Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers

Volume 7
Weldability of Austenitic Alloys

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List of Volumes of the Survey

This is Volume 7 of the report *Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers*. The titles of all of the volumes are as follows:

- **Overview**
- **Volume 1:** Phase Stability
- **Volume 2:** Oxidation and Corrosion
- **Volume 3:** Localized Corrosion and Stress Corrosion Cracking of Austenitic Alloys
- **Volume 4:** Stress Corrosion Cracking of Copper-Based Alloys
- **Volume 5:** Localized Corrosion of Copper-Based Alloys
- **Volume 6:** Effects of Hydrogen in Austenitic and Copper-Based Alloys
- **Volume 7:** Weldability of Austenitic Alloys
- **Volume 8:** Weldability of Copper-Based Alloys
### Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>AISI</td>
<td>American Iron and Steel Institute</td>
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<tr>
<td>ASME</td>
<td>American Society of Mechanical Engineers</td>
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<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
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<tr>
<td>bcc</td>
<td>body-centered cubic</td>
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<tr>
<td>CDA</td>
<td>Copper Development Association</td>
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<tr>
<td>CERT</td>
<td>constant extension rate test</td>
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<tr>
<td>CHLW</td>
<td>commercial high-level waste</td>
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<tr>
<td>DHLW</td>
<td>defense high-level waste</td>
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<tr>
<td>DOS</td>
<td>degree of sensitization</td>
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<tr>
<td>EPR</td>
<td>electrochemical potentiokinetic reactivation</td>
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<tr>
<td>fcc</td>
<td>face-centered cubic</td>
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<td>FZ</td>
<td>fusion zone</td>
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<tr>
<td>GMAW</td>
<td>gas metal-arc welding</td>
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<tr>
<td>GTAW</td>
<td>gas tungsten-arc welding</td>
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<tr>
<td>HAZ</td>
<td>heat-affected zone</td>
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<tr>
<td>IGSCC</td>
<td>intergranular stress corrosion cracking</td>
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<td>INCO</td>
<td>International Nickel Company</td>
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<tr>
<td>LTS</td>
<td>low-temperature sensitization</td>
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<tr>
<td>MIG</td>
<td>metal inert gas</td>
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<tr>
<td>MMA</td>
<td>manual metal arc</td>
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<tr>
<td>NNWSI</td>
<td>Nevada Nuclear Waste Storage Investigations Project</td>
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<tr>
<td>NRC</td>
<td>Nuclear Regulatory Commission</td>
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<tr>
<td>NWMP</td>
<td>Nuclear Waste Management Program</td>
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<tr>
<td>SAW</td>
<td>submerged arc welding</td>
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<tr>
<td>SCC</td>
<td>stress corrosion cracking</td>
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<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>SMAW</td>
<td>shielded metal-arc welding</td>
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<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
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<tr>
<td>TGSCC</td>
<td>transgranular stress corrosion cracking</td>
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<tr>
<td>TIG</td>
<td>tungsten inert gas</td>
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<tr>
<td>TTS</td>
<td>time-temperature sensitization</td>
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<tr>
<td>WZ</td>
<td>weld zone</td>
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Executive Summary

The candidate materials for the fabrication of containers for storing high-level nuclear waste include three austenitic alloys: Types 304L and 316L stainless steels and Alloy 825. The nuclear waste will be stored in containers at the prospective repository at Yucca Mountain, Nevada. This volume reviews the degradation modes that result from welding the austenitic candidates. Three specific areas of concern are discussed in depth: (1) resistance to corrosion, (2) hot cracking, and (3) formation of intermetallic phases. Corrosion resistance can decrease in weldments because of preferential corrosion, sensitization to intergranular corrosion, and susceptibility to stress corrosion cracking (SCC). Sensitization due to preferential grain-boundary precipitation of $\text{M}_2\text{C}_6$ carbides within the heat-affected zone (HAZ) of the weld decreases resistance to intergranular corrosion. It also increases susceptibility to intergranular stress corrosion cracking (IGSCC).

The formation of carbides is a nucleation and growth phenomenon affected by time, temperature, chemical composition, and thermal strain. We review models for intergranular corrosion based on localized chromium depletion due to precipitation of carbides at grain boundaries. A compositional model for sensitization is discussed that defines an effective chromium content. The effective chromium content accounts for the beneficial effect of elements such as chromium and molybdenum as well as the detrimental influence of carbon and nickel. Other elements such as silicon, nitrogen, sulfur, manganese, and phosphorus are reviewed with respect to their effects on carbide formation.

Of major interest to the Nevada Nuclear Waste Storage Investigations (NNWSI) Project is the effect of long storage times on nucleated carbides. This effect is typically described as low-temperature sensitization (LTS), i.e., service temperatures are below 400°C. Although some data are available on Type 304L stainless steel showing a loss of resistance to corrosion, there is a general lack of information on Type 316L stainless steel. The problem in prediction lies in the lack of available data on the long-term growth of the carbides at relatively low temperatures. Even less information is available on the LTS of Alloy 825; it would appear, however, that the high-nickel alloys are not subject to LTS.

Minimizing the carbon content is the most effective means of preventing sensitization. With proper welding procedures, neither of the low-carbon grades of austenitic stainless steels, Type 304L or Type 316L stainless steel, will sensitize as a result of weld fabrication. According to the compositional model and confirmations by available data, Type 316L stainless steel is more resistant to sensitization than Type 304L stainless steel. While Alloy 825 can be stabilized to impart immunity from traditional sensitization, there is a potential for sensitization after dissolution of the stabilized carbides in multipass welds. Specification of low carbon contents will prevent this susceptibility. In addition to the resistance of Alloy 825 to sensitization, its high nickel content and fully austenitic structure make it the least susceptible to SCC.

The susceptibilities of the weldment to cracking are reviewed with an emphasis on microfissuring of the HAZ. The formation of ferrite in the fusion zone (FZ) is discussed, and theories as to why ferrite provides such a positive countermeasure against grain-boundary cracking are presented. Basically, the ferrite serves to decrease the sensitivity to impurity contents. In terms of resistance of the weldment to cracking, Type 304L stainless steel is best, followed by Type 316L stainless steel and Alloy 825. As in the case of sensitization, there are very few data in the open literature on the causes of hot cracking in Alloy 825 weldments. Much of the reported information was obtained from private communications with individuals having experience in the nickel industry. The most generally accepted method of preventing hot cracking in Alloy 825 is to substitute a weld filler material of a different composition, namely Alloy 625.

The formation of intermetallic sigma phase ($\sigma$) can occur at elevated temperatures in austenitic stainless steels, and under certain conditions, it can remain stable at room temperature. Sigma, a hard, brittle, nonmagnetic phase, can result in the reduction of some mechanical properties, namely fracture toughness or impact resistance. Data are presented suggesting that the rate of formation of $\sigma$ and its effects on mechanical properties are increased by the presence of ferrite in the FZ. Sigma phase is more likely to form in the molybdenum-containing Type 316L stainless steel than in Type 304L stainless steel. Although no mention was found of immunity from formation of $\sigma$ in Alloy 825, its formation is considered highly unlikely on the basis of existing phase diagrams.

On the basis of resistance to corrosion-assisted degradation, the austenitic candidate materials are ranked as follows in terms of weldability: Alloy 825 (best) > Type 316L stainless steel > Type 304L stainless steel (worst).
Survey of Degradation Modes of Candidate Materials for High-Level Radioactive-Waste Disposal Containers

Volume 7: Weldability of Austenitic Alloys

Abstract

This volume surveys the effects of welding on the degradation modes of three austenitic alloys: Types 304L and 316L stainless steels and Alloy 825. These materials are candidates for the fabrication of containers for the long-term storage of high-level nuclear waste. The metallurgical characteristics of fusion welds are reviewed here and related to potential degradation modes of the containers. Three specific areas are discussed in depth: (1) decreased resistance to corrosion in the forms of preferential corrosion, sensitization, and susceptibility to stress corrosion cracking, (2) hot cracking in the heat-affected zone and the weld zone, and (3) formation of intermetallic phases. The austenitic alloys are ranked as follows in terms of overall weldability: Alloy 825 (best) > Type 316L stainless steel > Type 304L stainless steel (worst).

1. Introduction

The Nuclear Waste Management Program (NWMP) at Lawrence Livermore National Laboratory is responsible for developing the engineered barrier design to meet the Nuclear Regulatory Commission licensing requirements for the permanent disposal of high-level nuclear waste. This waste will include (1) spent fuel from civilian nuclear power plants (fuel assemblies from pressurized-water reactors and boiling-water reactors, and consolidated fuel pins), (2) commercial high-level waste (CHLW) in the form of spent-fuel reprocessing wastes contained in borosilicate glass, and (3) defense high-level waste (DHLW) contained in borosilicate glass. The waste package is being designed for emplacement in a geologic repository at a site at Yucca Mountain, Nevada. The reference horizon is located in the Topopah Spring Member of the Paintbrush Tuff, 350 m below the ground surface and 200 m above the static water table. The composition of the vadose water results in slightly oxidizing conditions in the repository.

The Metal Barrier Selection and Testing Task of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project has as its objective the selection of a candidate material to be used in the waste-package container that will meet the requirements set forth in the relevant federal regulations [1, 2]. Six candidate materials are currently under consideration, including these austenitic materials: Types 304L and 316L stainless steels and Alloy 825. The austenitic materials have been selected as a result of their relatively high strength and good corrosion resistance. The specified ranges of composition of these alloys are presented in Table 1. The remaining materials under consideration are three copper-based alloys: CDA 102 (oxygen-free copper), CDA 613 (Cu-7Al), and CDA 715 (Cu-30Ni).

The design criteria for the metal barrier require that the waste container maintain chemical and mechanical integrity for a period of about 50 yr after emplacement to permit the nuclear waste to be retrieved during the preclosure phase of repository operation [1, 2]. The engineered barrier system must provide substantially complete containment for at least 300 yr and perhaps as long as 1000 yr. During the containment period, the metal barrier will be exposed to a changing environment. Radioactive decay of the stored waste will result in substantial heat generation. Initially, many of the waste packages will be at a temperature of about 250°C (482°F). After 100 yr of storage, the temperature will drop to about 150°C (302°F). The resistance of the container material to corrosion over these time periods will have an impact on the mechanical behavior of the metal barrier. Degradation modes include
uniform aqueous phase corrosion and various forms of localized corrosion. Precipitation of carbides at grain boundaries can modify the local alloy composition, resulting in conditions favorable to intergranular stress corrosion cracking (IGSCC). The formation of sigma phase (σ) and the development of microcracks during the welding process can potentially reduce the fracture properties of the material.

This volume on the austenitic candidate materials reviews the basic metallurgy of the austenitic alloy system, discusses the effects of welding on corrosion, and examines the potential loss of toughness in weldments. Areas are highlighted in which significant data and results exist in the literature, and areas are identified in which very little data is found. The effects of welding on the copper-based candidates are surveyed in Vol. 8.

A discussion on the methodology and extent of the literature search can be found in the Overview.*

2. Basic Metallurgy of Welding

2.1 Nature of the Weld Process

From the viewpoint of the metallurgical effects of welding, the welding processes can be divided into fusion and solid-state techniques. Fusion welding involves heating the surfaces to be joined to above the melting point and, if necessary, adding filler metal to fill the joint gap. Solid-state joining processes require only the creation of clean surfaces and subsequent contact to allow formation of a metallic bond. Because fusion processes are normally required for joining large structures, and because fusion processes encompass more of the pertinent metallurgical concerns, this discussion will focus on the effects of fusion welding.

A fusion weld has been termed a microcosm that involves melting, solidification, and virtually every microstructural change that can be produced by thermal treatments [3]. The metallurgical effects of the welding process are heterogeneous, and it is therefore useful to describe discrete zones within a weldment. The fusion zone (FZ) consists of a composite of filler metal diluted by the surrounding base metal. This zone is surrounded by an unmixed zone consisting of base metal melted without mixing. Its outer edge defines the weld interface.

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Further from the FZ exists the partially melted zone, where localized liquid films may form at low solidus regions such as segregated grain boundaries. Beyond this region is the true heat-affected zone (HAZ), where all microstructural changes are restricted to the solid state. The fusion-welding process and process variables influence the extent and morphology of these zones. The widths of the partially melted zone and HAZ are inversely related to the steepness of the thermal gradient, which increases with the power density of the heat source. The extent of the unmixed zone decreases in processes that permit uniform melting and mixing of the filler metal. Processes such as cold-wire-feed gas tungsten-arc welding (GTAW) minimize the formation of unmixed zones, while more erratic weld-pool mixing, as in gas metal-arc welding (GMAW) or shielded metal-arc welding (SMAW), is more likely to produce unmixed zones [4].

