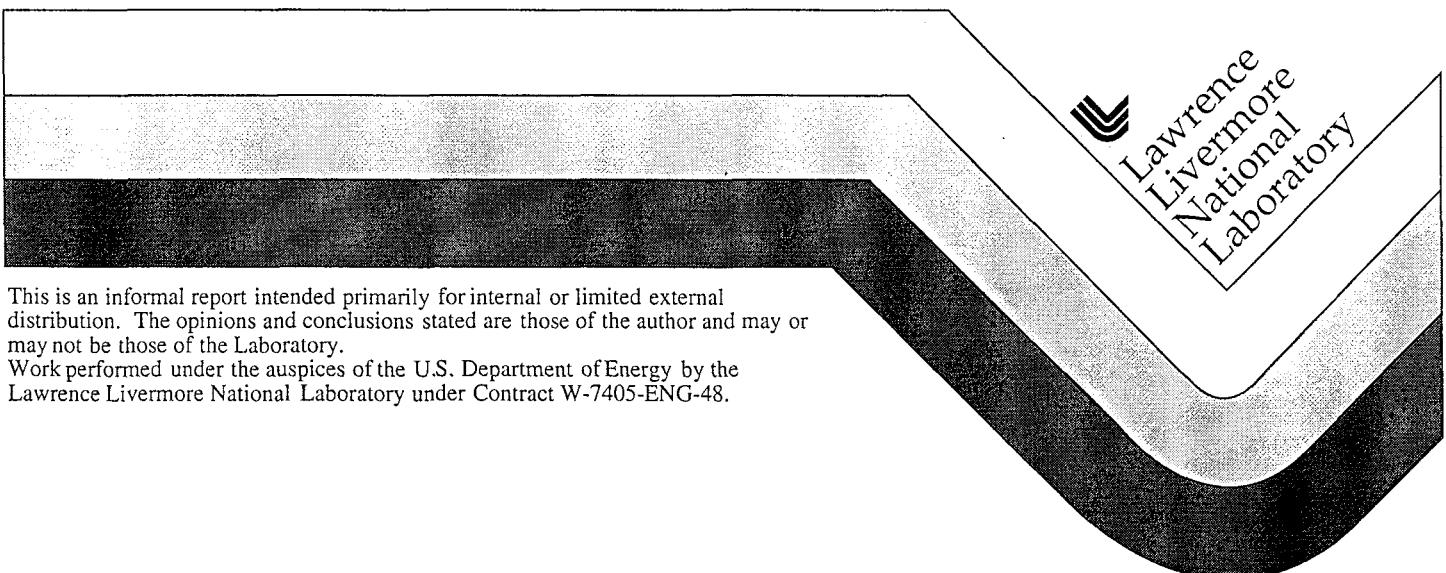


# Considerations on the Performance and Fabrication of Candidate Materials for the Yucca Mountain Repository Waste Packages: Highly Corrosion Resistant Nickel-Base and Titanium-Base Alloys

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November 30, 1995



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**CONSIDERATIONS ON THE PERFORMANCE AND FABRICATION  
OF CANDIDATE MATERIALS FOR THE YUCCA MOUNTAIN  
REPOSITORY WASTE PACKAGES:  
HIGHLY CORROSION RESISTANT NICKEL-BASE AND  
TITANIUM-BASE ALLOYS**

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# **CONSIDERATIONS ON THE PERFORMANCE AND FABRICATION OF CANDIDATE MATERIALS FOR THE YUCCA MOUNTAIN REPOSITORY WASTE PACKAGES**

## **1. Background**

Among the metallurgical factors that affect the performance of a material in a given environment are alloy composition, alloy segregation, depletion of alloying elements, non-uniform microstructures, precipitation leading to an increase in susceptibility to corrosion as well as decreases in ductility, residual plastic deformation, and residual stresses. Precipitation often occurs preferentially at grain boundaries, causing depletion of critical elements in regions adjacent to these boundaries. Continuous grain-boundary precipitates can lead to drops in ductility and toughness. The presence of non-metallic inclusions, if excessive and/or segregated, can also cause embrittlement. Segregation of alloying elements can result in localized galvanic action. Depletion of alloying elements as well as segregation can result in reductions in the concentrations of critical elements below those necessary to resist localized corrosion. Segregation and alloy depletion can also facilitate precipitation that could lead to embrittlement.

Compositional variations can arise from a number of sources, e. g., from the original cast structure, from joining sections made from different heats of the same alloy, from differences between filler metal and base metal, in fusion-welding, and from the cast microstructure in welded joints. Furthermore, depletion of alloying elements to below critical levels may occur in both the heat-affected and fusion zones of a weldment. Compositional variations, resulting from alloy partitioning and/or precipitation can also occur due to some thermal event, e. g., a faulty heat treatment, improper thermal cycles in welding, or elevated-temperature exposures in service.

In an as-fabricated component, compositional variations on a microscopic scale can be eliminated by an appropriate heat treatment, within the limitations of size and time of allowable exposure to the required temperature. By contrast, segregation occurring on a macro or larger scale, such as dendritic and coring segregation and through-thickness compositional gradients, can only be eliminated by a very lengthy, impractical, high-temperature homogenization treatment. In wrought materials, such a condition is

indicative of insufficient hot deformation in the breakdown of the cast structure and/or of problems in the casting and/or solidification of the original ingot. Improper welding could also lead to such a condition. Residual plastic deformation, that may be present from a forming operation, can be a causative factor in many localized-corrosion processes. Residual tensile stresses from welding may increase the susceptibility to stress-corrosion cracking and hydrogen-assisted cracking.

## 2. Environment

As a starting basis for the environment, one may consider the water composition from the J-13 Well, which is located near Yucca Mountain, and which draws water from the same tuffaceous rock that was selected for the repository. At the location of the well, this rock is below the water table and, thus, well below the proposed repository level which is to be located in an unsaturated zone about 213 to 426 m above the water table and about 91 to 366 m below ground.<sup>1</sup> The water is a sodium bicarbonate groundwater with a pH in the neutral to slightly alkaline range (Table 1).<sup>2</sup> The corresponding pH at the time of this sampling was 7.41. Electrochemical corrosion measurements and corrosion rates were obtained in J-13 well water for a number of austenitic stainless steels as well as for Alloy 825.<sup>3</sup> The results indicated that the corrosion potentials of these materials were insensitive to temperatures up to 90°C. Furthermore, no significant differences in their corrosion rates were observed up to 100°C, and with no indication of pitting. On increasing the chloride content of the well water, however, the corrosion potential of these materials became more negative as well as exhibiting enhanced susceptibility to pitting corrosion. Corrosion-rate studies in unmodified J-13 well water at temperatures from 50 to 150°C suggest that uniform oxidation and corrosion of Fe-Ni-Cr austenitic alloys will not limit container life in this environment.<sup>1</sup> The container life may be limited, however, for copper-based candidates for the same conditions.

The composition of the well water appeared to be a reasonable approximation to that of the vadose water.<sup>4</sup> The composition of this water, however, will change with time, depending on the relative rates of dissolution of the rock-constituents. Also, due to the changing heat flux produced by radioactive decay, the various species in the water will undergo significant changes in concentration

with time. Radiolytic products from gamma radiation will further modify the water composition. In addition, drill, diesel, and hydraulic fluids will be introduced into the repository with sulfides and carbonaceous material, encouraging the growth of microorganisms endemic to the site. Leaching of any engineered concrete or carbonaceous backfill can cause a significant increase in the pH value. Other constituents that may increase corrosion, such as sulfur, may also leach out from the materials used in engineered structures. Although corrosion tests have been performed in simulated J-13 well water, in view of the significant changes that might occur with time, the reliability of such tests in helping to accurately predict the long-time performance or even relative performance of candidate materials is questionable. For example, the evaporation of water in contact with the container could result in a significant increase in the concentration of the constituents present in any subsequent condensate formed at that location. On evaporation of 95% of J-13 well water at 90°C, the pH increased to 9.5 and the chloride concentration increased to 750 ppm.<sup>4</sup>

The reliability of the candidate materials to perform in a predictable manner in any given environment depends not only on a knowledge of their performance in that environment, but also on the ability to control, during the production and processing of the materials and the fabrication of the containers, the various factors that may affect such performance. The credibility in predicting the performance of a particular material over the critical time period may be questionable because of the uncertainty in the changing conditions of the repository environment with time. The repository environment will experience numerous physical and chemical modifications due to changes in temperature, moisture content, chemistry, radiolytic products, and microorganisms. These changes will affect the performance of the various candidate materials. Therefore, a conservative approach must be taken in the selection and performance prediction of a material.

The expected performance of some of the candidate materials in the various anticipated environments, especially of the more corrosion-resistant materials, is based on limited information frequently extrapolated from the behavior in laboratory tests that are usually performed in only partially-related environments. Performance of similar materials, although often limited, is also used as a guide. Concerns for the performance of high-level radioactive-waste containers, involving the choice of materials, the fabrication and

closure of the containers, their emplacement and residence in the repository, and the possible environmental changes, have been addressed in some detail by McCright.<sup>5</sup> With the ultimate goal being the prevention of radionuclide leakage, the performance of any selected material, the corrosion performance would be the major consideration in the overall selection of design, materials, fabrication, and final closure. Corrosion mechanisms, models, and scenarios have been presented that pertain to the various possible environments envisioned for the tuff repository.<sup>1,6,7,8</sup>

With an increase in knowledge of potential changes in the environmental conditions at the Yucca Mountain Site, with the introduction of alternative container designs, and with further evaluation of potential degradation modes, the selection of alternative candidate materials continues to be an evolutionary process. The task of developing procedures and/or recommendations for the fabrication and closure of the containers was initiated in FY86, with the major effort being performed by The Babcock & Wilcox Co. under an LLNL subcontract.<sup>9,10,11</sup> Alloy 825 and 70-30 cupronickel were the only materials of the current candidates that were evaluated in this task. Phase 1 was an engineering and screening study used to identify, assess, and rate a number of potential fabricating and closure processes for the containers. The study was on six candidate materials for a thin-wall container, about 10 mm thick, that was based on the current design at that time. Phase 2 was to produce and evaluate subscale mock-ups of a waste container as a basis for selecting the optimum fabrication and closure methods. In Phase 3, full-scale prototypes waste containers of the selected material were to be fabricated and sealed. Because of budget reductions, the project was terminated in the early stages of Phase 2 in FY89. Since the termination of this project, studies on the containers have been focused primarily on new container designs along with additional candidate materials, including materials having both more and less corrosion resistance than those which were previously considered.

### **3. Current Barrier Options**

The container design for the waste package and the selection of container materials have yet to be finalized. A typical conceptual design that was recently considered proposes a closed metal cylinder about 65 cm diameter, 300 to 500 cm long and with a wall thickness

of about 20 mm.<sup>2</sup> This wall thickness assumes the use of a highly corrosion-resistant material. The cylinder (or concentric cylinders if more than one barrier) might be fabricated from rolled-and-welded plate, or it might be cast or extruded. The bottom and top plates would likely be fabricated from rolled-plate and welded to the cylinder(s). All joints except those involved in the final closure could be annealed to relieve any fabrication stresses. Thus the region of final closure is of most concern in assuring the long-term integrity of the waste-package container.

Currently, several design options are being considered. One of these options envisions a metallic multi-barrier container having an outer barrier made from a corrosion-allowance material and an inner barrier consisting of a highly corrosion-resistant material.<sup>12</sup> The outer barrier would have an allowable and predictable corrosion rate. It would be of sufficient initial thickness, on the order of 102 mm, to assure containment and structural integrity of the waste package as corrosion proceeds during its lifetime service of 10,000 years. The most significant degradation mode assumed for the outer barrier would be that of general corrosion. With a correction factor for pitting, this would allow for a calculated wastage of the material and a prediction of its service life. The corrosion-allowance material, however, must not undergo excessive wastage as it must provide for structural integrity and radiation shielding. The inner barrier would consist of a relatively thin wall, about 20 mm in thickness, which must be immune to general corrosion as well as highly resistant to both crevice and pitting corrosion. The potential for stress corrosion cracking and/or hydrogen embrittlement of any candidate material must also be evaluated in the final design. In the event that the outer barrier is breached, resulting in infiltration of liquid, it would behave in an anodic manner to the nobler inner barrier and provide the latter with cathodic protection against corrosion.

A second design option would be to use a moderately corrosion-resistant material for the outer barrier in the event that the environment is too aggressive for the corrosion-allowance material. In this option, the moderately corrosion-resistant barrier would be of sufficient thickness to provide the required strength and shielding or, alternatively, would be thinner and protect the heavier corrosion-allowance material.

A third option would use a moderately corrosion-resistant material as an additional barrier between the highly corrosion-resistant and corrosion-allowable barriers. The moderately corrosion-resistant material would have degradation characteristics of both the two other types of materials. As a fourth option, where the environment initially may be especially aggressive over a significantly length of time, it may be desirable to have the outer barrier consist of the highly corrosion-resistant material.

The relative importance of the various properties of a material will depend on the role and location of the corresponding barrier. The properties to be considered include: resistance to oxidation, resistance to uniform corrosion, resistance to localized attack, resistance to environmentally-assisted cracking, phase stability, resistance to mechanical embrittlement, strength, and ductility. Also, the canisters must withstand handling in transportation, emplacement, and retrieval, as well as potential damage from falling rocks. It is proposed that the waste packages be emplaced horizontally in the drifts. The use of backfill in these drifts is yet to be decided. The backfill would absorb some of the shock from falling rock, if such an event were to occur. However, in being in contact with the container, the backfill may increase the chances for corrosion. For example, crevice corrosion could occur at contact locations; increased concentration of corrosive species can form in pockets of the backfill; leaching from the backfill material might contain constituents that could increase corrosion rates.

An important criterion in selecting the correct barrier option is the time period over which the container is in contact with water. This period is dependent on the thermal load from the radioactive-waste package. Two extremely different ranges of thermal loads are being considered, referred to as "high-thermal" and "low-thermal" loads, respectively.<sup>13,14</sup> In both cases, radioactivity causes the temperature of the container and surroundings to rise above the boiling point of water producing a dry environment shortly after emplacement of the waste package. Vapor-phase corrosion is expected to be the dominant degradation mode during the first part of the containment period.<sup>1</sup> In the low-thermal load case, the temperature of the outer surface of the container will fall below 100°C within a relatively short period of time after the emplacement. (With the pressure being at slightly below one atmosphere, the actual boiling point of the water in the repository will be about 96°C.) This drop in temperature will provide the potential for a wet environment and

subject the waste package to wet corrosion for almost its life in the repository.

With the high-thermal load case, the corresponding temperature after emplacement is expected not to fall below 100°C for over a thousand years, providing a relatively dry environment during this period of time, and wastage is restricted to oxidation or vapor-phase corrosion. A thick outer barrier of carbon or alloy steel would suffice here. The maximum temperature in both cases is expected not to exceed 250°C.<sup>2</sup> The different environmental scenarios created by the two extremes in the thermal loads will dictate different material requirements for the two containers. For example, if penetration of the outer barrier occurred under the high-thermal-load conditions, and the temperature had dropped sufficiently to form condensate, radioactivity from the waste material would then have been substantially lowered so that the consequence of radiation leakage would be significantly reduced. Any subsequent breach of the inner, more corrosion-resistant, barrier could be tolerated. Under low-thermal-load conditions, with the earlier condensation of water and the possibility of earlier breaching of the barriers, the higher dose of radiation leakage would be less tolerable as compared to the high-thermal-load case. Consequently, of the two scenarios, the more highly corrosion-resistant materials would be required for the low-thermal-load case.

#### 4. Current Candidate Materials

The candidate materials currently being considered for the multi-barrier containers at the Yucca Mountain repository are listed in Table 2.<sup>14</sup> The corrosion-resistant materials consist of high nickel-chromium-molybdenum alloys and titanium alloys. The high Ni-Cr-Mo alloys are separated into two groups, the superaustenitic stainless (Ni-rich) alloys and the Ni-Cr-Mo (Ni-based) alloys, distinguished primarily by their relative nickel and molybdenum contents. The titanium materials consist of Ti-Grade 12 and Ti-Grade 16, with near-alpha and alpha microstructures, respectively. The moderately corrosion-resistant alloys consist of two copper-nickel alloys, nickel-base Monel 400 and copper-base 70-30 cupronickel. Three low-carbon steels are proposed for the corrosion-allowance materials, two being wrought products and the third a casting grade. One of the wrought products (2<sup>1</sup>/<sub>4</sub> % Cr-1% Mo) corresponds to a pressure-vessel steel commonly used for nuclear reactors. Because information on

some of the candidate materials may be limited, reference will also be made to materials of similar or nearly similar compositions to the candidate materials.

Candidate materials must have the best-predicted overall performance and have acceptable properties in the following categories: 1) resistance to possible modes of degradation, 2) fabricability and cost, 3) mechanical strength and toughness, and 4) metallurgical phase stability.<sup>1</sup> Degradation modes listed are hydrogen embrittlement, hydrogen-induced degradation, uniform oxidation, uniform dissolution, pitting, crevice corrosion, stress-corrosion cracking, radiation-enhanced degradation, and microbiologically induced corrosion.

An expanded summary of the various properties, characteristics, and specifications of the candidate materials was presented in a recent report.<sup>15</sup> Highlights of this summary are presented here. Alloy 825 was proposed as the primary choice for the inner container. The alloy has adequate to excellent corrosion resistance in a number of environments, as well as having desirable mechanical properties, fabricability, and weldability. Alloy G-3, which contains more molybdenum than Alloy 825, was considered as a substitute for this alloy. The high chromium content in both alloys provided excellent resistance to highly oxidizing acidic conditions. In addition, the molybdenum will enhance the resistance to localized corrosion.

Alloys C-4 and C-22, containing concentrations of molybdenum considerably higher than are present in either Alloys 825 or G-3, were identified as alternatives to these two materials. Both Alloys C-4 and C-22 have excellent resistance to corrosion, especially to stress-corrosion cracking, in a wide variety of aggressive environments. The two alloys are resistant to grain-boundary precipitation in the weld heat-affected zone. Because of the very low carbon contents and the presence of stabilizing elements, post-weld thermal treatments are not necessary. Wrought forms are usually supplied in the solution-annealed condition.

Two titanium alloys, Ti-Grade 12 and Ti-Grade 16, have outstanding corrosion-resistance, low density and sufficiently high strength, and are considered as a third alternative for the inner container. Owing to its palladium content, Ti-Grade 7 is the most corrosion-resistant titanium alloy available. Because of the Pd content (0.12 to 0.25%), however, the alloy has a high cost that has limited its availability and

use. Ti-Grade 16 was developed as a lower-cost substitute having about one-third the amount of Pd with still excellent corrosion resistance. Ti-Grade 12 contains small amounts of nickel and molybdenum which improve the corrosion resistance over that obtained with unalloyed grades of titanium. As with most titanium alloys, care must be taken to avoid surface contamination and hydrogen pickup during manufacture of the containers.

