. The sigma phase, which has a tetragonal structure, can range in composition form B4A to A4B. The chi phase has a bcc-α Mn structure with the formula (FeNi)36Cr12Mo10 [17], while the Laves phase has a hexagonal structure with the formula Fe2Mo [20]. The occurrence of these phases is dependent on the electron/atom ratio, atomic size and atomic compressibility. The conditions under which these phases form are quite complex. This is compounded by the fact that these phases usually do not form independently. Hence, competition for a particular constituent atom can become a factor. These phases generally precipitate over the temperature range 600°C < T < 1150°C.

The sigma (σ) phase has been extensively studied due to its occurrence in alloys used at elevated temperatures. Sigma is a hard, brittle, nonmagnetic phase in stainless steel that was first noted by Bain and Griffiths [21]. In 304 stainless steel, sigma formation is promoted by the presence of silicon. Silicon appears to broaden the composition range over which sigma is stable. The addition of molybdenum, as in 316 stainless steels, tends to further broaden the sigma phase range of stability. Phase equilibrium diagrams for a 70% iron alloy containing Mo, Ni and Cr were determined by Bechtoldt and Vacher [20]. This study noted that in the region near the composition of 316L stainless steel (16-18 Cr, 10-14 Ni, 2-3 Mo), the equilibrium phases that are present change from (α + γ) at 1204°C to (α + γ + χ + γ) at 815°C. The formation of the sigma phase can result in equilibrium chl and Laves phases as molybdenum content increases.

The formation of sigma phase in austenitic alloys leads to a reduction in fracture toughness as shown in Figure 4. This reduction in toughness is most pronounced at ambient temperatures. This figure indicates a dramatic decrease in fracture toughness with increasing sigma content in high nickel, high chromium austenitic alloys. Although the effect will not be as pronounced in 316L, the formation of even a small amount of sigma phase can have significant impact on the mechanical properties. This effect is primarily a problem at temperatures below about 600°C [22]. Intergranular corrosion of alloys containing sigma phase is also a problem in an oxidizing environment [23]. Sigma phase is not resistant to strong oxidizing
media such as hot concentrated nitric acid. This can lead to intergranular attack when the sigma phase is distributed along grain boundaries.

Precipitation Studies

The most useful method of determining the stability of a particular alloy is to complete a precipitation study. Time-temperature-precipitation (TTP) diagrams indicate the conditions required for precipitation of equilibrium phases to be formed. Precipitation in the 304 alloy system as been adequately described in the Carbide Formation section presented previously, since $M_{23}C_6$ is the predominant precipitate phase. Time-temperature-precipitation diagrams for the 316 alloy system are presented in Figure 5 [17,19]. This figure shows the TTP diagram for 316 stainless steel and the variation in precipitate distribution as a function of time for a 316 specimen aged at 816°C for up to 10,000 hours. Note the increase in $M_{23}C_6$ concentration beginning almost immediately. The chi phase begins to precipitate at about 150 hours, while the sigma and Laves phases do not begin to precipitate until about 500 and 1000 hours, respectively. Similar plots, which have been constructed for 316L, indicate that thermomechanical history has a significant impact on precipitate formation.

Precipitate formation in 304L and 316L stainless steels can significantly impact the mechanical properties and corrosion resistance of these materials. The studies outlined here indicate that these alloys can undergo significant microstructural evolution at moderate temperatures ($T < 650°C$) over relatively short time periods ($t < 1000$ hours). Repository temperature, though somewhat lower ($T < 250°C$), could promote precipitation in the time period of interest for container retrieval ($t < 450,000$ hours). Low temperature phase transformations, which occur over long time periods, must be considered when selecting the metal barrier material for the extremely long term applications of high level nuclear waste storage.

Alloy 825

Alloy 825 is an austenite stable material throughout the entire temperature range from the solidus temperature to room temperature. It does not undergo transformation to martensite or ferrite as do the 304 and 316 alloys. Figure 6 indicates the difference in phase stability between 825 and the stainless steels. The stainless steels, which contain approximately 70% iron, have $\alpha$ and $\gamma$ in equilibrium at low temperatures. Alloy 825, which contains only about 30% iron has a stable $\gamma$ phase throughout the entire temperature range as inferred by the left side of Figure 6. The transition to full austenite stability occurs between an iron content of 60 and 70%.

The following studies on phase stability in alloy 825 were identified. Brown and Kirchner [24] completed a survey of the corrosion of high alloy weldments that included a brief description of the resistance of 825 to sensitization. Brown [25] evaluated a number of alloy 825 samples from two separate heats with various heat treatments in corrosive environments and
Figure 5. Time-temperature-precipitation diagram for 316 SS annealed at 1260°C [17].