2.1.1 Effects of Melting

Melting and subsequent resolidification in weldments result in significant compositional and microstructural changes relative to the wrought parent metal. A number of reactions can occur in the liquid metal. Protection of the molten surface from atmospheric oxygen and nitrogen is accomplished through the use of flux and/or protective atmospheres. Oxygen pickup and the content of oxide inclusions are minimized through the exclusive use of protective atmospheres, which may consist of inert-gas shielding or evacuation. Because the maximum temperatures in the FZ can approach the boiling point, vaporization losses may also occur. Elements with low vapor pressure will be preferentially depleted from the FZ and may necessitate the use of overalloyed filler metal to compensate for these losses.

Another means through which compositional heterogeneity occurs in weldments is by solidification segregation. Solidification in welds requires the redistribution of composition between the solid and liquid phases. The first solid to form is either enriched or depleted in alloying elements relative to the remaining liquid. This phenomenon leads to the formation of a concentration gradient at the solid-liquid interface. The rapid cooling rates characteristic of weldments limit compositional homogenization during solidification to the liquid phase and only by diffusion (mechanical mixing in the liquid and diffusion in the solid are not significant) [3]. In highly alloyed materials such as the austenitic alloys, these restrictions typically result in a cellular-dendritic mode of solidification and microsegregation. The solidification fronts grow epitaxially from the equiaxed parent metal grains as spikes along the major direction of heat extraction. The surrounding liquid is later consumed by lateral growth. Because of solute rejection at the solid-liquid interface, both the initial and final liquids to solidify can be of a significantly different composition than that of the average FZ. The extent of microsegregation is dependent on the equilibrium distribution coefficients of the solute species between the solid and liquid phases.

The last liquid to solidify is typically enriched in low-melting solutes and solidifies at a temperature well below the equilibrium (bulk) solidus. This has a marked influence on the resistance of the weldment to hot cracking. Solute elements that severely depress the effective solidus (temperature at which the last liquid actually solidifies) have the largest negative impact on resistance to hot cracking and microfissuring. Hot cracks are believed to initiate at liquated grain boundaries in the FZ and partially melted zone. Microfissuring occurs during reheating of underlying weld beads in multipass welds. The region of partial melting in the underlying weld bead is extended by the presence of microsegregation. The driving force for hot cracking and microfissuring is the tensile stress produced by the shrinkage strains during weld solidification and cooling. The residual stresses in a weld generally increase with increased restraint, as in thick-section welds, and can reach the ambient-temperature yield strength of the weldment.

2.1.2 Solid-State Thermal Effects

The thermal cycles in the HAZ vary with location and reach peak temperatures ranging from near-ambient to near the melting point. The cooling rates in the HAZ are dependent on factors such as the physical properties of the material, section sizes, ambient temperatures (or interpass temperatures), the power density of the heat source, and the heat input. The thermal history of a particular HAZ region is dependent on the total number of weld passes as well as geometric factors such as the width of the HAZ relative to the size of the weld beads. The width of the HAZ and the extent of thermal exposure above a critical temperature or within an elevated temperature range is dependent on the selection of the weld process and fabrication technique.
Exposure to elevated temperatures in the HAZ is limited by the use of a high-power-density process, low heat inputs, and low preheat and interpass temperatures.

In solid-solution alloys, the effect of HAZ thermal cycles is small. The most significant effect is grain growth at the regions of highest peak temperature near the partially melted zone. In previously cold-worked material, HAZ temperatures can also cause recrystallization. The effects on the HAZ in precipitation-hardened alloys or alloys subject to solute precipitation are more complex. The welding heat will re-solutionize the precipitates in regions of high peak temperature, and enhance precipitation or cause overaging at intermediate peak temperatures. Carbide precipitation in the HAZs of welds is a common concern in austenitic alloy weldments.

2.2 Weldability of the Austenitic Candidates

Several general review articles on the constitution and structure of stainless steels and austenitic alloys have been identified in the technical literature [e.g., 5-7]. A summary of these articles is provided here.

The austenitic candidate materials are all derived from the ternary iron-chromium-nickel system. The most basic phases encountered in this ternary system are dictated by the allotropic forms of iron, which can be identified in the chromium-iron binary phase diagram shown in Fig. 1 [8]. Between the melting point of 1539°C (2800°F) and about 1390°C (2558°F), pure iron exists as a body-centered cubic (bcc) structure that is usually called delta (δ) ferrite. From about

Figure 1. Chromium-iron binary equilibrium phase diagram [8].
1390 to 910°C (2550-1670°F), the structure of iron is face-centered cubic (fcc) and is called austenite or gamma phase (γ). Below 910°C (1670°F), iron again becomes bcc, with a structure identified as alpha (α) ferrite. There is no obvious microstructural difference between δ and α ferrite. This nomenclature has been adopted to provide a distinction between the conditions of formation of the ferrite.

The addition of chromium (up to about 7 wt%) to iron lowers the austenite temperature range, as indicated on the left side of Fig. 1. Above 7 wt% chromium, the temperature range over which austenite exists is gradually reduced. Above 13 wt% 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 used in stainless steels that behave similarly to chromium are molybdenum, silicon, aluminum, titanium, and niobium.

Austenitic alloys all contain more than 16 wt% chromium, which should produce an entirely ferritic material (Fig. 1). The effect of chromium is counteracted, however, by the addition of nickel. Figure 2 shows the equilibrium phase diagram for the iron-nickel system [8]. The austenite phase region is significantly increased by the addition of nickel to iron. Therefore, nickel is called an austenite-forming element. Manganese and cobalt are other examples of austenite-forming elements.

The effect of the balance of chromium and nickel additions on phase equilibria is shown in the pseudobinary-alloy phase diagrams for 63.5% iron alloys in Fig. 3, and for 50, 60, 70, and 80% iron alloys in Fig. 4. The iron-nickel-chromium ternary alloy phase diagram at 650°C (1202°F) is
shown in Fig. 5. The primary mode of solidification in austenitic welds and the resulting ferrite content are very important for the control of microfissuring and other second-phase concerns. Therefore, the concepts of chromium equivalent and nickel equivalent were developed. These values incorporate the tendency of additional alloying elements to stabilize either the austenite phase (as does nickel) or the ferrite phase (as does chromium). From these equivalent compositional values, a constitution plot mapping the amount of retained ferrite in weld FZs can be derived, as determined by Schaeffler (Fig. 6) and also by DeLong (Fig. 7).

As a class of materials, the austenitic alloys are considered the most weldable of any of the high-alloy steels. This is due to the good toughness of austenitic alloy weldments, even in the as-welded condition. Even so, there are three general concerns with respect to the weldability of these materials. These concerns are: (1) preservation of the corrosion resistance, (2) prevention of cracking, and (3) avoidance of harmful effects from intermetallic formation. The principal concern with respect to corrosion resistance of the weldment is prevention of sensitization to intergranular corrosion and intergranular stress corrosion cracking (IGSCC). Sensitization is basically a result of chromium depletion surrounding chromium-rich carbide precipitates in the HAZ. The susceptibility to sensitization can be reduced through compositional control of alloying-element additions and by limiting the extent of thermal excursions within the sensitization temperature range. Limitation of carbon contents, as in Types...
Fig. 4. Cross sections of iron-chromium-nickel ternary phase diagram [101].
Figure 5. Iron-chromium-nickel equilibrium phase diagram at 650°C (1202°F). Note the location of Types 304L and 316L stainless steels and Alloy 825, plotted using nickel and chromium equivalent values [4].

304L and 316L stainless steels, is the most effective means of decreasing the susceptibility to sensitization.

Cracking during solidification and reheating is also strongly dependent on alloy and impurity contents but is most easily avoided by an indirect effect of chemistry on solidification behavior. Solidification as primary ferrite or insurance of at least 3 to 5% residual ferrite in the final microstructure avoids most cracking concerns in these alloys. The precipitation of intermetallics such as \( \sigma \) phase can embrittle austenitic steels. Such embrittlement is dependent on the extent and distribution of intermetallic formation as determined by the composition, thermal history, and ferrite content (which can accelerate \( \sigma \) formation).

The high-nickel alloys such as Alloy 825 possess welding characteristics somewhat different from those of the austenitic stainless steels. In addition to the welding concerns for Types 304L and 316L stainless steels, three concerns can be listed. These are: (1) an increased necessity for cleanliness, (2) the inherently viscous weld metal, and (3) the characteristically low penetration. As pointed out by Kaiser [9], these concerns make the welding of high-nickel alloys different but not necessarily difficult. The necessity for increased cleanliness is twofold. First, unlike iron oxide, nickel oxide melts at temperatures above the typical temperature in the FZ and must be avoided to prevent lack-of-fusion or trapped oxide defects. Second, the sensitivity to cracking increases with nickel content, and deleterious impurities such as sulfur, lead, phosphorus, zirconium, and boron must be avoided [4]. Alloy 825 is fully austenitic and more susceptible to microfissuring than Type 304L stainless steel, especially in thick sections. Filler metals
Figure 6. A Schaeffler diagram [78].

Figure 7. A DeLong diagram [79].
designed for improved resistance to cracking, such as Alloy 625, reduce this concern. The viscous nature of high-nickel alloys requires special attention to arc manipulation to ensure complete fusion with the sides of the joint. This is typically achieved with proper weld procedures. Last, the characteristically low penetration of high-nickel alloys must simply be accepted to avoid overheating.

3. Corrosion

The resistance of the austenitic candidates to corrosion can be significantly altered by the welding process. Attention must be given to the potential for preferential corrosion in the FZ, sensitization in the HAZ, and enhanced susceptibility to stress corrosion cracking (SCC). Both the potential causes of weld-induced decreases in corrosion resistance and preventive procedures are discussed here. Corrosion resistance of the weldment equivalent to that of the parent metal can be achieved through control of parent-metal chemistry and the use of proper welding procedures. Proper welding procedures include the maintenance of cleanliness, selection of appropriate filler metals, and limitation of weld heat inputs, preheat, and interpass temperatures.

3.1 Preferential Corrosion of the FZ

Relative to the wrought parent metal, the FZ of a weldment is inhomogeneous in composition and microstructure. Because corrosive processes are selective, choosing the most susceptible region for attack, this inhomogeneous nature of the FZ can lead to preferential corrosive attack. Inhomogeneities may arise from the localized depletion of alloying elements by either alloy segregation during solidification or by sublimation during melting. This can result in preferential corrosive attack of these regions. Therefore, filler metals are often designed to compensate for these effects through overalloying. Microstructural differences in the FZ can also alter the corrosion resistance. Solidification segregation can enhance the formation of second phases such as intermetallics and stabilize the high-temperature ferrite. Weld filler metals for the austenitic alloys are commonly designed to initially solidify as δ ferrite to reduce susceptibility to microfissuring. This results in duplex austenitic/ferritic microstructures in the rapidly cooled FZ.

Localized depletion of alloying elements responsible for good corrosion resistance can result in accelerated corrosion within the FZ. Garner [10] has shown that molybdenum- and chromium-depleted regions in the dendritic structure of the FZ undergo preferential attack over a wide range of oxidizing conditions. This preferential attack is considered to be more of a problem in primary austenitic solidification, which leaves the dendrite cores depleted in molybdenum and chromium. Primary δ ferrite solidification results in molybdenum and chromium enrichment at the dendrite cores, with depletion of these elements in the interdendritic regions. David et al. [11] have shown that the retained ferrite is depleted in nickel as well as being enriched in chromium.

The influence of autogenous welding on resistance to pitting in the FZ has been quantified for several high-alloy stainless steels by Garner [10, 12]. Both potentiostatic and isothermal immersion tests in 10% FeCl₃ show reductions in the resistance of austenitic alloys to pitting after autogenous welding. The loss of pitting resistance relative to the unwelded parent metal increases with increasing molybdenum content in the high-alloy steels. A roughly linear relationship is observed between the critical pitting temperature and the molybdenum content for both parent and weld metal. The improvement in the pitting resistance in the weld metal, however, increases more gradually with increasing molybdenum content than in the parent metal. Because of this relationship, the pitting resistance of the parent metal can be achieved in the weld through the use of overalloyed filler metals enriched in molybdenum. For example, the pitting protection of the 3.2% molybdenum Type 317L stainless steel parent metal is achieved using a 3.8% molybdenum Type 317L stainless steel or higher-alloy filler metal. Alloys such as Type 304 stainless steel without molybdenum additions are typically welded with a filler metal of higher nickel and
chromium content (such as Type 308 filler, which is used for welding Type 304 stainless steel parent metal) [13].

While the use of overalloyed filler metals increases the corrosion resistance of the FZ, unmixed zones may also exist. Unmixed zones are essentially very thin autogenous welds with a chemistry similar to the parent metal. These unmixed zones are expected to possess the corrosion resistance of the welded parent metal. Skillful welding can avoid surface unmixed zones and prevent associated preferential corrosion in welds with enriched filler metals.