Average mechanical properties of the candidate corrosion-resistant alloys are given in Table 3. Limited data was available on Ti-Grade 16. Accordingly, properties on Ti-Grade 7 are included in the table, as these are expected to be close to those of Ti-Grade 16.

For a mostly-dry environment, a low-carbon wrought steel, ASTM A 516, Grade 55, was selected as the primary choice for the outer containment barrier. The composition limits are close to those of AISI 1020. Thus, information on property values which are readily available for the 1020 steel, and that may be lacking for A 516, could be used for the latter material. The steel can be either hot or cold formed. Welding might require preheating, depending on thickness and temperature, as well as stress-relief after welding. A low-carbon cast steel, such as ASTM A 27, Grade 70-40, was selected as an alternative to ASTM A 516. Castings should be heat treated by either full annealing, normalizing, normalizing and tempering or quenching and tempering. A second alternative candidate for the outer container is the low-carbon 2<sup>1</sup>/<sub>4</sub> % Cr-1% Mo pressure-vessel steel. This steel has a high degree of microstructural stability and excellent formability and weldability, as well as good resistance to aqueous corrosion and environmental cracking. The steel is used in either as-annealed, as-normalized-and-tempered, or as-quenched-and-tempered condition. A disadvantage of this steel is that it is subject to temper embrittlement in the temperature range of 300 to 600°C and, when so affected, is also susceptible to hydrogen embrittlement.

For a mostly-wet environment, Monel Alloy 400 was selected as a substitute for the steels. The alloy has excellent corrosion resistance to many environments, but it can be attacked in oxidizing solutions. It can readily be hot and cold worked; but it must be annealed in a reducing, sulfur-free atmosphere. It is readily machinable and weldable. A second alternative material and one that has been identified for fabricating the outer barrier of the defense high-level-waste glass-disposal container is Alloy C71500 (70% Cu-30% Ni or

cupronickel). The alloy is readily formable and weldable, and has excellent corrosion resistance to seawater and to processing fluids. A wide range of tensile properties is attainable with the Cu-Ni alloys in either the annealed-and-cold-worked or heat-treated conditions.

The two alloys are considered as being moderately corrosion-resistant relative to the environment at the Yucca Mountain Repository.

In this report we will consider in greater detail below the three series of corrosion-resistant materials listed in Table 2. A subsequent report will be prepared to cover the moderately corrosion-resistant and corrosion-allowance materials also shown in this table.

## 5. Superaustenitic Stainless and Ni-Cr-Mo Alloys

The superaustenitic stainless (Ni-rich) steels, may be considered as an extension of the more conventional austenitic stainless steels. The added alloying content, especially nickel, leads to an increase in corrosion resistance. Increased chromium additions improves the corrosion resistance in oxidizing media.<sup>16</sup> The candidate materials selected in this group are Alloy 825 and Alloy G-3. These alloys are highly resistant to chloride-induced stress-corrosion cracking, even in high chloride concentrations. They may be susceptible to pitting and crevice corrosion.<sup>5</sup>

The Ni-Cr-Mo (nickel-base) alloys are an extension of the superaustenitic stainless steels and possess further increases in corrosion resistance. Iron has been replaced by additional amounts of nickel and molybdenum. Two candidate materials were selected in this group, Alloys C-22 and C-4. Both groups contain small amounts of strong carbide formers and ultra-low carbon contents to minimize the possibility of sensitization<sup>6</sup>. Molybdenum, with tungsten to a lesser extent, improves corrosion resistance in reducing media.<sup>16</sup> The high nickel content increases the resistance to stress-corrosion cracking. The relatively high molybdenum content in the nickel-based alloys reduces the susceptibility to pitting and crevice attack that can occur in aggressive environments with the superaustenitic stainless alloys. In the most highly aggressive environments, Alloy C-22 appears to be more resistant than Alloy C-4; however, Alloy C-4, in possessing the better phase stability of the two alloys, may be more favorable for use in welding operations. The family of corrosion resistant alloys produced by Haynes International is shown

in Table 4, which also gives the composition and some of the performance features of the alloys.<sup>17</sup> Also included is Alloy 59 which is relatively new<sup>16</sup>. Comments on the corrosion resistance of Alloy 59 are given in Appendix A.

## 6. Phase Stability of Ni-Cr-Mo Alloys

### 6.1. Phase Relationships and Precipitation

An extensive survey of phase stability and degradation modes of four Ni-Cr-Mo alloys, including Alloys C-4 and C-22, the current candidates, and Alloys C-276 and 625, was presented by Gdowski in 1991.<sup>18</sup> The relative phase stability of the alloys was illustrated with reference to isothermal sections at several temperatures of the Ni-Cr-Mo equilibrium phase diagram. Locating the different commercial compositions on the isothermal sections was accomplished by assuming Ni, Cr, and Mo equivalents for the remaining elements. These equivalents were proposed by Cieslak *et al* as follows:

$$Mo_{eq} = \%Mo + \%W$$

$$Cr_{eq} = \%Cr, \text{ and}$$

$$Ni_{eq} = \%Ni + \%Fe + \sum \%X_i,$$

where  $\sum \%X_i$  is the total remaining alloy content not included in the other equivalents; percentages are in wt pct.<sup>19</sup> The isothermal sections demonstrate the shrinking of the austenite-phase region as the temperature is lowered, with the relative movement of the commercial alloys either towards or into the two- and/or three-phase regions containing intermetallic phases.

Figure 1 contains two isothermal Ni-Cr-Mo sections at 1250 and 850°C, with Alloys C-4, C-22, and C-276 located based on the compositional equivalent values.<sup>19</sup> As can be seen, at 1250°C all four alloys are within the austenite field. At 850°C, Alloys C-22 and C-276 are within a two-phase ( $\mu + \gamma$ ) region, whereas Alloy C-4 and 625 are shown still to be well within the austenite region. At still lower temperatures, all four alloys have crossed over the austenite-phase boundary. In addition to the  $\mu$  phase, and depending on the alloy, three other phases,  $P$ ,  $\sigma$ , and,  $\delta$  (delta ferrite) can be in equilibrium with the austenite phase. The  $\mu$ ,  $P$ , and  $\sigma$  phases are intermetallics, each having a small range of solubility, consisting of different nickel, molybdenum, and chromium contents. The chromium and molybdenum contents, which can be partially substituted for by

other elements present in the alloy such as tungsten, are significantly higher in these intermetallic phases than in the austenite phase.

Thus, if precipitation of the intermetallics occurs during processing, the austenite will be depleted in these elements. Precipitation can occur during thermal cycles involved in processing and fabrication. Depending on the extent and morphology of the precipitation, the precipitates may lead to embrittlement, while the depletion in critical alloying elements near the precipitates may lead to a drop in resistance to corrosion. Grain-boundary precipitation will be especially detrimental. In addition to the intermetallics, carbides, containing chromium and/or molybdenum, may also precipitate and likewise lead to a degradation in properties. The types of carbides that form are dependent on the amounts of alloying elements present and the temperature at which they form. It appears that at least some small amounts of carbides are usually present, although in concentrations that may not be harmful. In addition, ordering<sup>b</sup> may also occur in these alloys during either slow cooling or on heating below about 600°C and cause degradation of properties.

## 6.2. Aging Studies on Precipitation and Properties

Studies on the effects of aging at low and intermediate temperatures in Ni-Cr-Mo alloys were recently reviewed by Gdowski.<sup>18</sup> These studies showed that such aging can result in adverse changes in corrosion resistance and in mechanical properties. Of primary concern for the repository are the effects of long-term aging, (300 to 1000 years) at relatively low temperatures (50 to 260°C), for which conditions studies have not be reported.

The studies reviewed by Gdowski were divided into two temperature ranges. Above 600°C precipitation of intermetallics and carbides occurs, while below 600°C the precipitation is preceded by

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<sup>b</sup> Ordering refers to changing from a completely random arrangement of atoms at lattice-sites in the crystal structure between two or more species of atoms, to an ordered arrangement. This results from the attraction of unlike atoms, such that the nearest neighbors of one species are atoms of the second species. The ordered crystal structure may be either the same as or different from the random structure. In certain alloys, this occurs on lowering the temperature below some point (specific to the alloy), with the degree of ordering becoming more extensive as the temperature drops.

segregation of certain elements and ordering in the alloy. Surface and grain-boundary segregation of minor alloying elements and impurity elements occurred on aging both above and below 600°C. In the review, details on the sequences of aging and aging products are described for each alloy. Temperature-time-transformation (TTT) curves are presented for some of the aging products for Alloys C, C-276, and C-4 for temperatures ranging down to near 500°C.

Aging studies performed below about 500°C, and as low as 100°C, were performed on cold-worked Alloy C-276. Cold working accelerates the aging phenomena. Aging of the cold-worked alloy for one hour at temperatures ranging from 100 to 900°C developed significant differences in surface-impurity concentrations at the different aging temperatures. Other studies on aging with Alloy C-276 indicated that surface segregation may cause it to become susceptible to hydrogen embrittlement. Effects of aging for times up to 8000 hours at 540°C on mill-annealed Alloys C-4 and C-276 were also presented in the review.<sup>18</sup> Both alloys showed increase of about 100% in the yield strengths and about 40 to 45 % in the ultimate tensile strengths. The corresponding decreases in tensile ductility elongation were from 62 to 34% for Alloy C-4 and from 65 to 28 % for Alloy C-276. Samples aged for the 8000-hour period were evaluated for corrosion resistance in boiling 50% sulfuric acid containing 42 g/l ferric sulfate. The corrosion rate for C-276 increased from 5.7 mm/yr for the mill-annealed condition to 67.5 mm/yr for the aged condition; the corresponding values for Alloy C-4 were 3.3 and 5.4 mm/yr, respectively. In contrast to the behavior of Alloy C-276, Alloy C-4 showed virtually no detrimental effect on corrosion resistance due to aging.

A number of aging studies had been performed on Alloy C, indicating that minor alloying elements, especially silicon and carbon, accelerated the aging process, thereby increasing its susceptibility to embrittlement and corrosion. To reduce the aging kinetics for the precipitation of intermetallics and carbides, Alloy C-276 was developed as a modification of Alloy-C, wherein the maximum limits for carbon and silicon were reduced. Alloy C-276 was still readily susceptible to precipitation of the  $\mu$  phase<sup>c</sup> at high temperatures. For example, only six minutes at 900°C were required to precipitate sufficient  $\mu$  phase to significantly alter the corrosion rate.<sup>20</sup> This lack of stability of the austenite phase was attributed to the

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<sup>c</sup> The  $\mu$  phase is based on the crystal structure of  $\text{Fe}_3\text{Mo}_2$ .

presence of tungsten which later was either reduced or eliminated. An electron theory of stability of alloy phases predicted that by eliminating tungsten, precipitation from the austenite phase would be greatly reduced.<sup>21</sup>

Alloys C-4 and C-22 are modifications of Alloy C-276. In both alloys, the precipitation kinetics were further reduced relative to C-276, with C-4 being the least susceptible to microstructural changes. Thus, of the two candidates, Alloys C-4 and C-22, Alloy C-4, having the greater phase stability, would be more amenable to fusion-welding processes where avoidance and/or elimination of brittle precipitates can be a problem. Relative to C-276, tungsten is reduced in C-22 and is eliminated in C-4. The iron content is somewhat reduced, while the maximum carbon content is equally reduced in both alloys.

Reduction in both tungsten and iron, as well as in the carbon content, resulted in increasing the aging time for sensitization to occur in these alloys. To counteract tendencies for sensitization, titanium instead of vanadium is added to Alloy C-4 as a carbide stabilizer. These compositional modifications, including maintaining a low silicon content (0.08% max), eliminated the precipitation of intermetallics and significantly reduced the formation of carbides. The result was to greatly reduce the susceptibility to corrosion as depicted by corrosion tests performed on Alloys C-4 and C-276 following exposure period of up to 100 hours over the temperature range of 600 to 1000°C.<sup>18</sup>

The effects of aging at relatively low temperatures on mechanical properties and corrosion have been evaluated for Alloys C-4, C-22, and C-276 for times somewhat more relevant to repository performance.<sup>22</sup> Samples were exposed for 10,000 hours at 260, 340, and 425°C. Corrosion rates were measured using ASTM G-28, Methods A and B,<sup>d</sup> with exposures of 24 hours for both methods. Aged samples were compared with the original mill-annealed conditions. Charpy impact<sup>e</sup> and tensile-yield properties were reported. The

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<sup>d</sup> Method A consists of exposure to a boiling solution of 42 g/l of  $Fe_2(SO_4)_3$  in 50%  $H_2SO_4$ . Method B consists of exposure to a boiling solution of 23%  $H_2SO_4$ -1.2% HCl-1%  $FeCl_3$ -1%  $CuCl_2$ .

<sup>e</sup> Charpy impact tests are used to evaluate notch toughness. Small bar samples, notched on one face are fixed in a guide (in an impact testing machine) and

authors conclude that there is no long-term, low-temperature aging effect on either mechanical properties or corrosion resistance on these three alloys.

These studies were later extended to include higher aging temperatures and longer aging times.<sup>20</sup> Samples that were aged for 20,000 hours at 260, 340, and 425°C did not show any changes in the above properties. Additional aging at 425°C did result in an increase in strength and a drop in ductility, but, no change in the corrosion rate. Corrosion rates did not increase until after at least an aging period of over 38,000 hours at 482°C. On aging at 425°C for up to 20,000 hours, Alloy C-22 gave the lowest corrosion rate when corrosion tested according to ASTM G-28, Methods A and B; Alloy C-4 had significantly the highest corrosion rates using ASTM G-28 B, while Alloys C-4 and C-276 gave similar corrosion rates using ASTM G-28 A. Exposure of Alloy C-276 for over 53,000 hours at 538°C resulted in a significant drop in toughness and an increase in corrosion rate from 4.3 to 102 mm per year. This was attributed to grain-boundary precipitation of M<sub>6</sub>C. An ordered A<sub>2</sub>B phase<sup>f</sup>, which is believed to be Ni<sub>2</sub>(Cr,Mo), was also detected and can account for a slight increase in the corrosion rate. The formation of this phase was the only change that was observed in Alloy C-4 following exposure at 538°C for nearly 46,000 hours. The exposed alloy showed only a moderate increase in corrosion rate, namely, from 3.2 to 10.2 mm per year.<sup>20</sup> Extrapolating their observations, the authors predicted that at 260°C it would require 400,000 years to develop the ordered A<sub>2</sub>B phase and still longer to precipitate the carbide phase. As a result of their aging studies, the authors conclude that of the three alloys, C-22 is the best as a radioactive-waste-container material.

## 7. Comments on the Corrosion Resistance of Candidate Ni-Cr-Mo Alloys

Alloys C-4 and C-22 have exceptionally high resistance to corrosion in both reducing and oxidizing media for a wide variety of corrosive environments. Both are highly resistant to pitting and crevice corrosion and to stress-corrosion cracking.<sup>23,24</sup> The claim is made

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impacted on the face opposite the notch. The notch can be V-shaped, U-shaped, or key-hole shaped.

<sup>f</sup> In the formula A<sub>2</sub>B, A refers to the host element, such as Ni in this case, and B to one or more alloying elements.

that Alloy C-22 has the best overall corrosion resistance of all Ni-Cr-Mo alloys available.<sup>23</sup> The superiority of Alloy C-22 was illustrated by comparing corrosion rates of Alloys C-22, C-276, C-4, and 625 for a number of different aggressive media. The data from one of the examples (Table 5) show that Alloy C-22 is superior in all cases, with Alloy C-276 being next best and C-4 being third best.<sup>23</sup> The same order of merit was shown for the "critical pitting temperatures" (above 150, 150, 140, and 90°C) and "critical crevice-corrosion temperatures" <sup>g</sup> (102, 80, 50, and 50°C). The test solution consisted of 4% NaCl + 0.1% Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 0.01 M HCl with an acidity of pH2. It is assumed that the test materials were in the annealed condition. Because of the greater susceptibility of Alloy C-276 to precipitation than of Alloy C-4, it is expected that Alloy C-4 will exhibit better corrosion resistance than Alloy C-276 on exposure of the as-welded conditions in these media.

The benign nature of welding on the resistance to corrosion for Alloy C-4 is illustrated in Table 6, where the corrosion rates of the as-welded, annealed, and aged conditions are compared for eight different test media.<sup>24</sup> Both alloys, being highly resistant to the formation of grain-boundary precipitates in the weld heat-affected zone, are suitable for service in the as-welded condition in most corrosive environments. Intermetallic precipitates associated with other Ni-Cr-Mo alloys that form in the range of 650 to 1100°C have not been detected in Alloy C-4. Fine particles of M<sub>6</sub>C carbides can form, but their damaging effect is minimal. More detailed discussions on the relative corrosion resistance of Ni-Cr-Mo alloys are presented in Appendix A.

## **8. Technical Information and Fabrication Guidelines on Corrosion-Resistant Ni-Cr-Mo Alloys**

Technical information and fabrication guidelines for a number of corrosion-resistant Ni-Cr-Mo alloys are available in publications provided by Haynes International <sup>23,24,25</sup> and the Nickel Development Institute <sup>26</sup>. The following presentation is largely based on the information provided in these publications. Some of this

<sup>g</sup> The critical pitting and crevice-corrosion temperatures refer to the maximum temperature in each case at which no evidence of either corrosive action occurs under the test conditions studied. Typically, tests are performed at increasing temperatures in intervals of 5°C until a temperature is reached where evidence of corrosive activity is seen.

information was also presented in a recent LLNL report.<sup>15</sup> The focus here will be on Alloys C-4 and C-22.

Wrought forms of the Ni-Cr-Mo corrosion-resistant alloys are furnished in the solution-heat-treated condition unless otherwise specified. The alloys can be rolled, forged, hot upset, impact extruded, and cold formed. They are available in the form of sheet, strip, plate, bar, wire, billet, tubing, and covered electrodes. Although the alloys tend to work harden rapidly, they can be successfully deep-drawn, spun, press-formed, and punched.