Figure 6. Cross section of the Fe-Cr-Ni ternary phase diagram [2].

noted a wide variation in resistance to sensitization. This variation was noted for heats of similar composition with identical laboratory anneal conditions but different mill anneal conditions. Brown concluded that variability in resistance to sensitization is highly dependent upon the entire process history in alloy 825. Cron et al [26] reported inconclusive evidence for the presence of sigma phase in alloy 825. Raymond [27] studied the sensitization of alloy 825 due to $M_{23}C_6$
precipitation at grain boundaries. These studies represent the limited information identified in this study. A review of the nickel-based alloy literature was completed to provide general background with respect to phase stability in these systems [28-32]. No significant precipitation or intermetallic phase formation in alloy 825 was identified.

Precipitation of the $M_23C_6$ carbide was noted in alloy 825 by Raymond [27] for alloy 825 after various anneal times. Raymond completed transmission electron microscopy studies of 825 using extraction-replica techniques and jet-machined thinning processes. The extraction-replica technique permits the determination of the chemical composition of the carbide precipitates by x-ray diffraction, x-ray emission spectrography and wet chemical analysis. Using these data, Raymond constructed the TTP diagram for alloy 825 and noted a variation in the chemical composition of the precipitates as a function of time and temperature. This fluctuation in composition included a variation in the ratio of the metal atoms in the precipitate that ranged from 5Cr:84Ti to 43Cr:46Ti. For specimens above and below the C-curve, the precipitate is highly enriched in titanium. Specimens within the C-curve exhibited carbide compositions with almost equal concentrations of Cr and Ti. The variation in chromium content of the $M_23C_6$ precipitates has a significant impact on the corrosion resistance of the 825 alloy. The higher the Cr content of the precipitate, the greater the probability of sensitization which could result in intergranular corrosion. This is due to depletion of Cr in the region near the carbide precipitates, as discussed previously. The variation in Cr content of the $M_23C_6$ carbides could account for some of the inconclusive data described in the literature.

The precipitation of other intermetallic phases in alloy 825, such as $\sigma$, $\zeta$, or $\eta$, has not been noted in the literature. Brown [25] suggested the presence of submicroscopic sigma phase to describe the wide variation in corrosion behavior exhibited by alloy 825. This appears unlikely since increasing the nickel content of an austenitic alloy has been shown to reduce the tendency for sigma formation [2]. No data were identified which documented the formation of chi or Laves phases in alloy 825. This agrees well with the equilibrium phase diagrams for the Fe-Cr-Ni ternary system (Figure 1).

It should be noted that even though $M_23C_6$ carbide precipitation has been noted in alloy 825, this may not result in significant degradation of the corrosion resistance of the material. The composition of the carbide, which includes Ti, does not lead to significant depletion of chromium near the precipitate. This would result in little possibility of sensitization of the material. Hence, there is usually no significant loss of corrosion resistance. Austenite stability, the limited precipitation of carbides and the lack of significant intermetallic phase formation suggest that alloy 825 would provide the most metallurgically stable material among the three austenitic container material candidates.

SUMMARY

A review of the technical literature with respect to phase stability of the candidate austenitic materials 304L and 316L stainless steel and alloy 825 has been completed. Significant data dealing with phase stability was noted for the stainless steel alloys. The 304L and 316L were identified as metastable materials at repository relevant conditions. In the 304L and 316L stainless steels, the diffusion processes that permit precipitation are severely limited at low temperatures ($T < 600^\circ C$). The predicted maximum operating temperature of the candidate material in the repository ($250^\circ C$) is significantly lower than the temperature for significant diffusion ($600^\circ C$).

Carbide precipitation was identified in all of the austenitic candidate alloys. The precipitation of $M_23C_6$ carbides was predominant in the 304L alloy. Similar precipitation behavior was noted for 316L with somewhat shorter time periods for the onset of grain boundary $M_23C_6$ precipitation. Carbide precipitation in the stainless steels (304L and 316L) may lead to sensitization and the potential for intergranular stress corrosion cracking. Intermetallic phase formation was noted in 316L at relatively long times. These intermetallic phases include sigma, chi and Laves phases. Sigma phase formation was shown to significantly reduce the impact strength of austenitic alloys due to its hard brittle microstructure. No intermetallic phase formation was documented in alloy 825.

Very few phase instability data were identified for alloy 825. The limited data that were found dealt primarily with $M_23C_6$ carbide precipitation. The $M_23C_6$ carbides that precipitated in the 825 alloy had varying composition. The chromium and titanium contents of these $M_23C_6$
precipitates were a function of precipitation time and temperature. Increased Ti content in these precipitates limited the depletion of Cr near the precipitate and preserved the corrosion resistance of the alloy. Speculation about the possibility of "submicroscopic" sigma phase precipitation in alloy 825 was noted. However, no data was identified to substantiate this claim.

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REFERENCES