Preferential corrosion may also occur in the FZ due to the presence of second phases. Austenitic alloys commonly contain 5 to 10% retained δ ferrite in the FZ. This ferrite is present in the form of a continuous or nearly continuous dendritic network at these levels. As in the case of solidification segregation discussed above, compositional partitioning between the ferrite and austenite exists but with a sharp discontinuity in composition at the austenite/ferrite interface. This can result in galvanic coupling, and preferential attack of the ferrite has been observed [11, 14]. Preferential attack of the ferrite may occur in strong mineral acids and in strongly reducing media such as ammonium carbamate [14]. For this reason, ferrite levels may be limited to less than 2% (to ensure discontinuous networks) and special precautions taken to avoid the greater susceptibility to microfissuring. The influence of ferrite on SCC will be discussed below. Ferrite, and molybdenum- and chromium-rich regions, can also provide a fast transformation path for intermetallics enriched in these elements. At temperatures above 600°C, ferrite has been observed to transform to α or χ phases [10, 15, 16]. These molybdenum- and chromium-rich precipitates are not attacked under mild or moderate oxidizing conditions but are susceptible to attack in reducing acids or highly oxidizing acids [12]. Sensitization of weld microstructures to localized corrosive attack by the precipitation of semicontinuous chromium-rich carbides will be discussed below.

3.2 Sensitization of Iron- and Nickel-Based Austenitic Alloys

Sensitization due to welding is the most common cause of weld-related intergranular corrosion in austenitic alloy components of the chemical and power industries [17]. Sensitization describes a metallurgical condition in which the material is rendered susceptible to localized corrosive attack at the grain boundaries. The loss of corrosion resistance is generally a result of slow cooling through a particular temperature regime [18], within which chromium-rich carbide precipitation occurs. When weld sensitization occurs, it is associated with the HAZ of the weld.

Three theories have been proposed to explain the intergranular corrosion of sensitized austenitic steels: Bain et al.'s chromium depletion theory [19], the noble carbide theory [20], and the segregation theory [21]. Bain et al.'s classical chromium depletion theory seems to be the most credible. The noble carbide theory argues that intergranular corrosion is brought about by an electrochemical reaction between the carbide particles and the matrix and proceeds along a continuous path of connected carbide particles. The segregation theory described by Aust [21] explains intergranular corrosion as a result of a continuous grain-boundary path of either second-phase or soluble segregate resulting from solute-vacancy interactions. Some evidence exists supporting the role of grain-boundary segregation of phosphorus in accelerating grain-boundary corrosion in material without grain-boundary carbide precipitation [22].

The chromium depletion theory is based on two main assumptions: (1) the bulk material contains sufficient chromium to provide a protective passive film (generally agreed to be 13–15 wt% chromium), and (2) the material adjacent to a chromium-rich carbide particle precipitated in the sensitization range will have a chromium content below that required for passivation. Bain and his co-workers theorized that, during sensitizing heat treatments, chromium-rich carbides preferentially precipitate along grain boundaries. Chromium, having a much slower diffusion rate than carbon, is initially drawn from the surrounding grain-boundary regions. At sensitizing temperatures, the replenishment of chromium from the surrounding matrix is prevented by the slow matrix diffusivity of chromium. The chromium deficiency in the grain-boundary area surrounding the carbide creates a grain boundary susceptible to localized intergranular attack.

A susceptible microstructure results when chromium carbide precipitation at the grain boundaries depletes the chromium content of the surrounding grain-boundary area below the critical level required for passivity (Fig. 8). In the
absence of any strong carbide-forming element, the principal carbide formed is $M_{23}C_6$, where $M$ is primarily chromium, although other elements such as iron and molybdenum can partially substitute for the chromium. Precipitation of $M_{23}C_6$ takes place in the approximate temperature range of 450 to 950°C (842 to 1742°F) [23]. However, weld sensitization is only observed in a more limited temperature range, typically between 550 and 800°C (1022 to 1472°F), and is strongly dependent on composition as well as the strain state and thermal history [18, 24].

More recent theoretical and experimental studies [23, 25] have provided a more quantitative approach to the local chromium-carbon-carbide equilibrium at the grain boundary. The studies assumed that the local concentration of chromium immediately adjacent to a carbide particle could be calculated from the equilibrium constant for the solubility of chromium carbide in an austenite matrix:

$$23\text{Cr} + 6\text{C} \leftrightarrow \text{Cr}_{23}\text{C}_6$$

(1)

The equilibrium constant is given by:

$$k = \frac{1}{(\gamma_{\text{Cr}} X_{\text{Cr}})^{23} (\gamma_{\text{C}} X_{\text{C}})^6}$$

(2)

The activity coefficients of carbon, $\gamma_{\text{C}}$, and of chromium, $\gamma_{\text{Cr}}$, were obtained from available experimental data combined with a Wagner analysis [26], while unit activity is assumed for the carbide. With the determination of $\gamma_{\text{C}}$ and $\gamma_{\text{Cr}}$, the chromium composition at the grain boundary, $X_{\text{Cr}}$, in equilibrium with the carbide can be calculated from Eq. (2), assuming that the carbon activity, $\gamma_{\text{C}} X_{\text{C}}$, is fixed by the bulk chromium composition. This calculation seems reasonable since carbon has a much higher diffusion rate than chromium at sensitizing temperatures.

Figure 9 gives the calculated values for the chromium concentration in the grain boundary
Sensitization in the HAZ of the weld is an important determinant of the weldability of austenitic alloys for use in corrosive environments. The degree of sensitization (DOS) after welding is strongly dependent on both the composition and the thermal history of the HAZ. Strains due to prestrains or cooling strains during welding, as well as the microstructural characteristics of the weld, affect the kinetics of sensitization. These important factors in the control of sensitization and the resulting susceptibility to intergranular corrosion and IGSCC are discussed below.
3.2.1 Effects of Alloying Elements

Although chromium and carbon contents are both critical to sensitization of the grain boundaries by carbide precipitation, carbon content is the principal compositional variable determining the rate and extent of precipitation. Carbon has a wide range of acceptable composition in austenitic alloys (0.01 to 0.08 wt%) compared with the acceptable range for chromium of 18 to 20 wt% in Type 304 stainless steel and 16 to 18 wt% in Type 316 stainless steel. The reduction in time required for sensitization at 650°C with increased bulk carbon content in Type 304 stainless steel is
Figure 11. Time-temperature-sensitization curves determined by EPR tests on Type 304 stainless steel alloys of variable carbon contents [18].

Figure 12. Time-to-sensitization data as determined by modified Strauss or EPR tests at 650°C (1202°F), plotted as a function of bulk carbon content for Type 304 stainless steel [33].
shown in Figs. 11 and 12. Data on time for sensitization of Type 316 stainless steel at 650°C are included in Fig. 13. The scatter in the data can be partially attributed to differences in other elements affecting sensitization such as the chromium, molybdenum, and nickel concentrations of individual heats of Types 304 and 316 stainless steels.

Alloying elements can affect the process of sensitization and the susceptibility to intergranular corrosion and IGSCC in several ways. While carbon content is the dominant element controlling sensitization, the rate and extent of $M_23C_6$ carbide precipitation are altered by alloy and impurity additions. Composition also influences the corrosion/passivation properties of chromium-depleted zones. In addition, alloy elements can stabilize the alloy against sensitization by altering the chromium content of precipitated carbides. The alloying elements chromium, molybdenum, nitrogen, niobium, titanium, and manganese can be classified as beneficial in decreasing susceptibility to sensitization; carbon, nickel, sulfur, and phosphorus are detrimental.

Results of work by Briant et al. [27] on several different compositions with and without molybdenum and with varying amounts of chromium show that in a Strauss test [28], the alloys containing molybdenum required only 11 wt% chromium to prevent corrosion, whereas alloys without molybdenum required 15 wt% chromium to prevent corrosion. Consequently, a greater amount of chromium depletion is required before sensitization of the molybdenum-containing alloys is observed. A molybdenum
addition of 2% in an 18Cr-15Ni steel increased the critical time required for sensitization at all temperatures tested (approximately 400–850°C; 752–1562°F) in an acid copper sulfate solution [29], as shown in Fig. 14. Hall et al. [30] noted that no martensite was evident in molybdenum-containing alloys even after straining, which suggests that molybdenum also tends to prevent the formation of martensite in Type 316L stainless steel.

Tedmon et al. [25] studied the carbon activity coefficient in austenitic steel vs nickel content at 600°C (1112°F) for various chromium levels. From this work, nickel appears to increase the activity coefficient of carbon and thus the susceptibility toward sensitization, as shown Fig. 15. This increase in the activity coefficient caused by nickel is not totally unexpected because there is such a low solubility of carbon in nickel and because stable carbides of nickel are absent.

The concept of an empirical equation to include the variations in chromium, nickel, and molybdenum into an effective chromium content was developed by Cihal [31] and expanded by Fullman [32]. The equation is based on the concept that the important variable in determining the time required for sensitization of an alloy is the local chromium activity at the interface. The chromium activity at this interface depends not only on the chromium concentration but also on the concentration of the other elements, especially carbon. The effective chromium content, Cr_eff, is a reflection of the change in the chromium activity as a result of the presence of these other elements. Several such empirical relations have been proposed [27, 31, 33, 34]. The effective chromium relation given by Kass et al. [34], which accounts for the variability in carbon, molybdenum, and nickel may be written as:

$$Cr_{eff} = Cr + 1.7Mo - 100C - 0.2(Ni - 10) \quad (3)$$

Three observations can be made from Eq. (3): (1) carbon content is of principal importance, (2) an increase in molybdenum can be almost twice as effective as chromium in preventing sensitization, and (3) the contribution of nickel in low-alloy stainless steels to the degradation of chromium is small. Kass et al. [34] report that a Cr_eff of 16.2 or greater has been shown to confer immunity from intergranular cracking in boiling-water reactor environments after an isothermal treatment of 620°C for 24 hr. They also point out that a Cr_eff of 15.7 is more appropriate for the less severe thermal cycle due to welding.

Figure 16 shows the time-temperature susceptibility range for 18 wt% chromium austenitic stainless steels and alloys to intergranular corrosion for carbon contents between 0.005 and 0.087 wt% and nickel contents between 9 and 40 wt%.
Figure 15. Carbon activity coefficient in austenitic steel vs nickel content at 600°C (1112°F) for various chromium levels [25].

At a carbon level of 0.005 wt%, a change in nickel content from 9 to 40 wt% barely affects the susceptibility to intergranular corrosion, but at a carbon level of 0.021 wt%, a change in nickel content from 9 to 40 wt% significantly decreases the time required for sensitization. At 0.087 wt% carbon, the influence of nickel content on the time-temperature susceptibility range again diminishes.

Nitrogen can have a positive influence on the reduction of intergranular corrosion since it tends to retard the nucleation and growth of carbides at the grain boundaries [27, 35]. The response of Type 304L stainless steel to two levels of nitrogen is shown in Fig. 17. This figure shows that the addition of 0.13 wt% nitrogen increased the time necessary for sensitization at most temperatures although little effect is observed near 600°C (1110°F). In contrast to the above, some researchers have reported that perhaps nitrogen does not have such a positive effect on preventing sensitization. Cowan and Tedmon [24] postulated that nitrogen might play a role similar to carbon, causing the precipitation of chromium-nitrogen compounds and inducing grain-boundary chromium depletion. An investigation by Mulford et al. [35] found that in Type 316L stainless steel with high levels of nitrogen (0.16 wt%), many phases are found at the grain boundaries, including Laves phase Cr$_2$N as well as M$_2$C$_6$. The presence of these additional phases, however, did not appear to adversely affect the resistance to sensitization.
Figure 16. The effect of nickel content (9–40 wt%) and carbon content (0.003–0.087 wt%) on the susceptibility to intergranular corrosion (Rollason curve) in austenitic steels and alloys containing 18 wt% chromium, as found after testing in standard solution [31].

Figure 17. Response of Types 304LA (0.002 wt% nitrogen) and 304LN-A (0.13 wt% nitrogen) stainless steels to the modified Strauss test [35].
Auger spectroscopy has shown that both nitrogen and phosphorus have a tendency to segregate to grain boundaries in the sensitization temperature range [35]. Such impurity segregants can compete for grain-boundary sites [36], decreasing nitrogen levels (see Fig. 18). They may also independently increase the susceptibility of the steel to corrosion. Phosphorus segregation has been associated with accelerated intergranular corrosion in highly oxidizing solutions [22,37]. Although sulfur can also segregate to grain boundaries, its effect on corrosion and SCC is small [37]. This may be due in part to the precipitation of most of the sulfur as manganese sulphides.