### 8.1. Heat Treatment

In general, the only heat treatment that is acceptable for these alloys is a solution anneal. The solution-anneal heat treatments of Alloys C-4 and C-22 are performed by soaking at temperatures of 1066 and 1121°C, respectively, followed by rapid cooling. Water quenching is the preferred method; however, rapid air-cooling can be used on sections thinner than 9.5 mm (3/8 inch). The solution anneal will place the alloys in the optimum condition with respect to mechanical properties and corrosion resistance. Following all hot-forming and most cold-forming operations, a solution anneal should be done to restore these properties. Stress-relief temperatures commonly used for iron-based materials and some nickel-based alloys are not to be used, as heating to such intermediate temperatures will promote detrimental precipitation. The effects of cold working from various forming operations can be eliminated by holding a minimum of 5 to 10 minutes, depending on gage size, at the solution-anneal temperature. The holding time should be started when the entire section is at the proper temperature.

The following precautions are to be taken in heat treating:

- Remove any grease, graphite, paints, and all other foreign materials from surfaces. Avoid imbedding iron particles if wire brushing is used in the cleaning.
- Avoid any possibility of carburization; use neutral to slightly oxidizing atmosphere. Reducing atmospheres must not be used in order to prevent the possibility of carbon or hydrogen contamination.

### 8.2. Hot Working/Forming

Characteristics of the Ni-Cr-Mo alloys that must be considered during hot-working operations include relatively low melting temperatures, high hot strength, high strain-rate sensitivity, low thermal conductivity, relatively high strain-hardening coefficients, and a rapid increase in strength with a drop in temperature in the hot-working range. The alloys have a relatively narrow hot-working range with start-to-finish temperatures of 1177°C down to 954°C for Alloy C-4 and 1232°C to 954°C for Alloy C-22. Because of this, moderate reductions per pass with frequent reheating is recommended. Care must be taken during hot working to avoid excessive adiabatic heating, as well as excessive loss of heat, by controlling the rate of billet or ingot reduction. Care must also be taken to avoid furnace overheating. In addition, the original cast structure must be completely refined during the breakdown stage, that is, before the final hot-rolling or hot-forging operation. Following hot working, the alloys must be solution annealed for optimum corrosion resistance. The furnace atmosphere must be sulfur-free and slightly oxidizing.

### **8.2.1. Forging**

The following guidelines are recommended for forging:

- Soak billets or ingots at least 12 minutes per cm of thickness at forging temperature. Do not raise the furnace temperature above the forging-temperature range.
- Use a calibrated optical pyrometer to verify temperature.
- Avoid direct flame impingement on the stock.
- Turn stock frequently to present the cooler side to the furnace atmosphere and heat source.
- Forge immediately following withdrawal from the furnace.
- Use reductions of between 25 and 40% per pass, which are sufficient to maintain as much internal heat as possible, thus reducing the number of reheatings and minimizing grain growth.
- Avoid making radical changes in the cross-sectional shape during the initial reduction stages.
- Condition (remove) cracks or tears developed during forging. This can usually be done at intermediate stages between forging sessions.
- Limit hot-upsetting to stock with aspect ratios (length to diameter) no greater than three to one (3:1), with the temperature in the upper end of the hot-working range.

### 8.2.2. Hot Rolling

The guidelines listed for forging are generally applicable for hot-rolling operations with the following additions and modifications:

- Use moderate reductions of 15 to 20% in area per pass.
- Use rolling speeds of 6100 to 9100 surface cm per minute.
- Use frequent reheat to maintain temperature of the stock in the hot-working range.
- Soak workpiece thoroughly at the hot-working temperature before starting the rolling operations.

### 8.2.3. Other Hot-Forming Operations

The forming of plate into components such as dished heads is normally done by cold pressing or spinning with intermediate anneals. The shaping of large sizes and heavy sections, will require hot forming. The following additional guidelines are recommended for such hot forming operations:

- Set furnace temperature intermediate between the solution-anneal and finish forging temperatures (1066°C and 954°C for Alloy C-4; 1121°C and 954°C for Alloy C-22).
- Do not allow the temperature to drop below the lower hot-working temperature during hot forming.
- Avoid excessive surface chilling of the component by using preheated dies.

## 8.3. Cold Working/Forming

Cold working is the preferable method of forming these alloys.<sup>25</sup> Depending on the severity of the deformation, the alloys may require a number of intermediate forming stages to produce the final shape. For mild forming operations, the mill-annealed condition, which is a solution anneal, will generally have sufficient ductility without having the need for intermediate heat treatments. Where required, intermediate as well as final anneals should be performed at the solution-annealing temperature. Critical cold reductions in the range of about 2 to 10% must be avoided if solution annealing is specified. This precaution is to avoid the possibility of abnormal grain growth during subsequent annealing. The presence of cold work does not affect either uniform or pitting corrosion, but, heavy residual cold work can increase the susceptibility to stress-corrosion cracking in certain environments.<sup>25</sup> Lubrication during

forming is important and various lubricants are recommended, depending on the type and severity of the cold-working operation. Care must be taken to remove the lubricants or other foreign materials from the surface of the formed part prior to annealing, otherwise the mechanical and corrosion properties will be adversely affected. Lubricants that contain lead, zinc, or sulfur must be avoided as these elements tend to embrittle the Ni-Cr-Mo alloys.

The following guidelines are recommended for cold-working operations:

- Avoid reductions in the range of 2 to 10% if the reduction is to be followed by a solution anneal, otherwise abnormal grain growth may occur on such annealing.
- Solution anneal components with outer-fiber strains greater than about 7 to 10%.
- Perform a series of successive forming operations with intermediate anneals when relatively severe cold deformation is required to form the part; otherwise, cracking may occur.
- Remove scale by pickling or by mechanical means following an anneal prior to the next forming operation.
- Lubricate with lard oil or castor oil for mild forming operations. These oils are easily removable.
- Lubricate with metallic soaps, chlorinated oils, or sulfochlorinated oils for relatively severe forming operations. If sulfochlorinated oils are used, carefully clean workpiece in a degreaser or alkaline cleaner.
- Avoid lubricants that contain either white lead, zinc compounds, or molybdenum disulfide as they are difficult to remove, and they will embrittle the alloy during subsequent heat treatment.

#### 8.3.1. Cold Spinning

Spinning can be performed cold if excessive deformation is not required. There are two basic forms of spinning. In manual spinning, no appreciable thinning of the metal occurs. In power (shear) spinning, the metal is thinned as a result of the shear forces. The control of quality, including freedom from wrinkles and scratches as well as dimensional accuracy, is largely dependent on operator skill. The main parameters that should be considered are speed, feed rate, lubrication, alloy, strain-hardening characteristics, tool material, tool design, tool finish, and machine power. Lubrication must be

used in all spinning operations. During continuous operation, temperature changes of the mandrel and spinning tool may necessitate adjustment of pressure, speed, and feed. Mandrels must be hard, wear resistant, and fatigue resistant, and should have a finish no rougher than  $1.27 \mu\text{m}$  (50 microinches) and preferably  $0.38$  to  $0.76 \mu\text{m}$  (15 to 30 microinches).

For cold-spinning operations, the following additional guidelines and modifications apply:

- Make trial runs to determine speed and feed rate.
- Apply lubricant to the blank prior to loading in the machine.
- Add additional lubricants as needed during the operation.
- Flood workpiece and tools during spinning with coolant such as an emulsion of soluble oil in water.
- Do not use chlorinated or sulfurized lubricants, as spinning may burnish the lubricant into the surface, with embrittlement on subsequent heat treatment.

#### 8.4. Machining and Grinding

According to Haynes International, the Ni-Cr-Mo corrosion-resistant alloys are considered as being moderate to difficult to machine.<sup>25</sup> They work harden rapidly on machining, generate high heat during cutting, and may weld to the cutting-tool surface. Because of their high shear strength, they offer high resistance to metal removal. The alloys can be machined using conventional production methods at satisfactory rates. The alloys can be cut using any conventional plasma-arc-cutting system. Grinding wheels and corresponding coolants or lubricants recommended for different types of grinding operations are listed in Table 7. Recommended tool types and corresponding coolants for different machining operations are listed in Tables 8 and 9.

Guidelines on machining of Ni-Cr-Mo alloys are:

- Plasma-cut workpiece using a mixture of argon and hydrogen gases.
- Substitute nitrogen for hydrogen gas with a slight deterioration of cut quality.
- Avoid use of shop air or any oxygen bearing gases.
- Grind finish when very close tolerances are required.
- Use rigid machine, overpowered as much as possible.
- Maintain workpiece and tool held rigid and minimize tool overhang.

- Maintain tools sharp at all times; sharpen at regular intervals.
- Use carbide-tipped tools for most operations; high-speed tools can be used, giving lower production rates.
- Use positive rake angles for most machining operations.
- Use heavy, constant feeds to maintain positive cutting action.
- Use soluble oils lubricants, especially when using carbide tooling.

### 8.5. Welding

Welding guidelines, which are presented here for the welding of Ni-Cr-Mo alloys, are largely taken from information provided by Haynes International <sup>25</sup> and the Nickel Development Institute <sup>26</sup>. Welding processes that are commonly used with these corrosion-resistant alloys are gas tungsten-arc, gas metal-arc, and shielded metal-arc welding. Other welding procedures such as plasma-arc, resistance, friction, laser-beam, and electron-beam welding can also be used with these alloys. These methods are being used with increasing frequency.<sup>26</sup> Plasma-arc cutting is commonly used to cut plate and to make weld-joint preparations.

Oxyacetylene welding and submerged arc welding are not to be used. The first method has a high possibility of carbon pickup from the flame. The second method can result in hot cracking, chromium loss, silicon pickup, and excessive heat input. Oxyacetylene cutting should not be used.

A table showing the relative merits of a number of welding processes that had been considered for closure of containers for the Yucca Mountain Repository is reproduced as Table 10.<sup>9</sup> At that time, of the nickel-rich alloys, only Alloy 825 was a candidate. The need to adapt any of the selected processes for remote-control (hot cell) operations is an important consideration. Two of the methods, gas metal-arc welding and shielded metal-arc welding, that are recommended for welding of nickel-based alloys were not included in that evaluation. The relative merits in using these two methods as well as the gas tungsten arc welding method are presented in Table 11. The contents are based on information provided in bulletins published by Haynes International <sup>25,26</sup>

Liquid nickel-based alloys have relatively high viscosities, leading to defects associated with lack of fusion and shallow penetration in

multipass weld joints. To ensure sound welds with proper weld-bead junctions, care must be taken with joint design and weld-bead placement. The welding arc and filler metal must be manipulated so as to place the molten metal where it is needed. Although a weave technique is recommended to manipulate the viscous liquid-weld metal, wide welding-weave beads are not recommended. Stringer-bead torch-welding techniques, with some electrode manipulation, are preferred. The alloys have a tendency to crater-crack; therefore, grinding of starts and stops is necessary. Butt welds should be full-penetration welds to produce full strength and optimum performance in corrosive environments. Fillet welds need not be full-penetration welds as long as the sides and ends are welded closed to seal off voids, which favor the development of crevice corrosion.

Cleanliness is important in the welding of these alloys.<sup>27</sup> Embedded iron, which may arise in using iron-containing abrasives, can lead to localized corrosion. Contamination by grease, oil, corrosion products, and low melting-point elements such as lead and sulfur can lead to severe cracking problems.<sup>25</sup> Examples and sources of contaminating elements are listed in Table 12.<sup>26</sup>

Guidelines for welding of Ni-Cr-Mo alloys are:

- Control heat input in low to moderate range for the joint design being welded.
- Avoid wide welding weave beads.
- Use gas tungsten arc welding for depositing root pass in square butt or single vee joints.
- Make groove openings wide enough to allow proper torch or electrode manipulation and proper placement of the weld bead. This is necessary because of the high viscosity and low penetration of the liquid nickel-based weld metal.
- Use stringer bead torch/welding techniques with some electrode manipulation.
- Design joints and place weld beads to assure that sound welds with proper weld-bead tie-ins are achieved.
- Grind starts and stops to deter crater cracking.
- Take necessary steps to maintain cleanliness.
- Do not use oxyacetylene welding or submerged arc welding.
- Grind all thermally cut surfaces to bright, shiny metal prior to welding.
- Thoroughly clean welding surfaces and adjacent regions with appropriate solvent to remove all foreign matter prior to welding.

- Preheat to room temperature to avoid condensation if taken from a cold environment.
- Maintain interpass temperatures below 93°C.
- Wire-brush with stainless steel brushes between passes. If present, remove slag by chipping/grinding prior to wire brushing. If oxygen- or carbon dioxide-shielding gases are used, apply a light grind prior to wire brushing.
- Use fixturing/clamping and balance weld passes about the neutral axis (where possible) to minimize distortion.
- Avoid making concave-shaped root-pass weld beads, as this leads to cracking of the root pass.
- Use backing gas (100% argon) for the root pass when using either gas tungsten-arc or gas metal-arc welding.
- Store exposed shielded-metal arc process electrodes in ovens at 120 to 200°C to drive off moisture from the electrode-coating.
- Do not use wash passes or cosmetic welds because of the risk of weld cracking or reduced corrosion resistance.
- Prevent entrainment of air into the protective gas shield.
- Avoid stress relieving in the range of 500 to 700°C; if a stress-relief is required, use a solution heat-treatment.

In comparing the tensile properties of as-welded weldments with the base metals of Alloys C-4 and C-22, only minor differences are observed between the ultimate tensile values. By contrast, the welding often results in a significant increase in the yield strengths and a corresponding drop in ductility.<sup>23,24</sup> Some examples of this are shown in Table 13.

#### 8.5.1. Weld Cracking

The claim is made that cracking is rare during the normal fabrication of these Ni-Cr-Mo alloys.<sup>25</sup> Fabrication cracking can include hot cracking, stress cracking, and cracking related to heat treatment. Because of the complex and transient temperature-distributions developed during fusion welding, it is inevitable that stresses are created. These stresses, together with strain-intolerant microstructures that are temporarily present during solidification, and improperly shaped weld deposits, such as concave and tear-drop shapes, can lead to hot cracking. Hot cracking is generally confined to the fusion zone, but occasionally it can occur in the heat-affected zone. Excessive welding current with constrained welds can lead to hot cracking. An understanding of hot

cracking in terms of the solidification microstructures, the corresponding segregation, and the intermetallics formed in the fusion zone was presented by Cieslak *et al.*<sup>19,21</sup> Hot-cracking tests were performed on autogenous gas-tungsten-arc welds of Alloys C-4, C-22, and C-276,<sup>21</sup> as well as of Inconel Alloys 625 and 718.<sup>19</sup> Alloy C-4 showed the least sensitivity to hot cracking followed by Alloys C-22 and C-276 in that order, but, with little difference between the latter two alloys. Terminal molybdenum-rich phases were associated with the cracks in Alloys C-22 and C-276 and nickel-rich phases in Alloys 625 and 718. No terminal phases were observed for Alloy C-4, while Alloy 718 had the largest fraction of terminal solidification constituents. Alloy C-4 was also reported as having a better resistance to hot cracking than Alloy 59.<sup>16</sup> The dominant intermetallic phases in naturally-cooled weld-metals of Alloys C-22, C-276, and 625 are Mo-rich  $\sigma$ , Mo-rich P, and Nb-rich Laves structures, respectively. Alloy C-4 did not contain any intermetallics.

#### 8.5.2. Weld Filler Metal

The selection of welding filler material is a critical issue in the design of a corrosion-resistant weldment. In a review article on Ni-Cr-Mo welding consumables, Stephenson points out some of the problems encountered in the solidification of the weld metal.<sup>28</sup> Alloy depletion and dendritic/coring segregation<sup>h</sup> are two of the common microstructural occurrences that take place in the fusion zone. The degree of segregation (with reference to compositional variation) is decreased with an increase in heat input as observed with Alloy 625. However, the fraction of the interdendritic phase increased and the dendritic microstructure became coarser. The coarser structure, associated with the higher heat inputs were found to become more susceptible to corrosion. In using overalloyed filler

<sup>h</sup> In the solidification of an alloy, the composition of the solid freezing out from the liquid is continuously changing, at first being rich in those elements that raise the freezing point of the liquid, then becoming more and more enriched with those elements that lower the freezing point of the liquid as solidification continues. Therefore, composition gradients (segregation) develop as the molten alloy solidifies. Generally, the solidification occurs preferentially along specific crystallographic directions producing a christmas-tree-like (dendritic) pattern, which is revealed on etching due to the compositional gradients within the individual dendritic branches. The regions between the branches consists of the final liquid to solidify. The terms "coring" and "dendritic" are used interchangeably with the former term generally used where the segregation has a cored-like appearance.

metals<sup>i</sup> , high weld-heat inputs can result in unmixed fused parent metal at the fusion boundaries. If the unmixed region is sufficiently segregated, it may become corrosion-prone. Low weld-heat inputs and low interpass temperatures will diminish these tendencies.

The problems related to segregation can partially be compensated for by the use of an overalloyed filler metal. Based on the Haynes International "Suggested Filler Metal Selection Guide," however, Alloy C-22 filler weld metal (AWS Number ERNiCrMo-10) is suggested for use in the welding of Alloy C-22. Either weld filler metal of Alloy C-22 or C-4 (AWS Number ERNiCrMo-7) is suggested for the joining of Alloy C-4 components.<sup>25</sup> The corresponding AWS Numbers for the shielded metal arc welding electrodes are ENiCrMo-10 and ENiCrMo-7, respectively. Haynes International states that Alloy C-22 is the best alloy to use as a universal weld filler metal to resist corrosion of weldments[II]

Garner evaluated the relative effect of chromium content on the corrosion resistance of welded and unwelded alloys by investigating the influence of microstructural changes caused by autogenous (without filler metal) welding on the critical pitting temperature and critical pitting potential in 10%  $\text{FeCl}_3$  at a pH of about 1.0.<sup>29</sup> Studies were performed on 316L and 317L stainless steels with the former steel modified with various molybdenum contents up to about 5% Mo. Both critical values were lower for the welded areas than for the unwelded areas, with the differences between the two regions increasing with an increase in the molybdenum content. As expected, both of the critical values increased with an increase in molybdenum, which supports the beneficial role of increased molybdenum in suppressing localized corrosion.

#### 8.5.3. Comparison of Weld Metal and Base Metal Mechanical Properties

Differences in tensile properties between the as-welded condition and the base metal for Alloys C-4 and C-22 are shown in Table 13.<sup>23,24</sup> Alloy G-3, which can be considered to be within the family of corrosion-resistant Ni-Cr-Mo alloys, is included in the table.<sup>30</sup> The tensile strength is virtually unaffected by the welding, whereas there

<sup>i</sup> Overalloyed refers to enrichment in the filler metal of one or more of the critical alloying elements in concentrations greater than contained in the base metal.

is a significant increase in the yield strength and decrease in the elongation. The weldment samples had their tensile axis transverse to the welds. The all-weld filler metals give still higher as-welded yield strengths and slight increases in tensile strength compared to the values of the corresponding wrought metals, depending upon the welding method used. For example, Alloy C-22 and G-3 filler metals gave yield strengths ranging from 496 MPa to 524 MPa and 441 MPa to 469 MPa, respectively. The elongations of the filler metals generally fell below the values for the base-metal specimens.<sup>23,30</sup>

## 9. Comments on the Corrosion Resistance of Candidate Superaustenitic Stainless Alloys

### 9.1. Alloy G-3 (INCO Alloy G-3)

Alloy G-3 was developed as a substitute for Alloy G. It was first produced by Cabot Corporation (now Haynes International, Inc.) and was known as Hastelloy Alloy G-3. Its production was subsequently discontinued, being replaced by the more corrosion-resistant and costlier Alloy G-30. The alloy was then reintroduced by INCO Alloys International as INCO Alloy G-3. The information presented here on Alloy G-3 is based largely on bulletins published by both organizations.<sup>30,31</sup>

Alloy G-3 (Table 2) is similar in composition to Alloy G with the exception of changes in the concentration of two elements. The molybdenum content was increased from a range of 5.50 to 7.50% to 6.0 to 8.0%, while the maximum allowable carbon content was decreased from 0.05 to 0.015%. These modifications were made to improve the alloy's resistance to localized corrosion and to decrease the susceptibility of the alloy to sensitization, making it more ammenable to the use of weldments in corrosive environments. The molybdenum provides improved resistance to pitting and crevice corrosion, especially in oxidizing media, while the presence of copper (1.25 to 2.5%), as well as the high nickel content, enhances the corrosion resistance in reducing media. The high nickel content also provides the alloy with exceptional resistance to stress-corrosion cracking in chloride-containing environments. The extra low carbon content minimizes the susceptibility to intergranular corrosion that can result from exposure to elevated temperatures.

Alloy G-3 will withstand the corrosive effects of both oxidizing and reducing media, and can handle both acid and alkaline solutions. It

has excellent resistance to mixed acids, contaminated nitric acid, and flue gases. It has outstanding resistance to hot sulfuric and phosphoric acids. The alloy is resistant to stress-corrosion cracking based on U-bend tests made in boiling (155°C)  $MgCl_2 \cdot 6H_2O$  solution (ASTM G-30 and G-36)<sup>j</sup>.

The decreased susceptibility to various forms of localized corrosion obtained by lowering the carbon content is illustrated in Figure 2, in which the test results of Alloys G and G-3 are compared.<sup>31</sup> Both alloys were exposed to testing according to ASTM G-28, Method A. The significance of the results is that Alloy G-3 is expected to be significantly more corrosion resistant in the heat-affected zone than would be Alloy G.

The resistance to localized corrosion of Alloy G-3 compared to other corrosion-resistant alloys, as inferred by the relative pitting and crevice-corrosion temperatures, can be deduced from Table 14.<sup>30</sup> These two temperatures for Alloy G-3 are considerably higher than the corresponding temperatures for Alloy 825. Tests were performed in an acidic (pH 2), oxidizing  $NaCl-HCl$  solution (4%  $NaCl$  + 0.1%  $Fe_2(SO_4)_3$  + 0.01 M  $HCl$ ).

## 9.2. Alloy 825 (Incoloy 825)

According to Inco Alloys International,<sup>32</sup> Alloy 825 has a high level of corrosion resistance. In both reducing and oxidizing environments, the alloy resists general corrosion, pitting, crevice corrosion, intergranular corrosion, and stress-corrosion. It has a high resistance to cracking in chloride environments. It is highly resistant to most alkali solutions and most organic acids, and it has good resistance to general corrosion, pitting, and to crevice corrosion in sea water. It has good resistance to wet sulfur dioxide and to many sulfurous acid solutions. Alloy 825, however, is subject to biological fouling in continuous sea-water immersion. It is not resistant to oxidizing acid chlorides such as cupric or ferric chloride, nor to wet chlorine and hypochlorite solutions except in dilute solutions. It is only moderately resistant to hydrofluoric acid and to solutions of fluoride salts. The alloy is susceptible to being sensitized to intergranular corrosion if the titanium carbides are

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<sup>j</sup> ASTM G-30 describes procedures for making and using U-bend samples for the evaluation of stress-corrosion cracking (SCC) in metals. ASTM G-36 describes the procedure for evaluating SCC in a boiling magnesium chloride solution.

destabilized on exposure to temperatures in the range of about 650 to 760°C, as during welding or in service. Also, exposures to temperatures above 540°C can result in the precipitation of embrittling phases that may significantly lower the ductility and impact strength of the alloy.<sup>32</sup> In reviewing the literature published on Alloy 825, Strum *et al* noted that the corrosion rate for this alloy did not increase as a result of welding.<sup>33</sup> Welded samples and solution-annealed samples were exposed to a large number of different environments, but for short periods of time (4 to 168 hours).

## **10. Technical Information and Fabrication Guidelines on Candidate Superaustenitic Stainless Alloys**

### **10.1. Alloy G-3 (INCO Alloy G-3)**

Information on heat treatments, fabrication, and machining on Alloy G-3 appears to be limited to two brief bulletins.<sup>30,31</sup> The alloy is available in a wide range of wrought mill forms including rod, bar, plate, sheet, strip, and tubular products. The mill products are generally supplied in the solution-annealed condition. Solution annealing consists of heating to between 1150 and 1175°C and followed by either water quenching or rapidly cooling in air.

The alloy is readily fabricated by all the common methods. It can be readily both hot and cold worked. Forming operations are performed by standard procedures used for nickel alloys. The alloy is machinable using either carbide or high-speed-steel tools. The carbide tools are recommended for high cutting speeds and heavy feeds. Tools should have positive rake angles and should be operated with continuous cutting to avoid work hardening of the workpiece surface. As with other austenitic materials, the alloy work hardens rapidly.

Alloy G-3 has good weldability and does not need any post-heat treatment for restoring corrosion resistance. The alloy can be readily welded by gas metal-arc welding (GMAW), gas tungsten-arc welding (GTAW), and shielded metal-arc welding (SMAW). INCO welding electrode G-3 and filler metal G-3 are recommended for use with SMAW and with both GMAW and GTAW, respectively. Typical mechanical properties reported for welded 1/2-inch to 3/4-inch (12.7- to 19.1-mm) thick plate are shown in Table 13.<sup>30</sup>

It should be noted that although data specifically on Alloy G-3 is very limited, the information available on other nickel-base corrosion-resistant alloys should also be applicable here. For example, the operations, guidelines, and precautions presented in the discussions on Alloy 825 would be applicable to Alloy G-3.

## 10.2 Alloy 825

Much of the technical and fabrication data given in the following is based on information provided in the Inco Alloys International<sup>34,35</sup> and Nickel Development Institute<sup>26</sup> bulletins. Whereas the technical and fabrication information made available by Haynes International was generally applicable to all their corrosion-resistant Ni-Cr-Mo alloys, similar information presented by Inco Alloys International covered a wide range of nickel-based alloys, in many cases having quite different characteristics. Therefore, at times the information was questionable as to its relevance to Alloy 825 when extracting information from the general discussions on their alloys. Such questionable information is not included here. The precautions and guidelines specified for the fabrication and especially for the cleaning and heating of the corrosion-resistant Hastelloys would also be applicable here.

Alloy 825 has excellent fabricability and weldability and is readily machinable by conventional means. The alloy is available as rounds, flats, forging stock, pipe, tube, plate, sheet, strip, and wire. In all forms, the alloy is furnished in the solution heat-treated condition.

### 10.2.1. Heat Treatment

Solution annealing (stabilization) of Alloy 825 is performed in the temperature range of 927 to 982°C with the optimum stabilization being obtained at about 940°C. The optimum combination of softness and fine-grain structure as required for deep-drawing operations, without any loss in corrosion resistance, is obtained on heating to the upper limit of this temperature range. Fast cooling, ranging from rapid air cooling up to a water quench depending on section size, is necessary to prevent sensitization to corrosion. Unstabilized material can become sensitized on exposure to the temperature range between 650 and 760°C. Exposures to temperatures above 540°C can result in the formation of brittle phases that may significantly lower ductility and impact strength.

Depending on the initial microstructure, degree of cold work, and the annealing time, recrystallization can be achieved above about 650°C. For example, 20% cold reduction of fine-grain sheet requires about 15 minutes at 800°C for complete recrystallization. Above 1010°C, rapid grain growth occurs due to the dissolution of finely dispersed carbides. For work-hardened, carbide-stabilized nickel alloys, stress relief is usually done in the range of 480 to 870°C. Stress equalization is usually performed in the range of 260 to 370°C.

The metal must be thoroughly cleaned of all foreign substances, such as lubricants, storage and shop soil, paints, crayon markings, pickling liquids, and slag, prior to heating. Low-melting elements that embrittle the alloy are present in many of these substances. The workpiece should be protected during heating. Contact with any refractory materials (hearth or surrounding dust) must be avoided. Low-sulfur fuels must be used if heating fuels, rather than electrical heating, are used. The atmosphere must be sulfur-free and slightly reducing to neutral with care to avoid any intrusion of oxidizing conditions. A reducing atmosphere containing at least 2% carbon monoxide is recommended. Nickel alloys form an adherent oxide film on air cooling which is difficult to remove. Therefore, the alloy should be cooled under a protective atmosphere or, if at faster cooling rates, in a reducing quench bath.<sup>35</sup>

#### 10.2.2 Hot Working/Forming

The hot-working range for Alloy 825 is specified as 1175°C down to 870°C. Heavy reductions should be done above 1010°C; light reductions between 1010 and 870°C and between 650 and 540°C. The range between 870 and 650°C is to be avoided. To ensure maximum corrosion resistance, some reduction must be made in the range of 980 to 870°C during the final hot-working stage. Heavy sections may become sensitized during cooling from the hot-working temperature and be subject to intergranular corrosion. Thus, care must be taken to cool at a rate equal to or faster than air cooling, depending on section size. If the material is to be welded or subjected to further thermal treatment and subsequently exposed to an environment that may cause intergranular corrosion, the hot-working operation should be followed by a stabilizing anneal. The original cast structure must be completely removed during the breakdown stage of the ingot.

The Inconels and Incolloys require considerably higher hot-forming pressures (about double) compared to the pressures needed for austenitic stainless steels, as well as requiring more powerful equipment. Carbon-steel forging dies are adequate for production of small parts. Alloy-steel dies are recommended for large or intricate parts or for long runs. Only sulfur-free lubricants such as colloidal graphite, which are used to facilitate removal of the workpiece from the forging die, are to be used. To avoid chilling of the workpiece, tools and dies should be preheated to about 260°C. Excessively heavy forging should be avoided in order to prevent adiabatic<sup>k</sup> overheating into the range of rapid grain growth.

#### 10.2.3 Cold Working/Forming

In the annealed condition, Alloy 825 has excellent ductility and is adaptable to virtually all methods of cold fabrication. The high work-hardening characteristics (similar to austenitic stainless steels) combined with high ductility provides for a wide working range between the yield and ultimate values (Table 3) before cracking or tearing occurs.

To minimize the tendency towards galling, heavy-duty lubricants are recommended for most cold-forming operations. Unsaturated or polar fatty-acids oils and vegetable oils are suggested for less severe operations and, even when diluted, they are good lubricants for moderate deep-drawing operations. Ordinary petroleum greases and phosphates are normally not used in forming the high nickel alloys. Light-bodied mineral oils and water-based lubricants can be used only in light forming operations.

For severe deformations, sulfur- or chlorine-bearing lubricants are recommended. The sulfur and chlorine form compounds on the abraded deforming surfaces that increase the effectiveness of the lubricant. The compounds only form if sufficient heat is generated, as in heavy deformations or high-speed forming. These lubricants must not be used if the sulfur or chlorine cannot be completely removed after forming. Sulfur can embrittle the metal on exposure to elevated temperatures. Chlorine will cause the metal to become susceptible to pitting. Metallic coatings can be used as lubricants in

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<sup>k</sup> The term "adiabatic heating" refers to heat generated during the deformation of the workpiece which is retained in the workpiece, and raises its temperature.

severe cold-forming operations, but only when they can be properly removed after forming.

The sulfur- and chlorine-bearing lubricants should not be used in spinning, as this operation tends to burnish the lubricant into the metal surface. Similarly, molybdenum disulfide generally should not be used. Solid lubricants such as bar soap and beeswax are readily applied in spinning operations by holding the lubricant against the rotating workpiece.

Pigmented lubricants containing low melting compounds such as lead carbonate (white lead), zinc oxide, or other metallic compounds, must be avoided, as these compounds can cause embrittlement if not removed before heat treatment.

The high strain-rate sensitivity and frictional characteristics of the alloy dictate that all cold-forming operations, exclusive of high-energy-rate operations, be performed at relatively low speeds. Because of their galling tendencies on high nickel-bearing alloys, water-hardening tool steels should not be used in the cold forming operations. Oil-hardening steels offer some improvement. The highly alloyed air-hardening tool steels perform well. Carbide dies provide the maximum length of service, but they cannot withstand the high tensile and impact loads encountered in the forming of large parts. Soft die materials such as aluminum bronze will give superior surface finishes, but have a short service life. Nonmetallic die materials such as hardwood, synthetic rubbers, and plastics work well in light forming operations.

The nickel-based alloys can be drawn into any shape that is feasible with deep-drawing steel. For simple shapes, dies and tools designed for steel or copper-based alloys can be used. For complex shapes minor dimensional modifications of the dies may have to be made. Because of their higher mechanical properties compared to deep-drawing steel, less wall thinning occurs requiring an increase in die clearance. The rapid work hardening will also generally require an increase in the punch and die-ring radii.

During the various mechanical operations, either hot or cold, small particles of iron may become entrapped in the workpiece. The particles may become so embedded in the surface that they cannot be removed by the methods normally used to remove other foreign matter. Since the iron particles can become sites for localized

corrosion it is imperative that these particles be removed. Several different alternative chemical tests are suggested in order to detect the presence of any entrapped iron, as well as methods for its removal.<sup>35</sup> For example, applying a solution of 1% NaCl for from 12 to 24 hours will develop rust spots identifying the presence of the particles. The iron can then be removed by applying a cold solution of HCl and FeCl<sub>3</sub>, and followed by rinsing. The detection, removal and cleaning processes are repeated until all the particles are removed.

#### 10.2.4. Machining and Grinding

The discussion on machining is based primarily on information given in the bulletin on machining of nickel-based alloys.<sup>36</sup> The alloys are separated into several different groupings with Alloy 825 in Group C, the group that contains most of the Incoloy alloys. Alloy 825 normally has optimum machining characteristics in the annealed condition,<sup>32</sup> although, in general, the alloys in Group C are best machined in the cold-drawn or cold-drawn-and-stress-relieved conditions. It can readily be machined by any of the standard methods used for iron-based alloys. Because of the tendency to work harden rapidly, it is best to use heavy equipment, with cutting tools large and heavy enough to withstand the load and to quickly dissipate the generated heat. To minimize the effect of work hardening, use sharp cutting tools with positive rake angles, which cut rather than push the metal. The correct side- and end-relief angles must be used to provide the proper clearance between the tool flank and the workpiece. Feed rates and cut depths must be sufficient to prevent burnishing or glazing. To minimize distortion and to maximize dimensional stability, it is best to rough out the material slightly oversize, stress relieve, and finish to size.

Virtually any lubricant or coolant can be used, and in some cases none at all. Sulfurized mineral oils can be used with some precautions. Sulfur improves the lubricity, antiweld properties, and chip-forming action. If the oil and workpiece become too hot, a brown sulfur stain will appear on the workpiece. The stain must be removed prior to any heat treatment as the sulfur will cause intergranular attack. Exposure in the cleaning solution should be limited as prolonged exposures in some of the acid-cleaning solutions can result in intergranular corrosion. The sulfurized oils should also be avoided for high-speed operations using cemented carbide tooling. At the high temperatures that develop, the sulfur can embrittle the

cobalt or nickel matrix of the carbide tools. Nevertheless, cemented carbide tools are recommended for most operations involving uninterrupted cuts. Water-based coolants are preferred for high speed operations. For slow operations, such as drilling or boring, heavy lubricants with rich mixtures of chemical coolants are recommended. For simple turning operations, a spray-mist coolant is adequate. Some chemical activity is desired between the coolant and workpiece surface for most machining operations, and this is obtained through proprietary compounds added to the coolant by the manufacturer.

It is important that steady feed rates are used in drilling. If the drill is allowed to dwell, it will cause excessive work hardening of the metal at the bottom of the hole. This will make it more difficult to resume drilling and may result in failure of the drill. Heavy-duty high-speed drills with a heavy web are recommended. Cutting action with drills larger than 3/4 inch (19 mm) in diameter can be improved by grinding several small grooves through the lip and extending back along the lip clearance. Gun drills are used for deep holes up to 2.5 inches (63.5 mm) diameter, with highly sulfurized-oil coolant. If reaming is required, the speed should be 2/3 of the speed used for drilling the same material, but not so high as to cause chatter. Lack of rigidity, misalignment, and dull tools can also contribute to chatter.

In cold cutting heavy sections, it is best to use circular saws with insert teeth. An example is given for a 1.1 meter-diameter blade with 56 inserted high-speed teeth, which are ground and set in a specific manner.<sup>36</sup> The cutting is done at a saw speed of 7.6 meters per minute with a feed rate of 8.5 mm per minute. Sulfurized oil is used as the cutting fluid, with the usual precaution of its complete removal prior to subsequent heat treatment. Cutting-off operations can be done using a hand or power hacksaw, with high-speed-steel blades and the power hacksaw operating at 60 strokes per minute. Band sawing can also be used; high-speed-steel saws with flexible backs and as-tempered by the manufacturer are recommended. The workpiece for both band saws and hacksaws should be flooded with cutting fluid. In abrasive cutting, dry cutting can be used for sections up to 25.4 mm thick. Aluminum oxide resinoid-bonded wheels are recommended. Wet cutting is preferred for thicknesses over 25.4 mm. Here, the use of water containing a rust inhibitor is satisfactory. Surface speeds should be between 1,524 mm and

1676 mm per minute with a feed rate being the maximum permitted by the machine.

Grinding methods used for the high nickel alloys are similar to those used for steels. When only a small amount of metal is to be removed, the finishing operation may be done using rough and final fine grinds. Allowing the part to cool to ambient temperature after rough grinds allows redistribution of internal stresses, and any residual distortions can be corrected in the final grinding operations. Wet grinding is preferred, and the use of aluminum oxide wheels is recommended. Grinding pressure should be great enough to cause slight wheel breakdown.