Although manganese does not appear to have any detrimental effects on passivation, its beneficial effects are small. Briant et al. [27] showed that manganese retarded carbide precipitation in a specially prepared Type 304L stainless steel containing nitrogen at 600°C (1112°F). However, this effect was not observed at 650 and 700°C (1202 and 1292°F), the other temperatures tested.

The addition of stabilizing elements, such as niobium and titanium, can prevent chromium depletion by forming carbides that are thermodynamically more stable than chromium. The stabilized grades are essentially immune to isothermal sensitization when properly heat-treated, but can leave areas susceptible to subsequent sensitization, as in the "knife-line" corrosive attack in the HAZ of the weld. Dissolution of the niobium or titanium carbide in the HAZ occurs at sufficiently high HAZ temperatures, typically above 1205°C (2200°F) for niobium carbide. Subsequent rapid cooling can leave the carbon in solution, unsta- bilized and susceptible to sensitization. While large additions of stabilizer decrease the tendency for chromium-rich carbide co-precipitation, additions are limited by the corresponding increase in susceptibility to cracking in the HAZ.

### 3.2.2 Effects of Welding on Sensitization

Sensitization of weldments can result during fabrication or postweld heat treatments. The effects of thermal history, strain, and microstructure on the DOS are discussed individually below, following a description of techniques used to evaluate the DOS.

**Techniques for Evaluating Sensitization.** The accepted practices for determining the susceptibility to intergranular attack as recommended by ASTM are A 262, practices A-E [28]. Practice A is the oxalic acid etch test for classification of etch structures of austenitic steels. Practice B is the ferric sulfate-sulfuric acid test for detecting susceptibility to intergranular attack in austenitic stainless steels. Practice C is the nitric acid test
for detecting susceptibility to intergranular attack in austenitic stainless steels. Practice D is the nitric-hydrofluoric acid test for detecting susceptibility to intergranular attack in molybdenum-bearing austenitic stainless steels, and Practice E is the copper-copper sulfate-sulfuric acid test for detecting susceptibility to intergranular attack in austenitic stainless steels.

The simplest and least time-consuming is practice A (oxalic acid test), which is primarily considered to be a screening device; that is, specimens passing the oxalic acid test can be eliminated from further testing. Practices B, C, and D all use a weight-loss determination and therefore can provide a quantitative measure of the relative performance of specimens tested. Practice E is based on a visual examination of bend specimens and therefore is used to classify the specimen only as acceptable or unacceptable. Practice C is sometimes referred to as the Huey test and practice E as the Strauss test.

Some reports [33, 38, 39] that evaluate and discuss sensitization and DOS seem to indicate that, although ASTM A 262 [28] could provide the qualitative information as to whether or not a material was sensitized, it should not be used as a quantitative tool to determine the DOS. One of the quantitative techniques available is electrochemical potentiodynamic reactivation (EPR), as described by Clarke et al. [39]. This is basically a nondestructive electrochemical technique wherein a specimen is subjected to two potential sweeps in a de-aerated solution of sulfuric acid and KCNS. A reactivation peak is formed on the

![Figure 19. Schematic of the reactivation polarization curve, showing parameters of interest for EPR testing [39].](image-url)
The sensitivity to sensitization is dependent on weld fabrication techniques including heat input, number of weld passes, and overlap of HAZ thermal profiles in multipass welds. One technique useful for determining the dependence of sensitization on the location and thermal history of the HAZ is EPR profiling. The EPR technique is valuable in its capability of measuring and distinguishing between the low levels of sensitization in the HAZ. Using a bead-on-edge welding technique, samples are sectioned from several predetermined distances from the fusion line. Placement of thermocouples at various locations prior to welding allows recording of the weld thermal cycles. The normalized reactivation charge, Pa (coulombs per square centimeter of grain-boundary area) in the EPR test gives a measure of the DOS. A surface with a Pa number of 2.0 was determined by Lundin et al. [17] to correspond to the DOS at which the dual structure starts to occur in the oxalic acid test (ASTM A262-A). The test material was 0.06 wt% carbon Type 304 stainless steel.

Several test welds in Types 304LN and 316NG stainless steels were examined by Lundin [17] using EPR profiling. Autogenous gas tungsten-arc (GTA) edge-welds were produced using a heat input of 40 kJ/in. (1.57 kJ/mm) and preheat and interpass temperatures of 427°C (800°F). This is considered equivalent to welding a plate 1.5 in. (38 mm) thick with a heat input of 80 kJ/in. (3.15 kJ/mm) at 316°C (600°F). Such tests show a strong dependence of the DOS on the peak temperature. In a Type 304LN stainless steel single-cycle weld, the Pa number increases from a value of 0.1 at the fusion line to 0.6 at a distance of 0.17 in. (4.3 mm) from the fusion line. This increase corresponds to a peak temperature of 925°C (1700°F). The Pa number then decreases with distance to a value of 0.15 at a peak temperature of 705°C (1300°F) or lower. The same tests on Type 316NG stainless steel resulted in virtually no change in Pa number from the fusion line to the unaffected base metal.

The effect of multiple thermal cycles may be most simply treated as additive. Sensitization should be related to the time spent within the sensitization range. The effect of five thermal cycles (by the same GTA edge passes above) in Type 304LN stainless steel increases the maximum Pa number from 0.6 to 0.9. The peak temperature at maximum DOS remains near 925°C (1700°F), but the shape of the curve changes because of smaller increases in Pa number at higher and lower peak temperatures. Solomon [41] has pointed out that the effects of multiple cycles are not necessarily additive. Partial or complete dissolution of the carbides at high peak temperatures replenishes chromium-depleted regions and can wipe out the effects of previous cycles. There appears to be a general...
shortage of data in the literature on the effects of multiple thermal cycles, especially on the effects of overlapping HAZs.

Heat input in welding influences the cooling rates and times within the sensitization range. A heat input threshold for sensitization has been established through research by Gooch (see [13]). This threshold was measured to decrease with increasing carbon content from 68 kJ/in. at 0.06 wt% carbon to 40 kJ/in. at 0.08 wt% carbon. It was recommended that in common practice the weld heat input should be limited to a maximum of 30 to 35 kJ/in. for unstabilized alloys.

**Strain Effects.** Strain effects that can affect sensitization can be developed in two ways: (1) through the process of welding, and (2) through cold work before a thermal heat treatment or welding process. The weld-induced strain effect is developed during the welding process when a cold region surrounds the warmer HAZ and the molten fusion zone (FZ); the HAZ goes through a sequence of both tension and compression. The final stress state of the HAZ is dependent on the joint geometry and the welding process used. Unless some type of stress relief is applied, some part of the HAZ will contain stresses as high as the yield values at ambient temperature [42].

Very little data has been published on the effects of strain during exposure to sensitization temperatures [43, 44], but the limited data agrees with the significantly large amount of published data on cold work before isothermal heat treatments.

Pednekar et al. [64] studied the effect of prior strain (cold work) on sensitization. They used anodic polarization scans to determine sensitization, using varying amounts of prior strain at a sensitization temperature of 660°C (1220°F). Their results show that, with increasing amounts of prior cold work, the rate of carbide precipitation increased, first along the grain boundaries. Then, as the amount of prior cold work increased, the carbides preferentially precipitated within the grains. The DOS increases with initial cold work but then decreases with additional cold work as more and more carbides precipitate within the grains. This can be explained qualitatively using a dislocation model. With small amounts of cold work (less than 10%), one would expect a large increase in dislocation density in the grain-boundary region, which would result in the observed ease of precipitation and growth of carbides at the grain boundaries when the material is heated in the sensitizing temperature range. At the same time, the bulk diffusion rate for chromium would remain unchanged, resulting in chromium depletion in the vicinity of the carbide network. With increased cold work, the low stacking-fault energies typical of stainless steels result in dislocation pileups at slip-plane intersections. Consequently, as the amount of cold work increases, the carbide nucleation and precipitation process is increasingly favored within the grains. Bain et al. [19] and Tedmon et al. [25] also noted that a more uniform carbide distribution is developed. As explained by Bain et al. [19], this would shorten the diffusion path for chromium and ultimately result in quicker homogenization of the chromium content in the matrix between the bands of precipitated carbides within the grains.

The presence of martensite can also influence sensitization. Briant and Ritter [46] found that the temperature needed to cause sensitization is much lower in a material that contains some martensite than in a purely austenitic material. The time required for sensitization is also greatly reduced. They suggested that these effects were the result of higher diffusion rates of carbon and chromium in body-centered tetragonal martensite than in fcc austenite [46-49]. The solubility of carbon is also lower in martensite than in austenite. A comparison of sensitization in a Type 304 stainless steel with and without martensite is shown in Fig. 20. Even though martensite appears to have a negative effect on corrosion resistance, an increased resistance to susceptibility to SCC was observed when Types 304L and 316L stainless steels were cold-worked (10-15%) prior to heat treatment at 400°C (752°F) [45].

Solomon and Lord [44] modeled fusion-welding thermal cycles on Type 304 stainless steel to observe the effects of strain in conjunction with continuous cooling on sensitization. Figure 21 indicates that strain increases the propensity for sensitization as long as the strain is on the order of 5% or greater. Solomon and Lord also considered the effect of multiple welding passes and found that as little as 0.8% strain per pass can enhance sensitization, provided that multiple cycles are used with this strain, for peak temperatures of 800°C (1472°F) (Fig. 22). Solomon and Lord further postulated that dislocations generated as a result of strain increase the carbide nucleation and diffusion rates. The more carbon present, the greater the amount of carbide precipitated and the greater the influence of strain on sensitization.
Microstructural Effects. Microstructural characteristics that strongly influence sensitization include the presence of δ ferrite, differences in grain size, and carbide morphologies.

The presence of δ ferrite in the austenitic structure provides additional nucleation sites for M$_{23}$C$_6$ carbide precipitation. The ferrite-austenite interface is favored over austenite grain boundaries and twin boundaries as nucleation sites for precipitation [50]. Devine and Drummon [100] have shown that the resistance of two-phase austenite-plus-ferrite alloys to intergranular corrosion is related to the amount of the ferrite-austenite interfacial area. While small amounts of ferrite (1 to 2%) have only small effects on the DOS and susceptibility to intergranular corrosion, large amounts of ferrite (8 to 15%) decrease the susceptibility to intergranular corrosion.

While not subject to intergranular attack, quantities of ferrite that form a nearly continuous network can also provide a nearly continuous sensitized path. Devine and Drummon [100] have shown, however, that immunity to corrosion in these alloys can occur quite rapidly by replenishment of the relatively narrow depleted zone in the austenite. This phenomenon is due to the capability of the ferrite, which is enriched in chromium, to provide the principal source of chromium for carbide precipitation. They also point out that this ferrite is metastable in the sensitization range and will decompose. If the carbon has not consumed all of the ferrite, the rejection of chromium into the remaining ferrite as the ferrite decomposes into austenite can result in 0 formation. The influence of ferrite on preferential corrosion has been discussed earlier.

Grain size can also affect sensitization and SCC through its effect on grain-boundary area, and it influences SCC through its effect on the material's strength. Bain et al. [19] observed that...
Figure 21. Intergranular penetration (IGP) in an ASTM A 262, practice E test as a function of cooling rate for air-cooled (as-received) specimens cooled from 800°C (1472°F) [44].

Figure 22. Intergranular penetration in an ASTM A 262, practice E test as a function of the number of cycles of heating and cooling from 800 and 1000°C (1472 and 1832°F) [44].
Figure 23. Relative development of sensitivity in coarse and fine-grained alloys; chromium, 17.6; nickel, 8.8; carbon, 0.05 [19].

Figure 24. Time-temperature dependence of precipitation of M_23C_6 at different sites [50].

A very fine grain in the austenite steel predisposes an alloy to a retarded sensitization. Curves of the intergranular penetration vs exposure time to the sensitizing temperature show the difference between fine-grained and coarse-grained material (Fig. 23), and suggest that the relative proportion of normal crystalline material and grain-boundary material might exert some influence on the process of sensitization. The influence of grain size is most marked when sensitization results from relatively short-time exposures to the damaging temperatures. Material heated for long times (thousands of hours) is severely affected without regard to grain size.

The chromium carbides (Cr_23C_6) that precipitate at grain boundaries in sensitized stainless steels have complex and varied morphologies [24]. They can be present in continuous or discontinuous modes, and their
compositions can be variable. Up to about one-fourth of the chromium can be replaced by iron [23]. Mahla and Nielsen [51] separated and isolated chromium carbides from the grain boundaries of sensitized Type 304 stainless steel. Using transmission electron microscopy (TEM), they found that the carbides nucleated in grain boundaries, but that the carbides grew into adjacent grains. The carbides initially have a dendritic or flake-like structure, but with time and temperature, these flakes transform into more regular geometric shapes, whose habit is determined by metal lattice planes. They also found that the carbides were very thin [51], essentially forming a two-dimensional dendritic structure.