Surface grinding is best performed with coarse (40-60) grit. Low wheel contact and low pressure will help to prevent distortion. Reciprocating tables are preferred, as they have less wheel contact, generate less heat, and cause less distortion than do rotary tables.

Crush-form grinding (using shaped wheels) is best done with vitrified-bonded, medium-grade aluminum oxide wheels having medium-to-open structures. A high-grade grinding oil should be used with continuous filtering throughout all operations.

#### 10.2.5. Welding

Much of the material in this section is based on information presented in references 26, 34, and 37. Although different techniques than those used for other materials may be required, all conventional processes can be used for welding Alloy 825. The welding procedures are similar to those used for austenitic stainless steels. The thermal expansion characteristics of Alloy 825 are closer to carbon steels than to the stainless steels. This results in less distortion and lower residual stress in the superaustenitic stainless alloys than in the conventional stainless steels when using comparable welding methods. Preheating is usually not required except for the prevention of condensation on cold metal. Post-weld heating is also generally not required. Surfaces must be cleaned of all foreign matter before welding. Common contaminating elements and their possible sources are listed in Table 12.

The molten metal of the superaustenitic stainless alloys is considerably less fluid than that of carbon steels and somewhat less fluid than that of the conventional stainless steels. Weld penetration

is therefore more sluggish. Unlike carbon-steel weld metal, nickel-alloy weld metal does not spread. To spread the metal, it is often necessary to weave the electrode slightly, the amount of weave being dependent on the joint design and electrode type. The weave should not be wider than three times the core-wire diameter. Full penetration is important to avoid potential sites for crevice corrosion and possible loss of strength in butt and vee joints. To compensate for the lower fluidity, nickel-alloy joints have a wider bevel, narrower root face, and wider root opening than is used for carbon steels. The joint opening must be sufficient to permit the torch, electrode, or filler metal to extend to the bottom of the joint.

Choice of welding process will influence the weld-joint dimensions. For example, a spray-arc gas-metal-arc weld has a deeper penetration weld bead than other arc-welding processes so that thicker root faces may be used. Unless both sides of a joint can be welded, a backup material should be used wherever possible in welding plate or sheet. This will decrease the chance of crevices, voids, and excessive oxidation. The use of a backing protective gas is mandatory. The backing material should not be fused to the weld metal and should be removed after the welding. Copper is recommended as a backing material. Because of its high thermal conductivity and chilling effect, the copper will not be melted. Joints not held in fixtures must be tack-welded to maintain a uniform gap and alignment along the entire length with the first two beads made at the two extremities of a joint. The shape of the tack (or spot) bead should not cause a defect in the final weld. The bead shape is best controlled by using the gas tungsten-arc weld process. The beads should then be wire brushed and, if necessary, contour ground; also, any cracks or craters should be ground out. Where either welding on both sides or backing plates cannot be used, the gas tungsten-arc weld process, which provides the best underbead contour, should be used. For material over 9.5 mm thick, a double-U or V joint is preferred. To resist axial stresses, butt joints are preferred over lap or corner joints.

The choice of the welding process should be based on 1) thickness of metal to be joined, 2) design of the component, 3) design of the joint, 4) position of the joint, 5) need for fixtures or jigs, 6) special shop or field conditions, and 7) type of service exposure.

Shielded metal-arc, gas tungsten-arc, gas metal-arc and submerged-arc welding processes are the main joining methods in use for the superaustenitic stainless alloys. Plasma-arc, electron-beam, and

laser welding process are being used with increasing frequency. Although resistance welding is not mentioned in the Inco bulletin on welding,<sup>34</sup> in the Alloy Digests on the Carlson and Allegheny Ludlum alloys (Alloy C825 and AL 825 Alloy) equivalent to the Inco Alloy 825, resistance welding is also indicated as one of the common methods used for these alloys.

The shielded metal-arc welding process is used when the shapes and quantities do not justify the use of automatic welding. The filler-wire electrode is covered with a flux that decomposes and forms into a gaseous envelope that protects the molten metal from the environment. The same techniques for arc starting and stopping used for low-hydrogen carbon-steel electrodes are applicable for welding nickel alloys. The arc should be struck at a point in the joint that will be remelted. The arc should not be abruptly extinguished, as this is likely to cause a large weld crater. For control of the weld puddle, it is necessary to maintain a short arc length. The correct amount of weave and electrode manipulation depend upon the joint design, welding position and electrode type. This should be determined with practice runs. Under correct welding conditions, excessive spatter should not occur. If excessive spatter occurs, it may be caused by one of the following factors: 1) excessive arc length, 2) excessive current, 3) incorrect polarity, 4) excessive moisture in the electrode coating, or 5) magnetic arc blow. The problem can be readily corrected, with the corrective measures the same as those used for steels.

In the gas metal-arc welding process, the arc is established between a consumable, bare-wire electrode and the workpiece. This process has several advantages over the shielded metal-arc and gas tungsten-arc processes, namely. 1) faster welding speeds, 2) no slag, minimizing post-weld cleanup, 3) ease of automation, and 4) good transfer of elements across the arc. It has, however, more weld-parameters to control, making it more complex and more expensive than the other two processes. The type of metal transfer used in the gas metal-arc welding process has a profound influence on the process characteristics, and guidelines can differ for the different arc-transfer modes. The three most frequently used modes for welding the nickel-based alloys are the spray-arc, the short-circuiting-arc, and the pulsed-arc modes.

The spray-arc mode is characterized by high deposit rates and high heat inputs. It is generally limited to the flat position. The short-

circuiting-arc mode provides a low heat input and minimizes distortion in thin gauge materials. It has limitations when used on multiple-pass, thick joints. The process can be prone to lack-of-fusion defects. The weld beads tend to be convex, which would necessitate grinding each bead to assure full penetration to the side walls. The process is most useful for single-pass welding. The pulsed-arc mode is considered as an excellent compromise between the other two modes.

The shielding gas for all three modes normally contains at least 97.5% inert gas: argon, helium, or a mixture of the two. Some mixtures may also contain up to 2.5% CO<sub>2</sub> which may present additional work in the welding of chromium-rich stabilized alloys such as Alloy 825. The oxides of aluminum, titanium, and chromium that form are very refractory and tightly adherent, and must be removed by careful grinding between passes.

The gas tungsten-arc welding process is widely used and is well suited for welding nickel alloys. Argon is the preferable protective gas, with helium or mixtures of the two gases also being acceptable. When extinguishing the arc, the size of the weld pool should be gradually decreased, otherwise crater cracking is likely to occur as the weld solidifies. Proper arc-stopping practice is especially important in the root pass of welds that are welded only from one side. Ample shielding is recommended to protect both the weld puddle and the root side. The filler metal should be kept within the inert-gas envelope during welding. In some welds, inadequate filler can result in a concave bead that has a tendency for centerline cracking. Uneven melting of filler metal along with fast solidification rates can cause segregated spots of melted base metal and filler metal, respectively. Experience has shown that at least half of the fusion zone should consist of melted and re-solidified welding consumables.

Although the submerged-arc welding process is not recommended for use with the Ni-Cr-Mo alloys (for example, Alloys C-4 and C-22), this process is useful for joining thick sections of other nickel-based alloys. Inconel filler metal 625, which is one of the filler metals recommended for use with Alloy 825, is used with the submerged-arc process. Reference to the use of this process specifically for Alloy 825 could not be found. Nevertheless, because of its many advantages and its use with other nickel alloys such as Inconel 625 and Monel 400, as well as its possible use with Alloy 825, the process

is discussed here. Submerged-arc welding provides high deposition rates, thick beads, stable arc, and smooth as-welded surfaces. It is important to use the proper type and amount of flux. Only enough flux to prevent arc breakthrough should be used. Excessive flux can cause a deformed bead surface. Poor weld contour, flux entrapment, weld cracking, and inclusions can result when the wrong flux is used. Fluxes should be stored in a dry area, as they are subject to moisture pickup. Absorbed moisture can be eliminated by baking at about 400°C, followed by holding at 120 to 150°C until being ready to weld. The recommended filler metals are the same as the filler metals or electrode wires used for gas metal-arc and gas tungsten-arc welding. Slag entrapment is avoided with proper joint design and proper placement of the beads. Slag (solidified residue from the flux) must be removed from the weld bead, which may be inconvenient in multiple-pass welding. Beads should be placed so as to provide an open or reasonably wide root area for the next bead, with the beads having a slightly convex contour. The chemical composition remains virtually constant through the deposited metal with no accumulation of flux components. In addition to protecting the molten metal from atmospheric contaminants and providing arc stability, flux components contribute important additions to the weld metal.

Guidelines and precautions in the welding of Alloy 825 are:

- Remove all foreign material from surface, including any embedded particles, slag, and surface oxides, especially in the weld-zone areas.
- Remove all oxides and dross from thermal cutting before welding, as the oxides of chromium and titanium, having high melting points, will not be fused by the weld metal and will be entrapped as defects.
- Remove moisture from metal surface, as moisture can cause porosity in the weld metal. If the base metal is cold (below 3°C), preheat the area surrounding the weld zone to about 20°C to prevent condensation.
- Avoid flat or convex beads. Make all beads with slightly convex contours.
- Design the bottoms and attachments of containers for complete and free drainage to avoid crevice corrosion.
- Use backing material on the back side of a weld, where possible.
- Use tack welds for maintaining alignment when joints are not held in fixtures

- Design and space joints to facilitate full penetration of weld metal.
- Use gas tungsten-arc weld process for root pass when joints cannot be welded from both sides.
- Avoid uneven melting of filler metal.

#### 10.2.6. Weld-Filler Metals and Electrodes

Incoloy welding electrodes 112 (AWS A.5. 11 ENiCrMo-3), 122(AWS A 5.11 ENiCrMo-10), and 135 (DIN 1736 EL-NiCr28Mo) are recommended for the shielded metal-arc welding process.<sup>38</sup> Electrode 112 has relatively high strength (Table 15)<sup>38</sup> with exceptional corrosion resistance, including resistance to pitting and crevice corrosion. Electrode 122 is designed to offer protection against preferential weld-metal corrosion when used to welding molybdenum-containing nickel alloys. Electrode 135 has good resistance to pitting and general corrosion, especially in reducing environments such as phosphoric and sulfuric acids. As seen from Table 16,<sup>38</sup> electrode 122 has a much higher molybdenum content than electrode 135, while electrode 112 has a molybdenum content intermediate between the two. Electrodes 112 and 122 have about the same chromium content, which is significantly lower than that contained in electrode 135 (21 versus 28%). Other significant differences are in the carbon content and in the presence or absence of carbide stabilizers. The three electrodes can be operated in all welding positions.

Inconel filler metals 65 (AWS A5. 14 ERNiFeCr-1) 622 (AWS A 5.14 ERNiCrMo-10), and 625 (AWS A5. 14 ERNiCrMo-3) are recommended for the gas metal-arc and gas tungsten-arc welding processes.<sup>38</sup> Filler metal 65 is considered as highly corrosion resistant, especially in reducing environments. Filler metal 122 provides good resistance to pitting and crevice corrosion and offers protection against preferential weld-metal corrosion when used for joining molybdenum-containing nickel alloys. It is useful for joining many dissimilar metals. Filler metal 625 is considered as having exceptional corrosion resistance, including resistance to localized attack such as pitting and crevice corrosion. The main differences in composition are in the molybdenum content and in the carbide stabilizers (Table 16).

For Alloy 825, in applications requiring the highest resistance to pitting, use Inconel welding electrode 112 and Inconel filler metal 625, and use a stabilizing anneal following the welding. In general, the use of highly alloyed fillers to match the corrosion resistance of the base metal is recommended, and pre- or post-weld heating is usually required. The use of a maximum interpass temperature of 150°C, with an arc length as short as possible, is also recommended.

#### 10.2.7. Additional Comments on Welding

A note of precaution is made with respect to the welding of thick sections. In reviewing the bulletins containing information on Alloy 825 and published by Inco Alloys International,<sup>32,34,35,38</sup> data on properties of weldments were given without any reference to thickness. In a private communication reported by Strum *et al*, Lingenfelter noted that gas metal-arc and gas tungsten-arc weldments of Alloy 825 using filler metal 65 or electrode 135 exhibited microfissuring.<sup>33</sup> This was with reference to 25.4-mm-thick butt joints. He further noted that such austenitic alloys will frequently have adequate cracking resistance to produce crack-free welds up to 6.4 mm or perhaps 12.7 mm thick. The problem with the greater thicknesses arises due to the higher levels of restraint imposed by the added thickness. The authors note that there is very little information available on hot cracking of Alloy 825. They suggest the possible use of friction welding since this does not involve melting; the hot cracking occurs during the solidification process.

### 11. Titanium

#### 11.1. Comments on Corrosion

Commercially pure titanium, such as Ti-Grade 2, has excellent corrosion resistance in most aqueous salt solutions, including chlorides, hypochlorites, sulfides, sulfates, nitrates, and phosphates. The metal, however, is not especially resistant to non-oxidizing media, such as HCl and H<sub>2</sub>SO<sub>4</sub>. It has limited resistance to hot concentrated solutions of AlCl<sub>3</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, and ZnCl<sub>2</sub>. On hydrolizing, these salts form non-oxidizing acid solutions, and tend to pit the metal at high temperatures and high salt concentrations. Bomberger stated that unalloyed titanium should not be used in uninhibited acid-chloride solutions at high temperatures, and that

crevices should be avoided even in hot neutral chloride solutions.<sup>39</sup> He further stated that only corrosion-resistant titanium alloys should be used whenever crevices cannot be avoided or when used in uninhibited nonoxidizing acid solutions.

A small addition of a noble metal (Pd, Pt, or Ru) to Ti-Grade 2 greatly improves its corrosion resistance in non-oxidizing media without detracting from its corrosion resistance in oxidizing media. The addition of the noble metal also significantly increases the resistance to localized corrosion. The noble metal deposits on and enriches the surface of the alloy as it starts to corrode, reducing the hydrogen-evolution overvoltage. An example of the effect of small additions of a noble metal on reducing the corrosion resistance is illustrated in Figure 3<sup>40</sup> for exposure to boiling HCl solutions. The enhanced resistance imparted by the noble metal led to the development of several new alloys containing small amounts of either palladium or platinum, of which Ti-Grade 7 (0.12 to 0.25% Pd) became the most popular. However, the use of this alloy is limited because of its high cost.

To obtain a cheaper alloy that would be acceptable as a substitute for Grade 7 in most applications, Ti-Grade 12 (Ti-0.8Ni-0.3Mo) was developed (Table 2). It has similar, although somewhat inferior, corrosion properties to those of Grade 7.<sup>41</sup> A number of different mechanisms have been proposed to explain the passivation role of nickel, which is present in the passive film.<sup>41</sup> Most recently, some new alloys were developed containing additions of palladium.<sup>40,42</sup> One of these is Ti-Grade 16, which consists essentially of 0.05% Pd added to Ti-Grade 7 (Table 2). The corrosion resistance of Grade 16 is close to that of Grade 7, but with a significant reduction in cost Table 17.<sup>40</sup>

According to Schutz *et al*, the addition of nickel to unalloyed titanium improves its resistance to general corrosion in hot reducing acids as well as to chloride-crevice corrosion.<sup>43</sup> The addition of molybdenum enhances resistance to general corrosion in hot reducing-acid media, but with less potency than that of nickel. Limitations imposed by weldability, ductility and formability, together with various types of corrosion studies, led to the composition for Ti-Grade 12. The immunity of the alloy to crevice attack and pitting in near-neutral saturated brine up to 232°C demonstrated its improvement over the commercially pure (C.P.) grades of titanium. It is clear that, although

the additions of nickel and molybdenum to titanium greatly improved the performance of titanium in many corrosive environments, in the more severe environments, the corrosion resistance of Ti-Grade 12 does not meet the corrosion resistance of either Ti-Grade 16 or 7.

The relative resistance to crevice corrosion of Grade 12 (containing Ni and Mo) versus that of Grades 7 and 16 (both containing Pd) in naturally-aerated, saturated NaCl brine over a range of temperature and pH values is shown in Figure 4.<sup>40</sup> The authors lump together the alloys containing the noble metals (Pd and Ru), irrespective of the amounts of these elements present, indicating the commonality in the superior behavior of these alloys relative to that of the C.P. titanium grades (Ti-Grades 1 and 2) and Ti-Grade 12. The relative merits of Ti-grades 7, 12, and 16, reported by RMI Titanium Company, are shown in Table 18.<sup>44</sup>

Gdowski and Ahluwalia noted that Ti-Grade 7 and the two candidate materials, Ti-Grades 12 and 16 (Table 2), are likely to be very resistant to crevice corrosion under the conditions currently expected at the Yucca Mountain repository.<sup>45</sup> They also state that although Grade 7 has the highest resistance to crevice corrosion, it is not a candidate material because of its relatively high cost.

To evaluate the weldability of the more corrosion-resistant titanium alloys, comparisons of corrosion rates in boiling HCl at several different concentrations were made between the as-received base metals, weldments, and base metals that were heated to different temperatures and air cooled (simulation of heat-affected zones). Differences in the corrosion rates between the different conditions for Grade 16 and, especially, for Grade 7 were very slight (Figure 5).<sup>42</sup> Additional comments on the corrosion of titanium and its alloys are presented in Appendix A.

### 11.2. Microstructure

On heating, pure titanium undergoes a transformation at 885°C from an hexagonal close-packed crystal structure, referred to as the alpha ( $\alpha$ ) phase, to a body-centered cubic crystal structure, referred to as the beta ( $\beta$ ) phase. Alloying elements can be added to stabilize either one of these phases, forming the alpha, alpha-plus-beta, and beta series of alloys.

Ti-Grade 12 is a mixture of  $\alpha$ -Ti,  $Ti_2Ni$  intermetallic phase, and  $\beta$ -(Ti-Mo). The microstructure consists of alpha grains with 10 to 15% of beta phase. The beta phase is located primarily along grain boundaries and at triple points (intersection of grain boundaries of three or more grains). The intermetallic compound is seen at the boundaries between the alpha and beta phases and within the beta grains. Acicular (needle-like) alpha microstructures are found primarily in welds and in the heat-affected zones. The presence of the beta phase results in a significant increase in strength over that of the all alpha-phase material (compare the strength of Ti-Grade 12 with Grade 7 in Table 3).

Ti-Grade 16 is a relatively new alloy with very little available information.<sup>45</sup> It is an all alpha (single-phase) alloy. The microstructure is strongly dependent on the thermomechanical history of the alloy. On one extreme it can consist entirely of equiaxed alpha grains resulting from cold work and recrystallization. A sufficiently low forging temperature might also produce a recrystallized structure. On the other extreme, it can consist of various morphologies, such as acicular or Widmanstatten<sup>1</sup>, produced directly from the transformation of the beta phase on cooling. In addition, elongated grains may be present due to unidirectional deformation of the metal.

If the beta-to-alpha transformation occurs during deformation, the alpha separating from the beta takes on an equiaxed microstructure, called "primary alpha". This is due to the alpha continuously recrystallizing and undergoing grain growth into the transforming beta phase. However, if the deformation ends before the beta transformation is completed, the remaining beta transforms to the acicular-alpha microstructure.

## 11.2 Technical Information and Fabrication Guidelines on Titanium

Titanium Ti-Grade 12 is available as sheet, strip, plate, bar, billets, forgings, welded tubing, and welding wire. It is considered to be a

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<sup>1</sup>The term Widmanstatten refers here to a pattern of alpha platelets formed along specific crystallographic planes and directions of the beta phase during the final stages of transformation of beta to alpha on cooling at intermediate cooling rates. The morphology can vary from acicular (needle-like) to platelets, and if extensive it can have a basket-weave appearance.

low-medium strength, alpha-titanium alloy that is readily warm or cold formed and is highly weldable. It can be reduced up to 40% by cold working. The alloy responds to conventional heat treatments such as stress relief, mill anneal, and recrystallization. The alloy is normally used in the mill-annealed condition, which is obtained by heating to between 760 and 815°C for from 30 to 60 minutes, followed by cooling in air. Table 19, which is reproduced from an RMI Company data sheet, shows typical values of a number of physical and mechanical properties of Ti-Grade 12.<sup>46</sup> Other than ASTM minimum tensile requirements (Table 3), mechanical properties of Ti-Grade 16 were not available. It is assumed that they would be close to those of Grade 7. One disadvantage of titanium and most of its alloys is that their strength decreases rapidly with increasing temperature.

### 11.3. Heat Treatment

Flat-rolled products (sheet, strip, and plate) of Ti-Grade 12 are generally supplied in the final mill-annealed condition, depending on product form and/or customer requirements. Heat treatments range from 540 to 815 °C, similar to those for the C.P. grades. Annealing plate or strip products in the temperature range from 730 to 815°C will usually yield a recrystallized microstructure. For extensively-worked material, soaking at 700°C for 1/2 to 2 hours is sufficient. Normally, heat treatment following fabrication is not required; however, where close machining tolerances have to be held, stress relief may be required. For sheet products of Ti-Grade 12, a stress-relief anneal is performed on heating at 540 to 650°C for 1/2 hour and cooling at any convenient rate. With plate material, the recommended time is one hour per 25.4 mm of thickness. For Ti-Grade 7 the corresponding temperature range is 540 to 600°C.

The furnace atmosphere should be slightly oxidizing to minimize hydrogen contamination. Inert gases are recommended only for parts containing very thin sections that require multiple heating operations. Excessive exposure to oxidizing atmospheres at temperatures above 650 to 700°C may result in excessive oxidation. Above 800°C, scale formation in air can be quite rapid. Both oxygen and nitrogen are alpha stabilizers and show extensive solubility in the alpha phase. The two elements tend to embrittle titanium if present even in fairly small amounts. In air, oxygen contamination is negligible below about 540°C. Below this temperature, only a thin oxide film may form, causing a discoloration of the surface, while

above about 540°C, a definite oxide scale can form, with the formation of both film and scale depending on temperature and time. The scale formed in air (reaction of titanium with oxygen and nitrogen) is very adherent, hard, and difficult to machine, and is usually removed by pickling in strong reducing acids. The scale formed at the higher temperatures is generally more readily removable.

The formation of titanium hydride during the manufacture of the material is highly unlikely. But, the absorption of hydrogen from the environment with the formation of the hydride and followed by hydrogen-induced cracking is a distinct possibility.<sup>45</sup> Hydrogen can only be removed by vacuum annealing. An extensive review on the effect of hydrogen on titanium was presented by Paton and Williams.<sup>47</sup> These authors stated that with the advent of improved mill practice and fabrication procedures, the hydrogen content of the finished product has been steadily reduced, and failures due to hydrogen contamination are very rare.

#### 11.4. Forging

The initial breakdown forging of titanium alloys is usually done at temperatures above the beta transus (transformation temperature to all beta), since the beta phase is more ductile than the alpha phase and forging-pressure requirements are lower. Final forging is usually done at temperatures below the beta transus to prevent excessive beta grain growth, which results in a loss in ductility. Variations in strain rate have little effect on forgeability. The alpha and alpha-beta alloys are readily forgeable with either presses or hammers. For commercially pure titanium (as well as a number of the alloys), the initial breakdown of the ingot is carried out at temperatures between 925 and 1090°C.

Die forging of unalloyed grades is readily accomplished with blocking (forging with dies used to form a specific part) temperatures in the range of 870 to 925°C and finishing between 815 to 870°C (below the beta transus). For Ti-Grade 12, the recommended blocking temperature range is 900 to 925°C. Finishing below the beta transus will result in more uniform properties. As with the annealing processes, slightly oxidizing atmospheres must be used to minimize hydrogen pickup. Any scale or contaminated surfaces must be removed following any operation at elevated temperatures.

## 11.5. Forming

Ti-Grades 12 and 7 can be both cold and hot formed. The alloys can be cold formed on equipment used for stainless steels and for other titanium alloys. Ti-Grade 12 can be considered as being similar to Ti-Grade 3 for ductility and bendability. For design purposes, a minimum bend radius of twice the section thickness is appropriate at room temperature. Tighter radii require preheating to about 150°C.

Forming of titanium is best accomplished by one of four basic methods: hydropress, power brake, stretch, or drop hammer.<sup>44</sup> The method used will be governed largely by the configuration of the end product. Pressures should be applied more gradually than with steels. Blanks should be deburred to a round smooth edge to prevent the appearance of cracks or tears during the forming operation. Hot forming of titanium sheet is usually preferred over cold forming. In hot forming, the titanium blanks are heated so that the actual deformation takes place at 200 to 315°C for the commercially pure grades and at 425 to 700°C for the alloyed grades. Stress-relief heat treatments should be performed between cold-forming stages and following the final cold-forming operation.

The most important reason for hot forming titanium is to minimize springback and residual stresses associated with forming at lower temperatures. Hot forming also improves the forming characteristics of titanium by increasing its ductility. Variations in yield strengths between different heats of the same alloy are reduced on forming at elevated temperatures, allowing for greater uniformity in formed parts. Such advantages are also obtained, but to a lesser degree, by warm working (150 to 260°C).

With the alpha phase having an hexagonal close-packed crystal structure, textures (crystallographic alignments) and corresponding anisotropic properties are readily developed following unidirectional working of titanium, such as by cold rolling. The variations in ductility and yield strength, associated with the preferred textures, can affect the uniformity of a part being formed. An extensive treatise on textures and its effect on properties in titanium and its alloys was presented by Larson and Zarkades.<sup>48</sup>

## 11.5. Handling and Cleaning

All foreign material, such as stencil marks, grease, oil, solvents, solvent residues, and scrapings from straightening tools, should be removed before any heating operation associated with forming, heat treating, or welding. Surface oxides must be removed after hot forming. Surface oxides or scale should be removed before forming, as such coatings increase notch sensitivity during forming. Care must be taken to avoid nicks or scratches in blanks and parts. Such defects can lead to premature failure on forming the part or while in service. Foreign materials must be removed prior to any forming, heat-treating, or pickling operation.

Conventional cleaning, etching, and descaling procedures can be used. Specific details are covered in company specifications. Acid concentrations, temperatures, and etching rates should be carefully controlled to minimize local attack and dimensional changes. Heavy scale formed at elevated temperatures can be removed either by mechanical or chemical means. Mechanical descaling methods include tumbling, vapor blasting, and fine-grit blasting. Coarse-grit blasting and wire brushing should not be used due to the possibility of introducing stress risers. Small traces of scale remaining can be removed by hand, using fine emery grit (180 or finer). Thin oxide films can be removed by pickling in acid baths approved for use with titanium. Surfaces should first be cleaned to assure a uniform metal removal in etching bath.

#### 11.6. Machining and Grinding

Much of what is presented in the following on machining was obtained from information provided by RMI Titanium Company.<sup>44,49</sup> Machining may be done by all customary methods, but specific procedures must take into account the physical characteristics common to titanium. Machinability of the commercial grades of titanium are comparable to that of the austenitic stainless steels, with the alloyed-titanium materials being somewhat more difficult. The low thermal conductivity of titanium can result in a rapid buildup of heat, unless proper application of coolants is used. The use of sharp and proper tools is vital. Dull tools will accentuate heat buildup causing galling and seizing, leading to premature tool failure. Relatively slow speeds and heavy feeds must be used.

The modulus of elasticity of titanium is about half that of steel. Slender parts will tend to deflect under tool pressure, causing

chatter, tool rubbing, and tolerance problems. Consequently, rigidity of the entire machine-tool system is of considerable importance.

The turning operation is done with little difficulty. Carbide tools are preferred, with the "straight" tungsten carbide grades of standard designations C1 through C4 giving the best results. If high-speed steels are used, the cobalt type appear to be the best. Cast alloy tools, such as Stellite, Tantung, and Rexalloy, are preferred over the cheaper grades of high speed steels.

Milling of titanium is a more difficult operation than that of turning. Climb milling is recommended over conventional milling in order to minimize the tendency for the chip to adhere or weld to a tooth. Since a cutter tooth mills only part of each revolution, the chips tend to adhere to the tooth during that part of the revolution that the tooth does not cut. On the next contact, when the chip is knocked off, the tooth can be damaged if it is welded to the chip. In climb milling, the cutter is in contact with the thinnest portion of the chip, minimizing the adherence problem. For slab milling, the work should move in the same direction as the cutting tool; for face milling, the teeth should emerge from the cut in the same direction that the work is fed. A water-base coolant is recommended.

Successful drilling can be accomplished with ordinary high-speed steel drills. It is important that the unsupported section of the drill be no longer than is necessary for the chips to flow unhampered through the flutes and out of the hole. Use of "Spiro-Point" drill grinding is recommended.

In grinding, both alundum and silicon carbide wheels are used. Wheel speeds should be lower than those used in conventional grinding of steels. Water-soluble oils or cutting fluids with a high flash point must be used for all machining and grinding operations. Because of the high heat that is generated, a low flash-point fluid could be ignited. Parts must be thoroughly cleaned with a non-chlorinated degreasing solvent prior to exposure to any subsequent operation at elevated temperatures. Methyl-ethyl-ketone (MEK) is the preferred solvent for cleaning. Cutting fluids containing halogens (Cl, F, Br, and I) should not be used, to avoid corrosion problems that may arise from the use of such fluids with titanium and its alloys.

## 11.7 Welding

Molten titanium is extremely reactive with nitrogen, oxygen, and hydrogen, and can dissolve large quantities of these gases at temperatures above 540°C. These three elements tend to embrittle the metal. Consequently, any welding method must include provisions for shielding the molten weld metal and the adjacent heat-affected zone from these gases to temperatures as low as 300 to 400°C. The metal must also be protected against carbon contamination. The inert-gas tungsten-arc and inert-gas metal-arc processes, as well as laser, electron-beam, plasma-arc, resistance, spot, seam, and flash welding are methods used successfully for joining titanium and its alloys. Using the proper procedures, Ti-Grades 7, 12, and 16 are readily weldable with any of these methods. Ductile welds cannot be obtained using oxyacetylene welding or other forms of welding that use active gases, electrode coatings or fluxes.

The gas tungsten-arc welding (GTAW) method is the one most commonly used for joining titanium and titanium alloys in thicknesses less than about 3.2 mm.<sup>50</sup> Gas metal-arc welding (GMAW) is usually used for thicknesses over 3.2 mm. With GTAW, square-grooved butt joints can be welded without filler metal for thicknesses up to 2.5 mm. For thicker parts, the joints should be grooved and filler metal is required. Hot-wire GTAW can be used for thicknesses greater than 6.4 mm. Where possible, welding should be done in the flat position. GMAW is less costly than GTAW, especially for thicknesses over 12.7 mm due to the higher weld-metal deposition rates of the former process.

Plasma-arc welding (PAW) is faster than GTAW and can be used on thick sections, for example, as one-pass welding on plates up to 12.7 mm thick, using square-groove butt joints and the keyhole technique. In addition, the use of filler metal with PAW is optional for thicknesses less than 12.7 mm. PAW is closely related to GTAW. Heat is produced by a constricted arc, either between a consumable electrode and a workpiece or between a nonconsumable tungsten electrode and a constricting orifice. The ionized gas issuing from the orifice provides some shielding, which may be supplemented from an auxiliary source. The joining of titanium has been one of the major applications of plasma-arc welding.<sup>50</sup>

In general, welding techniques with titanium and its alloys are similar to those used for the austenitic stainless steels, except with the added feature of a trailing shield to protect the weldment as it solidifies. The trailing shield should cover the solidified weld and adjacent hot metal until they cool to below about 315 to 425°C. The underside of the weld must also be protected. This is typically done by using a grooved backup bar filled with inert gas. Backup shielding devices, contoured to fit internal surfaces, may also be used for the larger structures. The torch is designed to allow the protective gas to flow through it and cover the molten metal.

Either argon or helium, or a mixture of the two is used as the shielding gas. Argon, being less costly, is more widely used. Because of the high purity (99.985% min) and low moisture content, liquid argon is preferred. The dew point of the argon must be below -24°C. Excessive flow rates, which may cause turbulence and entrapment of contaminants, must be avoided. To minimize moisture pickup, non-porous flexible gas hoses like Tygon or vinyl plastic should be used. A rubber hose absorbs air, and it must not be used.<sup>50</sup>

The type of shielding used will affect the arc characteristics.<sup>50</sup> For example, at a given welding current, the arc voltage is much greater with helium than with argon. The heat liberated with helium is about twice that obtained with argon; consequently, with helium shielding, higher welding speeds and deeper penetrations can be obtained. Argon provides greater arc stability than that available with helium; thus, arc stability and weld-metal control are sacrificed on using only helium. A mixture of 75% Ar-25% He is frequently used as a compromise between stability and penetration for the shielding gas at the torch in automatic operations.

Both inert-gas-arc methods are adaptable to either manual or automatic welding of titanium. For manual gas-tungsten-arc welding, a water-cooled GTA torch equipped with a gas lens and a 19 mm ceramic gas cup should be used.<sup>51</sup>

Spot- and seam-welding procedures for titanium are similar to those used on other metals. Inert-gas shielding is not required here. Satisfactory welds are possible, with a number of combinations of current, time, and electrode force and are determined by trial. It is suggested to start with welding parameters used for austenitic

stainless steels, as the electrical and thermal conductivity of titanium are somewhat similar to these materials.<sup>44,52</sup>

In resistance and pressure welding, air is eliminated by intimate contact between pieces to be joined. In flash welding, since the molten metal at the faying surfaces is expelled at the time the weld is consummated, gas shielding is generally not needed. Shielding may be required with complex or hollow shapes and forged cross sections. When possible, use clamped joints rather than tack welds as the latter require the same shielding as other welds.

The welder should be able to visually inspect both face and root sides of the weld to see that shielding was effective. The solidified metal should have a bright silvery appearance. Joints can be prepared by sawing, machining, or grinding. They must be smooth and free of crevices and overlaps that could trap dirt and cleaning solvents. Avoid excessive heat, such as may occur in grinding. Any burns (oxides) due to overheating must be removed. Do not use finishing methods that can contaminate the weld with loosened particles, for example, by using sandpaper or steel wool. Rotary mechanical deburrers (rotary files) are recommended.

Before welding, mill scale as well as any light-colored oxide should be removed by rotary filing or acid pickling in a 35% HNO<sub>3</sub>-5% HF solution, and followed by a water rinse and then air dried. Grease and oils should be removed with a non-chlorinated degreasing solvent. The joint and workpiece must be meticulously cleaned on both sides of the joint at least 51mm beyond the width of the gas trailing shield. Interpass cleaning is not necessary if the weld deposit is bright and silvery. Light-colored oxide films (light yellow to light blue) should be cleaned off with a stainless-steel wire brush. Contaminated beads (dark blue, purple, gray, and loose white deposits) should be completely removed by grinding and then cleaned before welding continues. As a general rule, if the surface oxide is heavy, the weld is contaminated.

Excellent welds can be obtained in a welding chamber under a protective atmosphere. This may be impractical, as well as costly and time-consuming, for closure of the large containers designed for the repository, especially with the multiple barrier design. Unless the chamber is made sufficiently large to accommodate all the components, it would require frequent purging of the chamber and replenishing of the protective atmosphere.

Titanium welding normally does not require any preheat or postheat. Where the temperature is low or the humidity is high, preheating (35 to 65°C) to eliminate moisture is recommended. Weldments, after thorough cleaning, may be stress relieved at 540°C, for one hour per 25.4 mm of thickness. Post-weld heat treatments, however, are generally not required. The alpha and near-alpha alloys usually are welded in the annealed condition. In environments where the corrosion-resistant alloys, such as Ti-Grade 12 have been tested, the welds have shown corrosion resistance equivalent to the base metal.

#### 11.8. Weld-Filler Metals and Electrodes

Matching filler metal is recommended for Ti-Grades 7 and 12 to maintain the corrosion resistance of the base metals. The recommended AWS grades are ERTi-0.20 Pd and ERTi-0.8 Ni-0.3 Mo, respectively. Correspondingly, the filler metal for Ti-Grade 16 is likely to be designated ERTi-0.05. Normally, the welding wire is acid cleaned before spooling and packaging. Nevertheless, wires should be checked for cleanliness with a white cloth or glove; if dirty, the wire must be cleaned with a non-chlorinated solvent. The die lubricant used for wire drawing is the most likely contaminant, and it is readily removed using an acetone-soaked, lint-free cloth. Pickling in a nitric-hydrofluoric acid solution can also be used for cleaning. If, during welding, the wire is inadvertently taken out of the protective shield, the end should be clipped back about 12.7 mm to remove contaminated metal.

The recommended electrode is AWS 5.12-65T,<sup>51</sup> which is a two-percent thoriated-tungsten electrode. The particular shape used will depend on welder preference.