Stickler and Vinckier [50], using the techniques developed by Mahla and Nielsen [51], observed that carbides precipitate in stages: first on the δ ferrite-austenite interface, then on the grain boundaries, next on the incoherent grain boundaries, and finally on the coherent twin boundaries. These stages are illustrated in Fig. 24, which shows the time-temperature dependence of precipitation of $M_{23}C_6$ at each site. From these observations, it can be concluded that the carbides are not present as continuous films but rather that they assume complex, thin dendritic shapes and that their morphology is highly dependent on time and temperature.

3.2.3 Low-Temperature Sensitization

Povich [52] observed that Type 304 stainless steel could be sensitized at temperatures well below the normal isothermal sensitization range if chromium carbide nuclei were present. The combination of nucleation within the conventional sensitization temperature range and subsequent growth during low-temperature heat treatments has been termed low-temperature sensitization (LTS).

A schematic illustrating LTS is shown in Fig. 25. The shaded region shows the normal isothermal TTS zone. Neither path A nor B separately result in sensitization. However, combining paths A (high temperature) and B (long times) into C results in severe sensitization. Povich and Rao [40] postulated that LTS is a nucleation and growth phenomenon; that is, carbides are nucleated during a welding process.
Figure 26. Number of carbides per unit grain boundary area vs distance from the weld centerline before and after the 400°C (752°F)/10 day LTS heat treatment [52].

Figure 27. Plots of grain boundary carbide size as a function of distance from the weld centerline before and after the 400°C (752°F)/10 day LTS heat treatment [52].
or isothermal heat treatments, and long-term exposure to above-ambient temperatures brings about carbide growth.

Quantitative TEM studies on coupons from a pipe weld section have shown that no new carbides were nucleated during a 400°C (752°F) LTS heat treatment, but that carbides nucleated during welding increased in size, particularly along the direction of the grain boundary [40]. Povich and Rao [40] found an increase in the grain boundary coverage from 60% in the as-welded condition to 89% after a 400°C/10-day LTS heat treatment. These observations are shown in Fig. 26, which illustrates no change in the number of carbides after an LTS treatment, and Fig. 27, which shows a significant increase in the size of grain-boundary carbides after the 400°C/10-day LTS heat treatment.

From scanning electron microscopy (SEM) examination on welded specimens held for varying periods of time at 400°C (752°F), Kekkonen et al. [53] made several observations: the M_{23}C_6 carbides nucleate on high-angle boundaries during their short exposure to temperatures in the precipitation range. Relatively little carbide growth occurs during this stage. During the growth at low temperatures, the carbides seem to grow into one of the grains forming the boundary. After the carbides reach a certain size, retaining their geometrical shape, the grain boundary between the carbide particles starts to bow, and the carbides begin to coarsen. Both EPR and

![Figure 28. A temperature-time dependence for LTS based on the EPR test results [53].](image-url)
Sensitization of the Austenitic Candidates

3.2.4 Sensitization of the Austenitic Candidates

Types 304L and 316L Stainless Steels. There is a considerable amount of test data on sensitization of Types 304 and 316 stainless steels; however, such is not the case for Types 304L and 316L stainless steels. Table 2 provides a summary of the available test data on Types 304L and 316L stainless steels. This data suggests that resistance to sensitization significantly increases as the carbon content is lowered. While the low carbon specified in Types 304L and 316L stainless steels (maximum 0.03 wt% carbon) increases the resistance to sensitization in normal weld practice, the alloys are not immune from sensitization. Heat treatments in the sensitization range, as for stress relief, must still be avoided.

The compositional model for resistance to sensitization presented earlier can be used to predict the relative susceptibilities of Types 304L and 316L stainless steels. For purposes of comparison, the effective chromium is calculated from Eq. (3) using a carbon content of 0.03 wt% and from midspecification values for chromium, nickel, and molybdenum (Table 1). This results in a prediction that Type 316L stainless steel is more resistant to sensitization than Type 304L stainless steel, with effective chromium values of 17.8 and 16.0, respectively. Maximum effective chromium values at 0.03% carbon (using optimized compositions) are 20.1 for Type 316L stainless steel and 17.4 for Type 304L stainless steel. The calculated time required for sensitization at 650°C in these alloys was calculated from similar empirical relations by Bruemmer et al. [57]. For Types 304L and 316L stainless steel with 0.035 wt% carbon, the times to sensitize at 650°C are 2.9 and 5.8 h, respectively.

Alloy 825. Alloy 825 is an austenitic alloy containing a high percentage of nickel (42 wt%). It also contains titanium, which partially stabilizes the carbon against chromium-rich carbide formation. There seems to be a scarcity of available data on sensitization of this alloy. Scarberry et al. [103] reported on the corrosion rate in boiling HNO₃ of several stainless steel alloys after a sensitizing treatment of 1 h at 649°C (1200°F). After similar processing of Type 304 stainless steel and Alloy 825, there is a decrease by a factor of 30 with regard to the measured corrosion rates in Alloy 825.

Extrapolating Eq. (3) for the composition of Alloy 825, using the specified maximum of 0.05 wt% carbon and midspecification values for chromium, nickel, and molybdenum, results in an effective chromium value of 15.2. However, using two actual heat chemistries supplied by INCO Alloys International, much higher values are obtained. A value of 18.0 is calculated from an actual heat chemistry of 22Cr-44Ni-2.8Mo-0.02C, and a value of 19.7 from an actual heat chemistry of 22Cr-43.5Ni-3.2Mo-0.01C. Potential stabilization of carbon, as in Alloy 825, is not accounted for in Eq. (3). Therefore, the actual resistance to sensitization in Alloy 825 is expected
Table 2. Summary of available test data on Types 304L and 316L stainless steels.

<table>
<thead>
<tr>
<th>Material</th>
<th>Number of specimens</th>
<th>Type of test</th>
<th>Results</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 304L</td>
<td>4</td>
<td>Isothermal heat treatment</td>
<td>All specimens had step structure; 621°C/24 hr sample was deeply etched at grain boundaries</td>
<td>Oxalic acid screening and EPR</td>
<td>38</td>
</tr>
<tr>
<td>2. 304LA</td>
<td>1</td>
<td>Isothermal heat treatment, 600, 650, and 700°C</td>
<td>Sensitized in less than 1 hr</td>
<td>Strauss test</td>
<td>35</td>
</tr>
<tr>
<td>3. 316L</td>
<td>1</td>
<td>Isothermal heat treatment</td>
<td>Sensitized in more than 1 hr</td>
<td>Strauss test</td>
<td>35</td>
</tr>
<tr>
<td>4. 304L</td>
<td>9</td>
<td>Cyclic stress, oxygen level 8 ppm</td>
<td>No failure after 2000 to 6000 cycles</td>
<td>Controlled nitrogen, three welded + LTS (500°C/24 hr)</td>
<td>34</td>
</tr>
<tr>
<td>5. 316L</td>
<td>10</td>
<td>Cyclic stress, oxygen level 8 ppm</td>
<td>No failure after 2000 to 6000 cycles</td>
<td>Pipe welds 6 of 10 LTS (500°C/24 hr)</td>
<td>34</td>
</tr>
<tr>
<td>6. 316L</td>
<td>2</td>
<td>Cyclic stress, oxygen level 8 ppm</td>
<td>Failure 2885 cycles and 1256 cycles</td>
<td>Pipe welds + LTS, transgranular cracking</td>
<td>34</td>
</tr>
<tr>
<td>7. 304L</td>
<td>9</td>
<td>Fatigue</td>
<td>Degrees of cracking analyzed after 772, 1502, 2680, 5000, 10,000 cycles</td>
<td>No survival after 5000 cycles</td>
<td>34</td>
</tr>
<tr>
<td>8. 316L</td>
<td>8</td>
<td>Fatigue</td>
<td>Degrees of cracking analyzed after 772, 1502, 2680, 5000, 10,000 cycles</td>
<td>No survival after 5000 cycles</td>
<td>34</td>
</tr>
<tr>
<td>9. 304LN</td>
<td>—</td>
<td>Multiple and preheat welded specimens</td>
<td>EPR below sensitization value</td>
<td>EPR tests</td>
<td>17</td>
</tr>
<tr>
<td>10. 304L</td>
<td>5 heats, 2 specimens each heat</td>
<td>Isothermal heat treatments at 500, 600, 700, and 800°C</td>
<td>EPR tests, no DOS up to 1 hr at 600, 700, and 800°C</td>
<td>Results of additional 100 Type 304 tests were incorporated into plots</td>
<td>33</td>
</tr>
<tr>
<td>11. 316L</td>
<td>4 heats, 2 specimens each heat</td>
<td>Isothermal heat treatments at 500, 600, 700, and 800°C</td>
<td>EPR tests, no DOS up to 10 hr at 600, 700, and 800°C</td>
<td>Results of additional 100 Type 304 tests were incorporated into plots</td>
<td>33</td>
</tr>
<tr>
<td>12. 304L</td>
<td>4</td>
<td>Corrosion weight loss in boiling nitric acid</td>
<td>304L better than 304</td>
<td>Experimental work performed to validate model</td>
<td>102</td>
</tr>
</tbody>
</table>
Figure 29. TTS diagram for Alloy 825 annealed at 1093°C (2000°F) for 1 hr prior to sensitization treatment [40].

Figure 30. TTS diagram for Alloy 825 annealed at 941°C (1725°F) for 1 hr prior to sensitization treatment [40].

to be higher than predictions from bulk carbon contents of unstabilized alloys.

Brown and Kirchner [59, 60] evaluated 15 heats of Alloy 825, using ASTM A 262, practices B and C [28]. He found a wide variation in resistance to sensitization, which he felt could not be explained by compositional differences. He believed that variations in mill processing have a larger influence on resistance to sensitization than variations in composition within the nominal composition.

Raymond [61] used the Huey test (ASTM A 262, practice C) [28], TEM, and compositional analysis of chemically extracted carbides to evaluate the sensitization behavior of Alloy 825. He established that the alloy can be stabilized through a proper mill-annealing heat treatment. His results show that only 0.01 wt% carbon is stabilized as titanium-rich carbide in a heat containing 0.99 wt% titanium. Raymond postulated that the principal mechanism of
stabilization for Alloy 825 is that of precipitating the \( \text{M}_{23}\text{C}_6 \) at a temperature at which the diffusion of chromium is sufficiently rapid to prevent chromium depletion. Optimum thermal stabilization in Alloy 825 occurs in the range of 920 to 980°C (approximately 1700 to 1800°F). The effectiveness of higher-temperature anneals diminishes because of increased carbon remaining in solution. The carbon solubility increases from approximately 0.01 wt% carbon below 980°C (1800°F) to 0.02 wt% carbon at 1095°C (2000°F) and 0.04 wt% carbon at 1150°C (2100°F) \[61\]. The stabilized condition is quite resistant to isothermal sensitization, as shown by the low corrosion rates subsequent to exposure within the sensitization range in Figs. 29 and 30.

It should be noted that carbon solubility in 18Cr-8Ni steels is reported \[37\] to increase more rapidly with increasing temperature than in Alloy 825, exceeding 0.06 wt% carbon below 900°C (1650°F). For a thermal-stabilization mechanism dependent on the increased matrix diffusion of chromium relative to grain-boundary diffusion at high temperatures, the potential for thermal stabilization in 18Cr-8Ni steels is much lower than in Alloy 825.

The only review to evaluate the effects of welding on corrosion rates in Alloy 825 is that by Copson et al. \[62\]. The alloys investigated in this work are referred to as "Ni-O-Ne". The compositions of the materials investigated are listed in Table 3. Corrosion rates for alloy No. 12 were compared in three conditions: mill-annealed, isothermally aged at 650°C (1200°F) for 1 hr, and as-welded. The composition of alloy No. 12 is within the specifications for Alloy 825 listed in Table 1. A summary of results on corrosion rates in a wide range of media for alloy No. 12 are listed in Tables 4 and 5. Welded specimens did not show any signs of increased attack over the annealed material.

A summary of corrosion tests performed on Alloy 825 as reported in the literature is shown in Table 6.