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TABLE 1. COMPOSITION OF J-13 WELL WATER

Species	Concentration (mg/l)
Na	45.8
Si	28.5
Ca	13.0
K	5.04
Mg	2.01
B	0.134
Li	0.048
$\text{HCO}_3^-$	128.9
$\text{SO}_4^{2-}$	18.4
$\text{NO}_3^-$	8.78
$\text{Cl}^-$	7.14
$\text{F}^-$	2.18
pH=7.41	

TABLE 2. CANDIDATE MATERIALS FOR MULTI-BARRIER CONTAINERS

CORROSION-RESISTANT MATERIALS			
UNS No.	Common or Commercial Name	ASTM Number	Nominal Composition-Wt.%
<b>Nickel-rich Superaustenitic-Stainless Alloys</b>			
N08825	Alloy 825; Incoloy 825	B 424 (plate)	Ni 38.0-46.0; Cr 19.5-23.5; Mo 2.5-3.5; Fe balance; Cu 1.5-3.0; Ti 0.6-1.2; Mn 1.0 max; C 0.05 max; Si 0.5 max; S 0.03 max; Al 0.2 max
N06985	Alloy G-3; INCO Alloy G-3	B 582 (plate)	Ni balance; Cr 21-23.5; Mo 6.0-8.0; Fe 18.0-21.0; W 1.5 max; Co 5.0 max; Cu 1.5-3.0; Nb+Ta 0.5 max; Mn 1.0 max; C 0.015 max; Si 1.0 max; S 0.03 max; P 0.04 max
<b>Nickel-base (Ni-Cr-Mo) Alloys</b>			
NO6022	Alloy C-22; Hastelloy C-22	B 575 (plate)	Ni balance; Cr 20.0-22.0; Mo 12.5-14.5; Fe 2.0-6.0; W 2.5-3.5; Co 2.5 max; Mn 0.5 max; C 0.010 max; Si 0.08 max; V 0.35 max; S 0.02 max; P 0.02 max
N06455	Alloy C-4; Hastelloy C-4	B 575 (plate)	Ni balance; Cr 14.0-18.0; Mo 14.0-17.0; Fe 3.0 max; Co 2.0 max; Mn 1.0 max; C 0.010 max; Si 0.08 max; Ti 0.7 max; S 0.010 max; P 0.025 max
<b>Titanium-base Alloys</b>			
R53400	Ti-Grade 12	B 265 Grade 12	Ti balance; Ni 0.6-0.9; Mo 0.2-0.4; N 0.03 max; H 0.015 max; Fe 0.30 max; O 0.25 max; other, each 0.05 max; other, total 0.30 max
None to date	Ti-Grade 16	B 265 Grade 16	Ti balance; 0.05 Pd; N 0.03 max; H 0.015; Fe 0.30 max; O 0.25 max; C 0.10 max
<b>MODERATELY CORROSION-RESISTANT (INTERMEDIATE) MATERIALS</b>			
<b>Copper and Nickel Alloys</b>			
N04400	Alloy 400; Monel 400	B 127 (plate)	Ni 63.0 min; Cu 28.0-34.0; Fe 2.5 max; Mn 2.0 max; C 0.03 max; Si 0.5 max; S 0.024 max
C71500	70-30 Cupronickel; CDA 715	B 171 (plate)	Cu balance; Ni 29.0-33.0; Mn 1.0 max; Pb 0.02 max; Fe 0.4-1.0; Zn 0.5 max; C 0.05 max P 0.02 max; S 0.02 max
<b>CORROSION-ALLOWANCE MATERIALS</b>			
<b>Low-Carbon and Low-Carbon-Low-Alloy Steels</b>			
G10200	1020 Carbon Steel	A 516 (Grade 55)	Fe balance; C 0.22 max; Mn 0.60-1.20; Si 0.15-0.40; S 0.04 max; P 0.35 max
J02501	Centrifugally Cast Steel	A 27 (Grade 70-40)	Fe balance; C 0.25 max; Mn 1.20 max; Si 0.80 max; S 0.60 max; P 0.050 max
K21590	2 <sup>1</sup> / <sub>4</sub> Cr-1Mo Alloy Steel	A 387 (Grade 22)	Fe balance; Cr 2.00-2.50; Mo 0.90-1.10; C 0.15 max; Mn 0.30-0.60 Si 0.50 max; S 0.035 max

TABLE 3. AVERAGE MECHANICAL PROPERTIES OF CANDIDATE CORROSION-RESISTANT ALLOYS<sup>+</sup>

Alloy	Young's Modulus- $10^6$ psi (GPa)				0.2% Offset Yield Strength-ksi (MPa)				Tensile Stress-ksi (MPa)				Elongation-% Temperature-°C			
	25	100	200	300	25	100	200	300	25	100	200	300	25	100	200	300
825	29.8 (206)	29.2 (201)	28.3 (19.5)	27.3 (18.8)	47* (324)	40* (276)	36* (248)	34* (234)	100* (689)	95* (655)	92* (634)	91* (627)	45* (627)	44* (627)	45* (627)	41* (627)
G-3**	28.9 (119)	28.3 (195)	27.6 (190)	26.7 (184)	45 (310)	40 (276)	33 (228)	30 (207)	100 (689)	93 (641)	87 (600)	83 (572)	58	60	62	64
C-4#	30.8 (212)	30.1 (208)	29.3 (202)	28.4 (196)	49 (338)	43 (297)	38 (262)	36 (248)	117 (807)	110 (758)	105 (724)	103 (710)	63	70	61	65
C-22	29.9 (206)	293 (202)	28.4 (196)	27.4 (188)	54≠ (372)	48≠ (331)	42≠ (290)	36≠ (248)	114≠ (786)	106≠ (731)	99≠ (683)	95≠ (655)	62≠ (655)	65≠ (655)	66≠ (655)	68≠ (655)
Ti Gr 12 <sup>z</sup>	15.2 (105)	14.7 (101)	14.1 (97)	12.9 (89)	65 (448)	51 (352)	42 (290)	35 (241)	72 (496)			47 (324)	25			32
Ti Gr 16					40 <sup>x</sup> (275)				50 <sup>x</sup> (345)				20 <sup>x</sup>			
Ti Gr 7 <sup>z</sup>	15.2 (105)	14.7 (101)	14.1 (97)	12.9 (89)	51 (352)	35 (241)	23 (159)	17 (117)	57 (393)			27 (186)	28			37

<sup>+</sup> Values obtained or interpolated from data provided in bulletins and Alloy Digests published by producers/distributors

\* solution-annealed bar

\*\* solution-annealed plate

# solution-annealed 1/2-inch plate

≠ solution annealed 1/4- to 3/4-inch plate

<sup>x</sup> ASTM B minimum tensile requirements

<sup>z</sup> Modulii are average values; actual values depend on texture/orientation; ranges at 25°C are  $15.0 \times 10^6$ - $15.5 \times 10^6$  psi (103-107 GPa)

TABLE 4. HAYNES INTERNATIONAL HASTELLOY FAMILY OF CORROSION-RESISTANT ALLOYS

Alloy	Composition	Main Characteristics
Hastelloy B-2 (N10665)	69Ni(bal)-1Cr(max)-28Mo-2Fe(max)-1Co(max)-1Mn(max)-0.1Si(max)-0.01C(max).	Superior resistance to hydrochloric acid, aluminum chloride catalysts, and other strongly reducing chemicals. Excellent high-temperature strength in inert atmospheres or vacuum.
Hastelloy C-4 (N06455)	65Ni(bal)-16Cr-16Mo-3Fe(max)-2Co(max)-1Mn(max)-0.08Si(max)-0.01C(max)-0.7Ti(max).	High-temperature stability in the 650 to 1040°C range as evidenced by good ductility and corrosion resistance. Virtually the same excellent corrosion resistance as Alloy C-276.
Alloy C-22 (N06022)	56Ni(bal)-22Cr-13Mo-3Fe-2.5Co(max)-0.5Mn(max)-0.08Si(max)-0.01C(max)-3W-0.3V(max).	Better overall corrosion resistance and versatility than Alloys C-4, C-276, and 625. Outstanding resistance to localized corrosion, stress-corrosion cracking, and both oxidizing and reducing chemicals. Best alloy to use as a universal weld-filler metal to resist corrosion of weldments.
Hastelloy C-276 (N10276)	57Ni(bal)-16Cr-16Mo-5Fe-2.5Co(max)-1Mn(max)-0.08Si(max)-0.01C(max)-4W-0.3V(max).	Versatile corrosion-resistant alloy. Excellent resistance to both oxidizing and reducing corrosives, mixed acids, and chlorine-contaminated hydrocarbons.
Alloy G-30 (N06030)	43Ni(bal)-30Cr-5.5Mo-15Fe-5Co(max)-1.5Mn(max)-1.0Si(max)-0.03C(max)-2.5W-1.5Nb(max)-2Cu(max).	Many advantages over other metallic and non-metallic materials in handling phosphoric acid, sulfuric acid, nitric acid, fluoride environments, and oxidizing-acid mixtures.
Alloy G-50 (N06950)	50Ni( min bal)-20Cr-9Mo-17Fe-2.5Co(max)-1Mn(max)-1Si(max)-0.02C(max)-1W(max)-0.5Nb(max)-0.5Cu(max)-0.4Al(max)	Excellent resistance to stress-corrosion cracking in aggressive sour-gas environments. Mostly used as production tubing with yield strength in the range of 110 to 150 ksi.
Alloy H-9M (N06920)	45Ni(bal)-22Cr-9Mo-19Fe-5Co(max)-1Mn(max)-1Si(max)-0.03C(max)-2W	Equivalent or better localized corrosion resistance compared to Alloy 625, but, it is in a price range close to those of the superaustenitic stainless steels. The alloy also has good resistance to hot acids and excellent resistance to stress-corrosion cracking.
Hastelloy N (N10003)	71Ni(bal)-7Cr-16Mo-5Fe(max)-0.2Co(max)-0.8Mn(max)-1Si(max)-0.08C(max)-0.5W(max)-0.35Cu(max)-0.5Al+Ti(max)	Good resistance to aging and embrittlement. It has good fabricability, and excellent resistance to hot fluoride salts in the temperature range of 704 to 870°C.
Alloy 59 (N06059)	59Ni-23Cr-16Mo-1Fe	Excellent thermal stability (tungsten-free). Improved corrosion resistance in strong oxidizing media. Highest pitting index of the nickel-chromium-molybdenum family of alloys.

TABLE 5. CORROSION RATES OF FOUR Ni-Cr-Mo ALLOYS

Corrosive Medium	Corrosion Rate-mils (mm) per year			
	Alloy C-22	Alloy C-276	Alloy C-4	Alloy 625
10% FeCl <sub>2</sub> Boiling	1 (0.025)	2 (0.050)	140 (3.500)	>150 (>3.75)
1.5% HCl Boiling	11 (0.275)	29 (0.725)	65 (1.625)	>150 (>3.75)
2.5% HCl 90°C	<1 (0.025)	12 (0.300)	34 (0.850)	72 (1.800)
2% HF 70°C	9 (0.225)	9 (0.225)	17 (0.425)	20 (0.500)
5% HNO <sub>3</sub> + 25% H <sub>2</sub> SO <sub>4</sub> +4% NaCl Boiling	12 (0.300)	64 (1.600)	97 (2.425)	>150 (>3.75)
5% HNO <sub>3</sub> + 1% HCl Boiling	1 (0.025)	7 (0.175)	11 (0.275)	1.2 (0.030)
10% H <sub>2</sub> SO <sub>4</sub> Boiling	11 (0.275)	23 (0.575)	31 (0.775)	46 (1.150)
50% H <sub>2</sub> SO <sub>4</sub> 66°C	1 (0.025)	4 (1.000)	13 (0.325)	26 (0.650)
5% H <sub>2</sub> SO <sub>4</sub> + 0.1% HCl Boiling	27 (0.675)	42 (1.050)	49 (1.225)	>150 (>3.75)
25% H <sub>2</sub> SO <sub>4</sub> + 200 ppm Cl <sup>-</sup> 70°C	11 (0.275)	12 (0.300)	37 (0.925)	>150 (>3.75)
25% H <sub>2</sub> SO <sub>4</sub> + 1.2% HCl + 1% FeCl <sub>3</sub> + 1% CuCl <sub>2</sub> Boiling	7 (0.175)	55 (1.375)	>150 (>3.75)	>150 (>3.75)

TABLE 6. COMPARISON OF CORROSION DATA FOR DIFFERENT CONDITIONS OF ALLOY C-4

Medium	Conc., wt. %	Temp., °C	Average Corrosion Rate mils (mm) per year		
			Unwelded*	As-Welded <sup>+</sup>	Aged#
Formic acid	20	Boiling	2.9 (0.07)	3.5 (0.09)	3.5 (0.09)
Hydrochloric Acid	10	75	36 (0.91)	34 (0.86)	35 (0.89)
Nitric Acid	10	Boiling	5.9 (0.15)	7.1 (0.18)	9.2 (0.23)
Phosphoric Acid	85	Boiling	61 (1.5)	52 (1.3)	85 (2.2)
Sulfuric Acid	10	boiling	22 (0.56)	25 (0.64)	20 (0.51)
Sulfuric Acid	85	75	23 (0.58)	17 (0.43)	21 (0.53)
Hydrochloric Acid (2T Rad. Bend Test)	10	Boiling	250 (6.25)	285 (7.2)	276 (7.0)
ASTM G28 (50% H <sub>2</sub> SO <sub>4</sub> + 42 g FeSO <sub>4</sub> )		Boiling	100 (2.50)	111 (2.8)	114 (2.9)

\*Solution annealed at 1066°C and water quenched.  
+Gas tungsten arc welded.  
#Aged 100 hours at 899°C

**TABLE 7. GRINDING WHEELS FOR GRINDING Ni-Cr-Mo ALLOYS**

Type of Grinding	Wheels*	Manufacturer	Type of Work	Coolant
<b>Cylinder Grinding</b>				
Straight or Tapered O.D.'s	53A80-J8V127	Norton	Sharp corners and fine finish	Heavy duty soluble coolant 25:1 mix CASTROL 653
Form Work, Single Wheel Section Method	38A60-J8-VBE	Norton	Removing stock Sharp corner work Straight radius work	Dry
Form Work, Crush-Roll Method	53A220-L9VB	Norton	Precision forms Radius	Straight oil
Centerless	53A80-J8VCN	Norton	Thin-walled material Solid or heavy-walled material	Heavy duty soluble coolant 25:1 mix CASTROL 653
<b>Internal Grinding</b>				
Straight or Tapered	23A54-L8VBE	Norton	Small holes Medium-size holes Large holes Small counterbores	Heavy duty soluble coolant 25:1 mix CASTROL 709
<b>Surface Grinding</b>				
Straight Wheel	32A46-H8VBE 38A46-I-V	Norton Norton		Dry or any heavy duty soluble coolant 25:1 mix CASTROL 653
Double Opposed Disk Type	87A46-G12-BV 87A46-J11-BW	Gardner Gardner	Through-feed work Ferris wheel work Thin work	Heavy duty soluble coolant 10:1 mix CASTROL 653
Cylinder or Segmental Type	32A46-F12VBE	Norton	Thin work, bevels and close tolerance work	Sal-soda in water CASTROL 653
Single Wheel Section Method	32A46-F12VBEP	Norton	Profile work	Dry
<b>Thread Grinding</b>				
External Threads	A100-T9BH	Norton		VANTROL 5299-M or equivalent
<b>Honing</b>				
Internal	C120-E12-V32 C220-K4VE J45-J57	Bay State Carborundum Sunnen		VANTROL 5299-C or equivalent
<b>Rough Grinding</b>				
Cut-off (Wet) Cut-off (Dry)	86A461-LB25W 4NZA24-TB65N	Norton Norton		CASTROL 653 Dry
Snagging	4ZF1634-Q5B38	Norton		Dry

\*The wheels indicated have been optimized for speeds between 6000 and 6500 sfpm.

TABLE 8. CARBIDE TOOLS FOR MACHINING Ni-Cr-Mo ALLOYS

Operations	Carbide Tools
Roughing, with severe interruptions; Turning or Facing	C-2 or C-3 grade: Negative rake square insert, 45° SCEA <sup>1</sup> , 1/32 in. nose radius. Tool holder: 5° neg. back rake, 5° neg. side rake. Speed: 30-50 sfm, 0.004-0.008 in. feed, 0.150 in. depth of cut. Dry <sup>2</sup> , oil <sup>3</sup> , or water-base coolant <sup>4</sup> .
Normal roughing; Turning or Facing	C-2 or C-3 grade: Negative rake square insert, 45° SCEA, 1/32 in. nose radius. Tool holder: 5° neg. back rake, 5° neg. side rake. Speed: 90 sfm depending on rigidity of set up, 0.010 in. feed, 0.150 in. depth of cut. Dry, oil, or water-base coolant.
Finishing; Turning or Facing	C-2 or C-3 grade: Positive rake square insert, if possible, 45° SCEA, 1/32 in. nose radius. Tool holder: 5° pos. back rake, 5° pos. side rake. Speed: 95-110 sfm, 0.005-0.007 in. feed, 0.040 in. depth of cut. Dry or water-base coolant.
Rough Boring	C-2 or C-3 grade: If insert type boring bar, use standard positive rake tools with largest possible SCEA and 1/16 in. nose radius. If brazed tool bar, grind 0° back rake, 10° pos. side rake, 1/32 in. nose radius and largest possible SCEA. Speed: 70 sfm depending on the rigidity of setup, 0.005-0.008 in. feed, 1/8 in. depth of cut. Dry, oil, or water-base coolant.
Finish Boring	C-2 or C-3 grade: Use standard positive rake tools on insert type bars. Grind brazed tools as for finish turning and facing except back rake may be best at 0°. Speed: 95-110 sfm, 0.002-0.004 in. feed. Water-base coolant.

NOTES: 1 SCEA — Side cutting edge angle or lead angle of the tool.

2 At any point where dry cutting is recommended, an air jet directed on the tool may provide substantial tool life increases. A water-base coolant mist may also be effective.

3 Oil coolant should be a premium quality, sulfochlorinated oil with extreme pressure additives. A viscosity at 100°F from 50 to 125 SSU.

4 Water-base coolant should be premium quality, sulfochlorinated water soluble oil or chemical emulsion with extreme pressure additives. Dilute with water to make 15:1 mix. Water-base coolant may cause chipping and rapid failure of carbide tools in interrupted cuts.