### 3.3 SCC of the Austenitic Candidates

SCC refers to the accelerated corrosive attack resulting in crack propagation at stresses below that required in the absence of a corrosive environment. The critical stress intensity for unstable crack growth can be significantly

<table>
<thead>
<tr>
<th>Alloy No.</th>
<th>Ni (wt%)</th>
<th>Cr (wt%)</th>
<th>Mo (wt%)</th>
<th>Cu (wt%)</th>
<th>Mn (wt%)</th>
<th>Si (wt%)</th>
<th>C (wt%)</th>
<th>Ti (wt%)</th>
<th>Fe (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>41.1</td>
<td>19.9</td>
<td>2.92</td>
<td>1.62</td>
<td>0.63</td>
<td>0.30</td>
<td>0.017</td>
<td>0.46</td>
<td>Bal.</td>
</tr>
<tr>
<td>2</td>
<td>41.3</td>
<td>19.8</td>
<td>3.21</td>
<td>1.73</td>
<td>0.57</td>
<td>0.36</td>
<td>0.022</td>
<td>0.48</td>
<td>Bal.</td>
</tr>
<tr>
<td>3</td>
<td>41.1</td>
<td>20.6</td>
<td>3.20</td>
<td>1.78</td>
<td>0.62</td>
<td>0.35</td>
<td>0.023</td>
<td>0.44</td>
<td>Bal.</td>
</tr>
<tr>
<td>4</td>
<td>41.4</td>
<td>20.6</td>
<td>3.30</td>
<td>1.90</td>
<td>0.55</td>
<td>0.39</td>
<td>0.035</td>
<td>0.55</td>
<td>Bal.</td>
</tr>
<tr>
<td>5</td>
<td>43.2</td>
<td>18.6</td>
<td>3.26</td>
<td>1.30</td>
<td>0.55</td>
<td>0.30</td>
<td>0.04</td>
<td>0.47</td>
<td>Bal.</td>
</tr>
<tr>
<td>6</td>
<td>43.3</td>
<td>20.8</td>
<td>3.07</td>
<td>1.70</td>
<td>0.74</td>
<td>0.39</td>
<td>0.05</td>
<td>0.42</td>
<td>Bal.</td>
</tr>
<tr>
<td>7</td>
<td>37.2</td>
<td>20.5</td>
<td>1.98</td>
<td>1.09</td>
<td>0.68</td>
<td>0.28</td>
<td>0.05</td>
<td>0.22</td>
<td>Bal.</td>
</tr>
<tr>
<td>8</td>
<td>41.5</td>
<td>19.6</td>
<td>3.21</td>
<td>1.44</td>
<td>0.96</td>
<td>0.58</td>
<td>0.05</td>
<td>0.63</td>
<td>Bal.</td>
</tr>
<tr>
<td>9</td>
<td>42.6</td>
<td>19.5</td>
<td>3.21</td>
<td>1.52</td>
<td>0.90</td>
<td>0.62</td>
<td>0.04</td>
<td>0.83</td>
<td>Bal.</td>
</tr>
<tr>
<td>10</td>
<td>42.1</td>
<td>19.6</td>
<td>3.23</td>
<td>1.60</td>
<td>0.92</td>
<td>0.59</td>
<td>0.04</td>
<td>1.34</td>
<td>Bal.</td>
</tr>
<tr>
<td>11</td>
<td>42.3</td>
<td>21.6</td>
<td>2.94</td>
<td>1.91</td>
<td>0.69</td>
<td>0.23</td>
<td>0.03</td>
<td>0.69</td>
<td>Bal.</td>
</tr>
<tr>
<td>12</td>
<td>40.0</td>
<td>21.4</td>
<td>3.01</td>
<td>1.70</td>
<td>0.63</td>
<td>0.23</td>
<td>0.03</td>
<td>0.81</td>
<td>Bal.</td>
</tr>
<tr>
<td>13</td>
<td>41.0</td>
<td>19.6</td>
<td>4.03</td>
<td>1.91</td>
<td>0.90</td>
<td>0.40</td>
<td>0.05</td>
<td>0.54</td>
<td>Bal.</td>
</tr>
<tr>
<td>14</td>
<td>40.5</td>
<td>20.8</td>
<td>3.04</td>
<td>2.00</td>
<td>0.51</td>
<td>0.30</td>
<td>0.04</td>
<td>0.47</td>
<td>Bal.</td>
</tr>
<tr>
<td>15</td>
<td>41.1</td>
<td>21.7</td>
<td>3.14</td>
<td>1.86</td>
<td>0.57</td>
<td>0.42</td>
<td>0.03</td>
<td>0.57</td>
<td>Bal.</td>
</tr>
<tr>
<td>16</td>
<td>45.7</td>
<td>17.2</td>
<td>3.11</td>
<td>1.58</td>
<td>0.65</td>
<td>0.28</td>
<td>0.05</td>
<td>0.49</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Table 4. Corrosion tests on alloy No. 12 in sulfuric acid [62].

<table>
<thead>
<tr>
<th>Acid concentration (%)</th>
<th>Temperature (°F)</th>
<th>Time (hr)</th>
<th>Corrosion rate (in./yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mill-annealed</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Boiling</td>
<td>4</td>
<td>0.035</td>
</tr>
<tr>
<td>10</td>
<td>Boiling</td>
<td>4</td>
<td>0.056</td>
</tr>
<tr>
<td>20</td>
<td>Boiling</td>
<td>4</td>
<td>0.197</td>
</tr>
<tr>
<td>40</td>
<td>Boiling</td>
<td>4</td>
<td>0.135</td>
</tr>
<tr>
<td>60</td>
<td>Boiling</td>
<td>4</td>
<td>0.531</td>
</tr>
<tr>
<td>80</td>
<td>Boiling</td>
<td>4</td>
<td>17.0</td>
</tr>
<tr>
<td>96</td>
<td>Boiling</td>
<td>4</td>
<td>0.829</td>
</tr>
<tr>
<td>5</td>
<td>Boiling</td>
<td>20</td>
<td>0.028</td>
</tr>
<tr>
<td>10</td>
<td>Boiling</td>
<td>20</td>
<td>0.051</td>
</tr>
<tr>
<td>20</td>
<td>Boiling</td>
<td>20</td>
<td>0.034</td>
</tr>
<tr>
<td>40</td>
<td>Boiling</td>
<td>20</td>
<td>0.065</td>
</tr>
<tr>
<td>60</td>
<td>Boiling</td>
<td>20</td>
<td>0.324</td>
</tr>
<tr>
<td>80</td>
<td>Boiling</td>
<td>20</td>
<td>4.0</td>
</tr>
<tr>
<td>96</td>
<td>Boiling</td>
<td>20</td>
<td>0.213</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>4</td>
<td>0.004</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
<td>4</td>
<td>0.005</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>4</td>
<td>0.009</td>
</tr>
<tr>
<td>40</td>
<td>150</td>
<td>4</td>
<td>0.040</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>4</td>
<td>0.033</td>
</tr>
<tr>
<td>80</td>
<td>150</td>
<td>4</td>
<td>0.053</td>
</tr>
<tr>
<td>96</td>
<td>150</td>
<td>4</td>
<td>0.283</td>
</tr>
<tr>
<td>5</td>
<td>150</td>
<td>20</td>
<td>0.001</td>
</tr>
<tr>
<td>10</td>
<td>150</td>
<td>20</td>
<td>0.001</td>
</tr>
<tr>
<td>20</td>
<td>150</td>
<td>20</td>
<td>0.001</td>
</tr>
<tr>
<td>40</td>
<td>150</td>
<td>20</td>
<td>0.036</td>
</tr>
<tr>
<td>60</td>
<td>150</td>
<td>20</td>
<td>0.030</td>
</tr>
<tr>
<td>80</td>
<td>150</td>
<td>20</td>
<td>0.124</td>
</tr>
<tr>
<td>96</td>
<td>150</td>
<td>20</td>
<td>0.246</td>
</tr>
</tbody>
</table>

*Tests at 150°F were aerated, and specimens were moved at 16 ft/min.

decreased under conditions of SCC. Three principal factors must coexist for the operation of SCC [17, 24, 63]: a critical stress intensity, a critical environment, and a susceptible microstructure. SCC can be prevented by the elimination of any of these factors. Welding-induced microstructural changes can influence the susceptibility of the austenitic candidate materials to SCC. In particular, the effects resulting in preferential corrosion in the FZ and sensitization in the HAZ of weldments can create SCC-susceptible microstructures.

Three microstructurally specific modes of SCC have been observed in weldments: intergranular stress corrosion cracking (IGSCC), transgranular stress corrosion cracking (TGSCC), and interdendritic SCC. The susceptibility of a weldment to any of these three modes of SCC is
Table 5. Corrosion tests on alloy No. 12 in other acid environments [62].

<table>
<thead>
<tr>
<th>Environment</th>
<th>Temperature (°F)</th>
<th>Time (hr)</th>
<th>Corrosion rate (in./yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid, 60%</td>
<td>Boiling</td>
<td>20</td>
<td>Mill-annealed: 0.008 1 hr at 1200°F: 0.012 Welded: 0.015</td>
</tr>
<tr>
<td>Phosphoric acid, 70%</td>
<td>Boiling</td>
<td>20</td>
<td>Mill-annealed: 0.007 1 hr at 1200°F: 0.013 Welded: 0.018</td>
</tr>
<tr>
<td>Phosphoric acid, 80%</td>
<td>Boiling</td>
<td>20</td>
<td>Mill-annealed: 0.051 1 hr at 1200°F: 0.038 Welded: 0.052</td>
</tr>
<tr>
<td>10% H$_2$SO$_4$</td>
<td>150</td>
<td>20</td>
<td>Mill-annealed: 0.001 1 hr at 1200°F: 0.002 Welded: 0.001</td>
</tr>
<tr>
<td>10% H$_2$SO$_4$ + 5% HNO$_3$</td>
<td>150</td>
<td>20</td>
<td>Mill-annealed: 0.002 1 hr at 1200°F: 0.002 Welded: 0.002</td>
</tr>
<tr>
<td>10% H$_2$SO$_4$ + 5% NaCl</td>
<td>150</td>
<td>20</td>
<td>Mill-annealed: 0.203 1 hr at 1200°F: 0.181 Welded: 0.222</td>
</tr>
<tr>
<td>Acetic acid, 10%</td>
<td>Boiling</td>
<td>120</td>
<td>&lt;0.001 1 hr at 1200°F: 0.002 Welded: &lt;0.001</td>
</tr>
<tr>
<td>Formic acid, 10%</td>
<td>Boiling</td>
<td>120</td>
<td>&lt;0.003 1 hr at 1200°F: 0.003 Welded: 0.003</td>
</tr>
<tr>
<td>Lactic acid, 10%</td>
<td>Boiling</td>
<td>120</td>
<td>&lt;0.001 1 hr at 1200°F: &lt;0.001 Welded: &lt;0.001</td>
</tr>
<tr>
<td>Maleic acid, 10%</td>
<td>Boiling</td>
<td>120</td>
<td>&lt;0.001 1 hr at 1200°F: &lt;0.001 Welded: &lt;0.001</td>
</tr>
<tr>
<td>Oxalic acid, 10%</td>
<td>Boiling</td>
<td>120</td>
<td>&lt;0.020 1 hr at 1200°F: 0.015 Welded: 0.016</td>
</tr>
<tr>
<td>Phthalic acid, 10%</td>
<td>Boiling</td>
<td>120</td>
<td>&lt;0.001 1 hr at 1200°F: &lt;0.001 Welded: &lt;0.001</td>
</tr>
<tr>
<td>Aluminum chloride, 25%</td>
<td>86</td>
<td>168</td>
<td>0.005 1 hr at 1200°F: 0.005 Welded: 0.005</td>
</tr>
<tr>
<td>Zinc chloride, 25%</td>
<td>86</td>
<td>168</td>
<td>0.0001 1 hr at 1200°F: 0.0002 Welded: 0.0002</td>
</tr>
<tr>
<td>Sodium bisulfite, 25%</td>
<td>86</td>
<td>168</td>
<td>&lt;0.0001 1 hr at 1200°F: 0.0002 Welded: &lt;0.0001</td>
</tr>
</tbody>
</table>

*aSolutions were aerated; specimens were moved at 16 ft/min.

*bNo air was added to solutions; specimens were moved at 16 ft/min.

Table 6. Summary of tests performed on Alloy 825.

<table>
<thead>
<tr>
<th>Number of specimens</th>
<th>Type of test</th>
<th>Results</th>
<th>Comments</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Boiling 42% magnesium chloride</td>
<td>No cracking in 30 days</td>
<td>Solution heat treated</td>
<td>103</td>
</tr>
<tr>
<td>2</td>
<td>Boiling 65% magnesium chloride</td>
<td>Corrosion rate = 36 mils per yr</td>
<td>Sensitized (649°C for 1 hr)</td>
<td>103</td>
</tr>
<tr>
<td>?</td>
<td>ASTM A 262, practices B and C [28]</td>
<td>Corrosion rate in nitric and ferric showed wide heat to heat variation</td>
<td>Effect of sensitization on various ranges of compositions within specifications. 15 heats examined.</td>
<td>60</td>
</tr>
</tbody>
</table>
dependent on both the composition of the alloy and thermomechanical history. IGSCC results from the development of grain-boundary sensitization in the HAZ of the weldment. TGSCC can occur in the FZ, and interdendritic SCC has been observed at the austenitic/ferritic interfaces in duplex weldments.

In a study of SCC in single-pass autogenous GTA weldments in Type 304L stainless steel (in boiling 24% MgCl₂) by Sherman et al. [14], none of the failures occurred by an intergranular mode. Carbon contents of 0.016 and 0.028 wt% resulted in high and low ferrite levels, respectively. In tests of transverse weldment sections, failure always initiated outside of the FZ. In the high-ferrite alloy, transgranular cracking initiated in the parent metal, while in the low-ferrite alloy, transgranular cracking occurred in the grain-coarsened HAZ. The high-ferrite alloy retained ferrite in the high-temperature region of the HAZ, significantly reducing the maximum HAZ grain size. In tests of all-weld-metal samples, the samples failed in an interdendritic mode following the ferrite-austenite interfaces.

Using ferrite in the FZ to prevent hot cracking raises the issue of the effect of a two-phase structure and its inherent corrosion problems. Stalder and Duquette [65] observed the effect of a two-phase ferrite-plus-austenite structure in a weld on its corrosion resistance as compared with a fully austenitic structure. In an SCC test, they found that fracture occurred preferentially along ferrite-austenite interfaces regardless of temperature, whereas in annealed material, fracture occurred intergranularly or transgranularly, depending on the test temperature.

Baeslack et al. [66] conducted an SCC study of Type 304 stainless steel containing welds with varying degrees of ferrite. They concluded from observations of the failure microstructure and measurements of reduction of area that the fully austenitic Type 304 stainless steel cracks in a transgranular manner and is less susceptible to SCC than is the two-phase weld metal. The crack morphology of the duplex weld metal indicates preferential dissolution of the ferrite and SCC of the austenite. In addition, they found that the ferrite content does have an effect on the susceptibility to SCC; those structures showing a continuous network of ferrite appear to be more susceptible to cracking.

Gooch et al. [67] have used potentiostatic polarization techniques to study the localized corrosion of stainless steel weld metals in aqueous environments. All steels studied were austenitic and included Types 304, 316, and 321 stainless steels. The welding processes investigated included tungsten inert gas (TIG), metal inert gas (MIG), manual metal arc (MMA), and submerged arc welding (SAW). Various filler materials were used, some containing a small percentage of niobium, a carbide-former capable of suppressing the formation of Cr₂₃C₆ precipitated near the weld. Most atmospheres present during the welding operation were either pure argon or argon with 2 wt% oxygen. Most welds were made from 1/4-in.-thick plates, although a few samples were made from either 1/8- or 5/8-in.-thick plates. Transverse cross sections were polished to a 1-mm finish with diamond paste. Active areas were defined using lacquer masks. All corrosion tests were performed with solutions consisting of 20 wt% sulfuric acid and 0.5 g/l ammonium thiocyanate. In all experiments, the potential was controlled relative to the mercury/mercurous sulfate reference electrode, which has a standard half-cell voltage of 664 mV on the hydrogen scale.

Initially, Gooch et al. [67] attempted to characterize samples with potentiodynamic polarization experiments. The potential of the working electrode (test specimen) was swept from -900 to +1500 mV at a rate of 300 mV/hr. Polarization curves exhibited all of the qualitative characteristics expected, including active loops, active-passive transitions, passivity, and transpassive regions. These experiments demonstrated that the addition of molybdenum tends to stabilize passive films on stainless steels and make them more noble. For example, Type 316 stainless steel had a lower peak current density (active loop) than did Type 304 stainless steel. Furthermore, it was also determined that the ferrite phase in welds was preferentially attacked.

Although the potentiodynamic tests were useful, better results were obtained by anodic polarization of samples at various potential levels, followed by microscopic examination and characterization of corroded specimen surfaces. Several general types of localized corrosion were identified, including fusion-boundary attack, grain-boundary attack, and preferential attack of the ferrite phase. Deep attack of the fusion boundary occurred in specimens containing molybdenum, and those specimens polarized anodic to the potential required for breakdown of
the passive film. Most welds will never be polarized to the extent necessary for attack of the fusion boundary. Grain-boundary attack was observed at potentials near the active-passive transition (positive side of active loop), but only in specimens containing more than 0.08 wt% carbon and no molybdenum. Such attack is probably due to the precipitation of Cr$_{23}$C$_6$ particles, which depletes chromium near grain boundaries. Localized depletion of chromium and the general lack of molybdenum could prevent formation of stable passive films in these regions. Welds maintained near the corrosion potential (negative side of active loop) suffered preferential attack of the ferrite phase. Since the potential of a metal in aqueous solution remains near the free corrosion potential, localized attack of the ferrite phase should be the predominant mode of weld-metal corrosion. The process used to make the welds had no significant effect on either overall corrosion behavior or susceptibility to preferential attack. However, in multiple-pass welds, the first-pass weld metal was more susceptible than the weld metal of subsequent passes; the reason for this difference may be related to the additional thermal cycles imposed by subsequent weld passes.

4. Defects and Defect Tolerance

4.1 Hot Cracking

The causes and prevention of hot cracking of welds in austenitic alloys are well documented [68]. In reviewing the subject of hot cracking, consideration must be given not only to hot cracking of the FZ but also to the HAZ. It is generally accepted [69-72] that the presence of ferrite in the weld metal will reduce or prevent the problem of hot cracking. This review presents background material on the causes of hot cracking (both in the FZ and HAZ), and means for its control.

A review by Thomas [73] discusses the theories of hot cracking of HAZs and the effects of composition. The observation that HAZ cracks are almost always intergranular in nature has suggested that compositional segregation of some sort is responsible for hot cracking. This segregation or partitioning of alloy elements can result in localized liquation. Sulfur and phosphorus are common segregants contributing to cracking [99, 107]. Cracking is also exacerbated in those stainless steel alloys containing niobium and titanium as stabilizers. The niobium and titanium both form low-melting eutectics with carbon.

Several theories [68] have been proposed to account for the hot cracking that occurs in stainless steel welds. Of these, the phenomenology proposed by Borland [70, 72] and Borland and Younger [71] seems to be the most generally accepted. In this view, the mechanism of hot cracking comprises four stages:

1. Primary dendrite formation occurs, in which the solid is dispersed and the liquid is continuous, and no cracking is possible.

2. The dendrites become interlocked, with the liquid circulating between the dendrites. If the cracks are pulled apart, the cracks are refilled and healed by the interconnecting liquid.

3. The "critical solidification range" occurs, in which cracks cannot be healed by liquid because of the lack of interconnections among liquid volumes.

4. The remaining liquid completely solidifies and no cracking occurs.

In multicomponent systems containing potentially dangerous impurities such as phosphorus and sulfur, the solidus can be severely depressed. This depression leads to a wider temperature range during stage 3 for development of thermal stress, and severe cracking susceptibility.

It has long been recognized [74] that the presence of ferrite has a positive effect on the reduction of hot cracking, and many theories have been proposed as an explanation. To understand the presence of ferrite in the solidified weld metal, it is helpful to review Fig. 3. The figure shows a vertical cross section of the iron-chromium-nickel phase diagram at 63.5 wt% iron. Ternary alloys with compositions typical of stainless steel welds (within the broken vertical lines) should solidify as austenite plus δ ferrite. Either phase can solidify first, depending on the nickel and chromium equivalents. Most of the δ ferrite formed at high temperature transforms to austenite by a solid-state reaction. The amount of retained δ ferrite at ambient temperatures is dependent on the cooling rate as well as the composition.

There are at least five different theories explaining the beneficial effects of ferrite in
reducing or eliminating hot cracking. The most popular of these [70, 71] start with the assumption that ferrite has a greater solubility than austenite for those impurities that generally form low-melting phases. The presence of some ferrite can therefore reduce the amount of liquid films and the temperature range over which they persist by decreasing impurity segregation during the solidification process. Borland and Younger [71] tabulated the solubilities of various elements in austenite and ferrite and, from this, inferred that elements such as phosphorus, sulfur, silicon, and oxygen would partition to the δ ferrite. It has also been suggested that the interphase boundary between ferrite and austenite benefits as a sink for impurities [70]. Astrom et al. [75] performed an x-ray analysis of a welded stainless steel specimen doped with sulfur and phosphorus. They concluded that sulfur was the cause of hot cracking and that, in a fully austenitic weld, manganese remains largely in solution and is not available at the final stages of solidification to break up the sulfide films. In terms of absolute amounts, 5 wt% ferrite [76] is considered to be a preferred value in the weld metal to prevent hot cracking.

Morishige et al. [69] conducted a statistical study of 39 commercial heats of Types 304, 316, 321, and 347 stainless steels. Using a tungsten arc weld, they performed hot ductility tests (Fig. 31) at 1300°C (2372°F) on these specimens, which had 0 to 10% δ ferrite present. The results show no correlation between the presence of ferrite and reduction of area. This work emphasizes the importance of solidification behavior vs consideration of ferrite content alone. Matsuda et al. [77] proposed from their experimental work that δ ferrite prevented hot cracking by a peritectic/eutectic reaction. They reasoned that the residual liquids were confined to liquid drops within the austenite grains. Primary δ ferrite solidification also reduces the level of impurities in the final liquid.

Schaeffler [78] and DeLong [79] examined the combined effect of alloy additions on the constitution of weld deposits. Their diagrams enable the user to design a FZ with any desired ferrite content (Figs. 6 and 7). However, this approach has not been completely effective since there have been instances where, predictions notwithstanding, cracking has occurred in the FZ. Lippold [108] observed that the welding process could affect the prediction of the ferrite composition in the FZ. He found fully austenitic regions in deep electron-beam welds where the DeLong diagram had predicted 2 to 3% ferrite. In laser welds made at Lawrence Livermore National Laboratory on Types 304 and 316 stainless steels, cracks occurred in fully austenitic microstructures which, by Schaeffler/DeLong predictions, should have contained 5 to 10% δ ferrite [83]. The relatively large melt

Figure 31. Hot ductility as a function of the δ ferrite tendency [69].
undercooling and high cooling rates in laser and electron-beam processes can have a significant influence on solidification and retained ferrite levels.

Hot cracking is generally avoided if roughly 3 to 5% δ ferrite is retained in the as-solidified structure. However, the optimum resistance to cracking requires primary solidification as δ ferrite vs austenite. For this reason, Types 304L and 308 fillers, which solidify as primary δ ferrite, are more resistant to weld cracking than Types 316 and 316L stainless steel, which can solidify as primary austenite. Both can be welded without cracking using proper control of ferrite content and impurity levels.

Little data is available on weld cracking of the fully austenitic Alloy 825. Because of this lack of published information, much of the data in this section is derived from personal communications and from extrapolations from alloy systems similar in composition to Alloy 825.

Although Alloy 825 has been known to hot-crack, definitive work has not yet been published. Some work has been conducted on Alloy 800, which is similar to Alloy 825 (see Table 7). This alloy also has been known to hot-crack [80]. Lippold [80] compared four different heats of Alloy 800, using the Varestraint test as a measurement of cracking susceptibility. Using optical microscopy, SEM, and Auger surface analysis, he observed that the heat most susceptible to cracking contained the largest amount of silicon (in this case, 0.39%), with the cracking occurring primarily at the grain boundaries of the FZ. Lippold observed high concentrations of silicon, titanium, and niobium at these grain boundaries, which he postulated developed as a result of partitioning during solidification. These constituents then acted to depress the solidification temperature. The sulfur and phosphorus contents were on the order of 0.01 wt% or less and were not evident in the region of fracture.

<table>
<thead>
<tr>
<th>Alloy 825a</th>
<th>Alloy 800b</th>
<th>Alloy 625c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni 38.0 min</td>
<td>30.0 min</td>
<td>58.0 min</td>
</tr>
<tr>
<td>Fe 22.0 min</td>
<td>39.5 min</td>
<td>5.0 max</td>
</tr>
<tr>
<td>C 0.05 max</td>
<td>0.10 max</td>
<td>0.10 max</td>
</tr>
<tr>
<td>Cu 1.5 max</td>
<td>0.75 max</td>
<td>—</td>
</tr>
<tr>
<td>Si 0.50 max</td>
<td>1.0 max</td>
<td>0.50 max</td>
</tr>
<tr>
<td>Ti 0.6 min</td>
<td>0.15 min</td>
<td>0.4 max</td>
</tr>
<tr>
<td>Mo 2.5 min</td>
<td>—</td>
<td>8.0 min</td>
</tr>
<tr>
<td>Cb + Ta —</td>
<td>—</td>
<td>3.15 min</td>
</tr>
<tr>
<td>Al 0.2 max</td>
<td>0.15 min</td>
<td>0.4 max</td>
</tr>
<tr>
<td>S 0.03 max</td>
<td>0.015 max</td>
<td>0.015 max</td>
</tr>
</tbody>
</table>

* From [104].
*b From [105].
* From [106].
Cheng [81] stated that it was possible to weld Alloy 825 without cracks by using the TIG process and plates with thicknesses less than 0.5 in. Cheng and others interviewed solved the problem of joining thicker sections by using Alloy 625 (a nickel, chromium, molybdenum alloy) as a weld filler metal. Bishel [82] considered solidification stresses a primary cause of hot cracking. Composition is probably the most significant factor, but he could not place the blame on any one constituent. Bishel does not believe that there is a problem with the corrosion resistance of weld metal Alloy 625 and base metal Alloy 825 because the weld is the more noble of the two compositions.

Witherell [83], responsible for much of the developmental work on weld filler metals for Alloy 625, supports the above comments on the use of Alloy 625 for welding. He also points out that an attempt to modify the composition of Alloy 825 so as to reduce or eliminate the fissuring essentially changes the alloy to such an extent that it can no longer be considered to be Alloy 825. Witherell thinks oxygen and nitrogen lock in the grain boundaries during solidification, and the thermal strain (which cannot be accommodated) then causes cracking.

Alloy 625 has more molybdenum than Alloy 825 and therefore creates a more passive film. Consequently, Alloy 625 is more resistant to crevice corrosion and pitting than Alloy 825 [84].

Lingenfelter [85] stated the following:

Alloy 825 was developed in the 1950s and was originally marketed as NIONEL, prior to the adoption of the current alloy numbering system by its producer, INCO Alloys International. It has been used historically in aqueous corrosion environments, particularly where pitting and crevice corrosion are a problem and in oxidizing acids where intergranular attack is the problem.

Most of the early applications were for pickling hooks and other hardware which did not require nuclear quality weldments, i.e., weldments free or virtually free of porosity, fissuring, and other linear defects. A matching composition filler wire for use with GMAW and GTAW (Filler Metal 65) as well as a coated electrode (Welding Electrode 135) were developed and marketed for a number of years. Weldments produced with these products exhibited microfissuring to the extent that they would not consistently meet the high-quality standards demanded by the Navy Nuclear Code [86] or Section 8 of the ASME Boiler Code [87]. It should be noted that these codes require a full one-inch-thick butt joint for qualification of a welding product. The same fully austenitic alloys (such as Alloy 825 represents) will frequently have adequate cracking resistance to produce crack-free welds up to one-quarter-inch or perhaps one-half-inch thickness. These same materials will not meet the standards at one-inch thickness due to the higher levels of restraint imposed by the added thickness.

In conclusion, on the basis of the information available on Alloy 825, there are two observations that should be made: (1) if Alloy 825 is to be a viable candidate, it is important that the causes of hot cracking be understood so that whichever technique is chosen for joining, the potential problems will have been considered and addressed, and (2) because hot cracking is the result of a melting and solidification process, the possible use of friction welding as a joining method is very attractive since it does not involve melting.

4.2 Toughness

While the toughness of as-welded austenitic alloys is generally excellent, there are several areas of concern. Weld thermal cycles and high service temperatures can cause precipitation of carbides such as M23C6 and intermetallics such as σ phase. The presence of ferrite is of some concern regarding the cryogenic toughness, but more important, it can increase the extent of degradation of toughness due to σ formation. The presence of weld discontinuities such as microfissures can potentially limit operational stresses.

The effect of aging treatments within the sensitization range on the toughness of Types 304 and 308 stainless steels with Types 308 and 16-8-2 stainless steel welds was measured by Mills [88]. The fracture toughness was measured by multiple-specimen $J_{q}$-curve techniques after 10,000-hr thermal exposures at temperatures of 427 to 538°C (800 to 1000°F). Thermal aging at 427°C resulted in no loss in toughness in either...
the parent materials or the weld metal. Thermal aging at 538°C resulted in a 10 to 20% reduction in fracture toughness \( J_c \) for both the parent materials and the weld metal. These toughness levels are high enough to preclude any possibility of nonductile fracture. The aging treatments caused a partial transformation of the residual ferrite into carbides and \( \sigma \) phase, which lowered values of toughness by providing microvoid nucleation sites.

Lefebvre et al. [89] measured the influence of severe thermal cycles on the notch toughness of Type 316 stainless steel filler metals. Compositions ranged from 17.7 to 19.4 wt% chromium and 3 to 10% \( \delta \) ferrite. After an isothermal aging treatment of 100 hr at 750°C (1382°F), values of Charpy V-Notch impact strength at 20°C were maintained above 15 J for all compositions. The impact values decreased with increasing chromium and ferrite contents. An optimized chromium level of 18.3% and a ferrite content of 4% resulted in aged impact strength values of 25 to 30 J. After the aging treatment, the residual ferrite had obviously fully decomposed, and \( \sigma \) phase is believed to be primarily responsible for the decrease in impact values.

Alloy systems based on transition metals iron and nickel that also contain titanium, vanadium, or chromium can form a number of intermetallic phases. The austenitic alloys can form \( \sigma \), \( \chi \), and Laves phases that are thermodynamically stable. The compositions of these phases may adhere strictly to the prescribed stoichiometric ratios, or the phases may exist over a range of compositions. The \( \sigma \) phase, which has a tetragonal structure, can range in composition from \( \text{B}_2\text{A} \) to \( \text{A}_2\text{B} \). The \( \chi \) phase has a bcc-\( \alpha \text{Mn} \) structure with the formula (FeNi)\(_{24}\)Cr\(_{12}\)Mo\(_{10}\) [90], and the Laves phase has a hexagonal structure with the formula Fe\(_2\)Mo [91]. The occurrence of these phases can be correlated with the electron/atom ratio, atomic size, and atomic compressibility. The conditions under which these phases form are quite complex, and this complexity is compounded by the fact that these phases do not form independently. They generally precipitate over the temperature range 600°C < \( T < 1150°C \) (1112°F < \( T < 2102°F \)).

The \( \sigma \) phase has been extensively studied because it occurs in alloys used at elevated temperatures. Sigma is a hard, brittle, nonmagnetic phase in stainless steel that was first noted by Bain and Griffiths [92] in 1927. In Type 304 stainless steel, the formation of \( \sigma \) is promoted by the presence of silicon, which appears to broaden the composition range in which \( \sigma \) is stable. The addition of molybdenum, as in Type 316 stainless steels, tends to further broaden the range of stability of \( \sigma \) phase. Phase equilibrium diagrams for a 70 wt% iron alloy containing molybdenum, nickel, and chromium were determined by Bechtold and Vacher [91] and are presented in Fig. 32. Note that, in the region near the composition of Type 316L stainless steel (16-18 Cr, 10-14 Ni, 2-3 Mo), the equilibrium phases change from \( \alpha + \gamma \) at 1204°C (2200°F) to \( \alpha + \gamma + \chi + \text{Laves} \) at 815°C (1500°F). The formation of the \( \sigma \) and \( \chi \) phases can result in equilibrium \( \chi \) and Laves phases as molybdenum content increases.

The formation of \( \sigma \) phase in austenitic alloys generally leads to a reduction in fracture toughness. This reduction in toughness is most pronounced at ambient temperatures, as shown in Fig. 33. This figure indicates a dramatic decrease in fracture toughness with increasing \( \sigma \) content in high-nickel, high-chromium austenitic alloys. Although precipitation will not be as pronounced in Type 316L stainless steels, the formation of even a small amount of \( \sigma \) phase can have a significant impact on the mechanical properties.

Sigma-phase formation is primarily a concern at temperatures below about 600°C (1110°F) [93]. Intergranular corrosion of alloys containing \( \sigma \) phase has been observed in oxidizing environments [94]. Sigma is not resistant to strong oxidizing media such as hot concentrated nitric acid, which leads to intergranular attack when the \( \sigma \) phase is distributed along grain boundaries. Recognizing that \( \sigma \) phases can potentially develop, it is equally important that the kinetics of the reaction be evaluated [95, 96].

Willingham and Gooch [95] present data on \( \sigma \) formation in Type 316L stainless steel in times as short as 2 min at a temperature of 850°C (1562°F). It has generally been accepted that the formation of \( \sigma \) requires times considerably longer than that suggested above. Nevertheless, once initiated, \( \sigma \) formation might be rapid, should the bulk material structure promote further transformation. Blenkinsop and Nutting [96] examined \( \sigma \) and carbide formation and concluded that carbide \( \text{M}_2\text{C}_6 \) does not nucleate \( \sigma \) phase. They also suggested that cold work could produce \( \sigma \) nucleation sites and that, the greater the deformation, the more extensive the effect.
Figure 32. Phase equilibrium diagrams for high-purity iron-chromium-nickel alloys containing 70 wt% iron [91].
In terms of potential $\sigma$ formation, Alloy 825 has to be treated differently from Type 316L stainless steel since it is an austenite-stable material throughout the temperature range (from the solidus to room temperature). Figure 4 shows a cross section of the iron-chromium-nickel phase diagram as a function of temperature and alloy content. Note that Alloy 825 would correspond to an iron content of approximately 30%, which is beyond the left side of this figure. Type 316L stainless steel contains between 60 and 70% iron and could be considered a metastable austenitic alloy as shown in Fig. 3. Below about 70% iron, the $\gamma$ phase is stable throughout the entire temperature range. This points out the unlikelihood of $\sigma$, $\chi$, or $\lambda$-phase formation in Alloy 825; no data have been identified that document the formation of these phases. This information agrees well with the equilibrium phase diagram for the iron-chromium-nickel ternary system shown in Fig. 5. Investigation of the stability of a potential filler metal (Alloy 625) for Alloy 825 indicated no intermetallic formation following extended heat treatment in the temperature range of 593 to 927°C (1100 to 1700°F) [97].

The presence of microfissures is another concern with respect to the toughness of weldments. In a review [68], Lundin notes that despite the known presence of fissure-like discontinuities in austenitic alloy weldments, no documented evidence exists linking these defects to failures. On the contrary, investigators have found little if any consequence of microfissures on the mechanical properties of austenitic alloys. Static tests show no influence on the tensile strength of weld joints unless the microcracked area exceeds 5% of the weld cross section. In toughness and impact testing of Types 316 and 310 stainless steels containing microcracks, no unstable crack propagation occurred from +18°C to -196°C. Microcracks had no influence on fatigue life in the same weldments. Fatigue-crack initiation sites were distributed between microfissures, specimen corners, and acceptable discontinuities such as inclusions, with no dominance of one type over another. Basically, the critical flaw size in austenitic alloys is much larger than the sizes of any microcracks normally found.
5. Summary

The complexity of the fusion-welding process gives rise to several concerns regarding potential degradation modes in austenitic weldments. The principal concerns are: (1) resistance to sensitization and SCC, (2) weld cracking, and (3) brittle intermetallic formation. None of the three austenitic candidates dominates in its resistance to all of these concerns. Therefore, priority is placed on the material- and service-dependent concerns of corrosion and embrittlement. Weld cracking is a fabrication concern amenable to control by the proper selection of filler-metal chemistry and welding procedures.

Compositional models relate increased resistance to sensitization to increases in chromium and molybdenum contents and decreases in carbon and nickel additions. From such analysis, and from available data, the resistance of Type 316L stainless steel to sensitization is rated superior to that of Type 304L stainless steel. Extension to actual heat chemistries of Alloy 825 predicts further improvement in resistance to sensitization. The degree of sensitization (DOS) is most effectively lowered by reductions in carbon content. Excellent resistance to sensitization can be achieved by stabilization of the carbon otherwise available for sensitization in a form that does not result in nonpassivating chromium-depleted regions. While Alloy 825 is partially stabilized by titanium and is amenable to thermal stabilization, specification of low carbon content is recommended.

Susceptibility to IGSCC is expected to be related to the DOS. In as-welded (unsensitized) stainless steels containing ferrite, however, SCC can also occur by preferential interphase attack or by TGSCC outside the FZ. Alloy 825 is predicted to be immune from TGSCC in the parent metal because of its high nickel content.

The principal concern regarding the cracking of weldments in the austenitic candidates is microfissuring. Considerable doubt exists with respect to the significance of these typically small cracks on the mechanical behavior of ductile materials such as the austenitic alloys. However, it is well documented that the presence of δ ferrite in the FZ will severely limit microfissuring. At equivalent δ ferrite levels, Type 304L stainless steel is more resistant to microfissuring than Type 316L stainless steel. Prevention of fissuring in fully austenitic steels requires special control of impurity levels and may require fabrication constraints. Substitution of Alloy 625 filler metal may be the best method of ensuring proper resistance to cracking in Alloy 825. This filler metal is noble with respect to Alloy 825 and is also resistant to intermetallic formation.

The ranking of these austenitic candidates in terms of resistance to welding-induced degradation is: Alloy 825 (best) > Type 316L stainless steel > Type 304L stainless steel (worst).

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