TABLE 9. HIGH-SPEED TOOLS FOR MACHINING Ni-Cr-Mo ALLOYS

Operations	High Speed Steel Tools	Carbide Tools
Facing Milling	M-2, M-7, or M-40 series <sup>5</sup> : Radial and axial rake 0°- pos. 10°, 45° corner angle, 10° relief angle. Speed: 20-30 sfm. Feed: 0.003-0.005 in. Oil <sup>6</sup> or water-base coolant. <sup>7</sup>	Carbide not generally successful, C-grade may work. Use positive axial and radial rake, 45° corner angle, 10° relief angle. Speed: 50-60 sfm. Feed: 0.005-0.008 in. Oil or water-base coolants will reduce thermal shock damage of carbide cutter teeth.
End Milling	M-40 series or T-15: If possible, use short mills with 4 or more flutes for rigidity. Speed: 20-25 sfm. Feed: 0.002 in. tooth 1/4 in. dia. 0.002 in. tooth 1/2 in. dia. 0.003 in. tooth 3/4 in. dia. 0.004 in. tooth 1 in. dia. Oil or water-base coolant.	Not recommended, but C-2 grades may be successful on good setups. Use positive rake. Speed: 50-60 sfm. Feed: Same as high speed steel. Oil or water-base coolants will reduce thermal shock damage.
Drilling	M-33, M-40 series or T-15: Use short drills, heavy web, 135° crank-shaft, grind points wherever possible. Speed: 10-15 sfm. Feed: 0.001 in. rev. 1/8 in. dia. 0.002 in. rev. 1/4 in. dia. 0.003 in. rev. 1/2 in. dia. 0.005 in. rev. 3/4 in. dia. 0.007 in. rev. 1 in. dia. Oil or water-base coolant. Use coolant feed drills if possible.	C-2 grade not recommended, but tipped drills may be successful on rigid setup if no great depth. The web must be thinned to reduce thrust. Use 135° included angle on point. Gun drill can be used. Speed: 50 sfm. Oil or water-base coolant. Coolant-feed carbide tipped drills may be economical in some setups.
Reaming	M-33, M-40 series or T-15: Use 45° corner angle, narrow primary land and 10° relief angle. Speed: 10-20 sfm. Feed: 0.003 in. tooth 1/2 in. dia. 0.008 in. tooth 2 in. dia. Oil or water-base coolant.	C-2 or C-3 grade: Tipped reamers recommended, solid carbide reamers require very good setup. Tool geometry same as high speed steel. Speed: 50 sfm. Feed: Same as high speed steel.
Tapping	M-1, M-7, M-10: 2 flute, spiral point, plug tap 0°-10° hook angle nitrided surface may be helpful by increasing wear resistance but may cause chipping or breakage. Tap drill for 60-65% thread, if possible, to increase tool life. Speed: 7 sfm (cutting). Use best possible tapping compound, sulfochlorinated oil base preferred.	Not recommended
Electrical Discharge Machining	HASTELLOY alloys can be easily cut using any conventional electrical discharge machining system (EDM) or wire EDM.	

NOTES: 5 M-40 series High Speed Steels include M-41, M-42, M-43, M-44, M-45 and M-46 at the time of writing. Others may be added and should be equally suitable.

6 Oil coolant should be a premium quality, sulfochlorinated oil with extreme pressure additives. A viscosity at 100°F from 50 to 125 SSU.

7 Water-base coolant should be premium quality, sulfochlorinated water soluble oil or chemical emulsion with extreme pressure additives. Dilute with water to make 15:1 mix.

TABLE 10. RANKING OF CLOSURE PROCESSES FOR HIGH-LEVEL WASTE CONTAINERS FOR THE TUFF FACILITY

Process	Advantages	Disadvantages
Friction Welding	Small HAZ, small fusion zone, minimum risk for second phases, low residual stress, low distortion, good inspectability, ease of in-cell maintenance, low frequency of maintenance, fast weld speed, few welding variables to monitor.	ID and OD scarf (requires OD machining) massive equipment, expensive equipment, repair difficult, (full reweld of second process repair), may impact container design, additional safety considerations.
Electron Beam Welding	Low heat input, relatively small fusion zone and HAZ, relatively low residual stresses and distortion, good inspectability, fast weld speeds, chance for repair welding without machining, no filler metal.	Could experience poor crown surface condition and defects in spike areas, expensive equipment, in-cell vacuum chamber required, in-cell maintenance expensive, safety considerations.
Plasma Arc Welding	Low to medium heat input, no filler metal with keyhole, relatively low-cost equipment, much previous closure experience, versatile equipment, repair welding with same process, arc length more forgiving than with gas tungsten arc welding.	Many weld variables to monitor, in-cell monitors (guidance and real-time controls) could be required, fairly complex torch, possibility for porosity in keyhole mode, medium inspectability, higher possibility for second phases if filler metal is used, machining for repair welding possibly required,
Laser Beam Welding	Same as electron beam welding.	Pushing current technology with required material thicknesses, expensive equipment, beam must penetrate cell wall at some point, maintenance could be expensive.
Gas Tungsten Arc Welding	Medium heat input, low-cost equipment, fewer variables than plasma arc welding, much previous in-cell experience, repair welding with same equipment, easier in-cell maintenance, less expensive than all of the above processes.	A greater volume of material affected by high residual stresses and greater distortions than all of the above processes, filler metals required, repairs require re-machining, larger fusion zone and larger HAZ, lower inspectability, higher possibility for second phases, in-cell guidance and real-time controls may be needed.

TABLE 11. RELATIVE MERITS OF THREE WELDING METHODS FOR WELDING OF NICKEL-BASED CORROSION-RESISTANT ALLOYS

Process	Advantages	Disadvantages
Gas Tungsten Arc Welding (GTAW)	Very versatile, all-position process; adapts to both manual and automatic operations; offers great control; no slag to remove; no weld splatter; no alloy loss during welding; minimal postweld surface cleanup/finishing; most readily used for making small repair welds; weld can be made by fusion of the base metal without any filler metal.	Major drawback is low productivity; manual weld-deposition rates are low.
Gas Metal Arc Welding (GMAW)	Provides considerable increase in productivity over GTAW; suited for both manual and automatic situations; easily automated; faster welding speeds than GTAW and SMAW; provides possibility for three modes of metal transfer (short-circuiting, globular, and spray transfer); constant current, fixed frequency pulse, variable slope/inductance, and synergic welding power supplies can all be used; no slag formed; better transfer of elements across arc as compared to GTAW and SMAW.	Control and ease of operation are somewhat reduced relative to GTAW; since electrode holder must be close to the workpiece it is less adaptable than SMAW for welding in difficult-to-reach situations.
Shielded Metal Arc Welding (SMAW)	Versatile, can be used in all welding positions; can be operated easily in remote locations; equipment is less complex, more portable, and less costly than for other arc-welding processes.	Limited to manual operations; electrode requires a short time to begin generating a protective atmosphere from the electrode flux coating, and this can result in start-up porosity; removal of slag required between passes; visibility during welding is impaired by slag; not suitable for very thin sheet; electrodes are sensitive to moisture pickup.

TABLE 12. CONTAMINATING ELEMENTS ON WELDING NICKEL-RICH ALLOYS

Elements	Effect/Defect	Common Sources of Elements
Sulfur, Carbon	Reduced corrosion resistance	Hydrocarbons, such as cutting fluids, grease, oil, waxes , and primers
Sulfur, Phosphorus	Cracking in weld and in HAZ	Marking crayons, paints, and temperature-indicating markers
Lead, Zinc, Copper, and other low melting point metals	Cracking in weld and in HAZ	Tools, such as lead hammers, copper hold-down or backing bars, zinc-rich paint, and galvanized steel
Shop dirt	Any of the above	Any of the above

TABLE 13. COMPARISON OF ROOM-TEMPERATURE  
TENSILE PROPERTIES OF AS-WELDED WELDMENTS  
AND BASE METAL OF ALLOYS C-4, C-22, AND G-3

Alloy	Thickness inches	Sample Source	Yield Strength ksi (Mpa)	Tensile Strength ksi (Mpa)	Elong. in 2 inches—%
C-4	0.5	Base metal	48.6 (335)	116.8 (805)	63
C-4	0.5	GTAW*	68.3 (471)	112.7 (777)	40
C-22	0.25-0.75	Base Metal	54 (372)	114 (786)	62
C-22	0.5	GTAW	65 (448)	114 (786)	47
C-22	0.5	GMAW <sup>+</sup> Short Arc	63 (434)	109 (752)	38
C-22	0.5	GMAW Spray	67 (462)	110 (758)	37
C-22	0.75	SMAW <sup>#</sup>	56 (386)	111 (765)	44
G-3	Plate	Base Metal	45.1 (311)	100.4 (692)	58
G-3	0.5-0.75	GTAW	47.3 (326)	95.9 (661)	49
G-3	0.5-0.75	SMAW	52.9 (365)	101.8 (702)	42
G-3	0.5-0.75	GMAW	51.1 (352)	98.3 (678)	39

\* GTAW—Gas Tungsten Arc Welding

<sup>+</sup> GMAW—Gas metal Arc Welding

<sup>#</sup> SMAW—Shielded Metal Arc Welding

TABLE 14. COMPARATIVE IMMERSION PITTING AND CREVICE-CORROSION TEMPERATURES IN OXIDIZING NaCl-HCl SOLUTION\*

Alloy	Pitting Temperature		Crevice-Corrosion Temperature	
	°C	°F	°C	°F
Alloy C-276	150	302	80	176
Alloy 625	101	214	25	77
Alloy G-3	75	167	25	77
Alloy G	75	167	25	77
Alloy 255 (FERRALIUM)	50	122	35	95
Alloy 904L	45	113	20	68
Type 317LM Stainless Steel	35	95	15	59
Type 317L Stainless Steel	25	77	10	50
Alloy 825	25	77	≤-5	≤-23
Alloy 20 Cb-3	20	68	≤-5	≤-23
Type 316 Stainless Steel	20	68	≤-5	≤-23

\* 4% NaCl + 0.1% Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 0.01 M HCl. Solution contains 24,300 ppm chlorides and is acidic with a pH 2.

TABLE 15. MINIMUM AS-WELDED MECHANICAL PROPERTIES OF WELDING PRODUCTS FOR INCOLOY ALLOY 825

	Tensile Strength		Elong.	Hardness
	ksi	Mpa	%	R <sub>B</sub>
Inconel Welding Electrode 112 (AWS A5.11 ENiCrMo-3; ASME F43; ASME SFA-5.11; UNS W86112)	110	758	30	
Inconel Welding Electrode 122 (AWS A 5.11ENiCrMo-10; UNS W86022)	115	793	40	100
Incoloy Welding Electrode 135 (DIN 1736 EL-NiCr28Mo; Werkstoff Nr. 2.4653; VdTUV 1042.00)	85	586	30	
Incoloy Filler Metal 65 (AWS A5. 14 ERNiFeCr-1; ASME F45; ASME SFA-5. 14 ERNiFeCr-1; UNS N08065)	80	552	25	
Inconel Filler Metal 622 (AWS A 5. 14 ERNiCrMo-10; UNS N06022)	115	793	40	100
Inconel Filler Metal 625 (AWS A5. 14 ERNiCrMo-3; ASME F43; ASME SFA-5. 14 ERNiCrMo-3; UNS N06625)	105	724	30	

TABLE 16. COMPOSITIONS OF WELDING PRODUCTS FOR ALLOY 825<sup>++</sup>

	Inconel Welding Electrode 112	Inconel Welding Electrode 122	Incoloy Welding Electrode 135	Incoloy Filler Metal 65	Inconel Filler Metal 622	Inconel Filler Metal 625
Ni	55.0 min**	Remainder	35.0-40.0*	38.0-46.0*	Remainder	58.0 min
Fe	7.0 max	2.0-6.0	Remainder	22.0 min	2.0-2.6	5.0 max
Cr	20.0-23.0	20.0-22.5	26.5-30.5	19.5-23.5	20.0-22.5	20.0-23.0
Mo	8.0-10.0	12.5-14.5	2.75-4.50	2.5-3.5	12.5 -14.5	8.0-10.0
C	0.10 max	0.02 max	0.08 max	0.05 max	0.015 max	0.10 max
Mn	1.0 max	1.0 max	1.25-2.50	1.0 max	0.50	0.50 max
P	0.03 max	0.03 max		0.03 max	0.02 max	0.02 max
S	0.02 max	0.02 max	0.03 max	0.03 max	0.02 max	0.015 max
Si	0.75 max	0.2 max	0.75 max	0.50 max	0.08 max	0.50 max
Co		2.5 max			2.50 max	1.0 max <sup>#</sup>
V		0.3 max			0.35 max	
Ti				0.60-1.20		0.40 max
Al				0.20 max		0.40 max
Cu	0.50 max	0.50 max	1.0-2.5	1.5-3.0	0.50 max	0.50 max
Nb	3.15-4.15 <sup>+</sup>					3.15-4.15 <sup>+</sup>
W		2.5-3.5			2.5-4.5	
Others	0.50 max	0.50 max	0.50 max	0.50 max	0.50 max	0.50 max

\* Includes cobalt. \*\* Includes cobalt, 0.12 max Co when specified. <sup>+</sup> Includes tantalum. <sup>#</sup> If determined.

<sup>++</sup> All compositions in wt. %.

TABLE 17. APPROXIMATE MILL-PRODUCT-COST RATIO\*

Alloy	ASTM Grade	Cost ratio
Unalloyed Ti	2	1.00
Ti-0.3Mo-0.8Ni	12	1.10
Ti-0.1Ru	—	1.12
Ti-6Al-4V-0.1Ru	—	1.34
Ti-0.05Pd	16	1.35
Ti-3Al-2.5V-0.1Ru	—	1.37
Ti-6Al-4V-0.05Pd	24	1.57
Ti-3Al-2.5V-0.05Pd	18	1.60
Ti-0.15Pd	7	1.90
Hastelloy C-276	—	1.90

\* Corrected for density and for 6.3 mm plate

TABLE 18. RELATIVE MERITS OF Ti-GRADES 7, 12, AND 16

Feature	Relative Merit
Corrosion resistance in reducing acids	Grade 16 ≈ Grade 7 > Grade 12
Pitting potential	Grade 16 ≈ Grade 7 > Grade 12
Resistance to crevice corrosion	Grade 16 > Grade 7 > Grade 12
Resistance to hydrogen absorption	Grade 16 > Grade 7 > Grade 12
Mechanical and physical properties	Grade 16 ≈ Grade 7 ≈ Grade 12
Formability	Grade 16 ≈ Grade 7 > Grade 12
Weldability	Grade 16 ≈ Grade 7 ≈ Grade 12
Relative cost	Grade 7 > Grade 16 > Grade 12

TABLE 19. PHYSICAL AND MECHANICAL PROPERTIES OF Ti-GRADE 12

Property	Typical Values	
Yield Strength (0.2% Offset) 50 ksi min. ] per ASTM 345 MPa min. ] Specs.	448 MPa @24°C	65 ksi @75°F
	414 MPa @93°C	60 ksi @200°F
	365 MPa @149°C	53 ksi @300°F
	303 MPa @204°C	44 ksi @400°F
Tensile Strength 70 ksi min. ] per ASTM 483 MPa min. ] Specs.	538-586 MPa @24°C	78-85 ksi @75°F
	448-517 MPa @93°C	65-75 ksi @200°F
	379-469 MPa @149°C	55-68 ksi @300°F
	324-393 MPa @204°C	47-57 ksi @400°F
Elongation 18% min. ] per ASTM Specs.	20-25% @75°F (24°C)	
	22-28% @200°F (93°C)	
	25-30% @300°F (149°C)	
	27-32% @400°F (204°C)	
Reduction in Area	>25% @≥75°F (≥24°C)	
Elastic Modulus	1.03 x 10 <sup>5</sup> MPa @24°C	15.0 x 10 <sup>6</sup> psi @75°F
	0.99 x 10 <sup>5</sup> MPa @93°C	14.4 x 10 <sup>6</sup> psi @200°F
	0.96 x 10 <sup>5</sup> MPa @204°C	13.9 x 10 <sup>6</sup> psi @400°F
Hardness	HRB ~95-98	
Charpy Impact Energy	16-34 Joules @24°C	12-25 ft-lbs @75°F
Thermal Conductivity	19 W/m·°C @20°C	14.3 BTU/ft·hr·°F @68°F
	18 W/m·°C @100°C	13.5 BTU/ft·hr·°F @212°F
	17 W/m·°C @150°C	12.8 BTU/ft·hr·°F @302°F
Electrical Resistivity	51 x 10 <sup>-6</sup> ohm·cm @20°C	20 x 10 <sup>-6</sup> ohm·in @68°F
	65 x 10 <sup>-6</sup> ohm·cm @100°C	26 x 10 <sup>-6</sup> ohm·in @212°F
	74 x 10 <sup>-6</sup> ohm·cm @150°C	29 x 10 <sup>-6</sup> ohm·in @302°F
Thermal Expansion Coefficient	9.8 x 10 <sup>-6</sup> (°C) <sup>-1</sup> over 0-370°C range	5.3 x 10 <sup>-6</sup> (°F) <sup>-1</sup> over 32-600°F range
Specific Heat (at 25°C)	544 J/kg·°C	0.13 BTU/lb·°F
Density (at 25°C)	4.54 gm/cm <sup>3</sup>	0.163 lb/in <sup>3</sup>

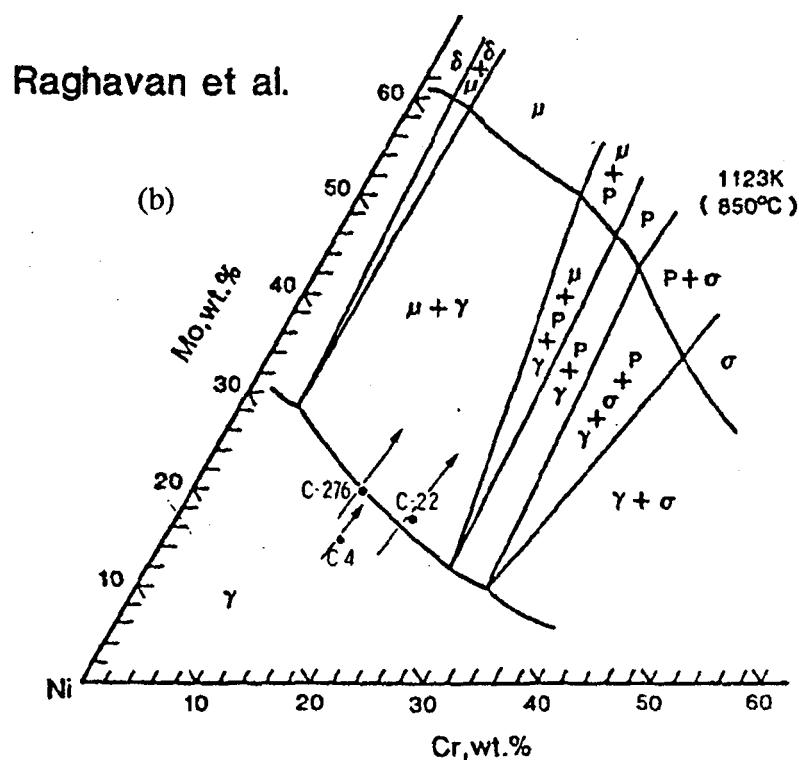
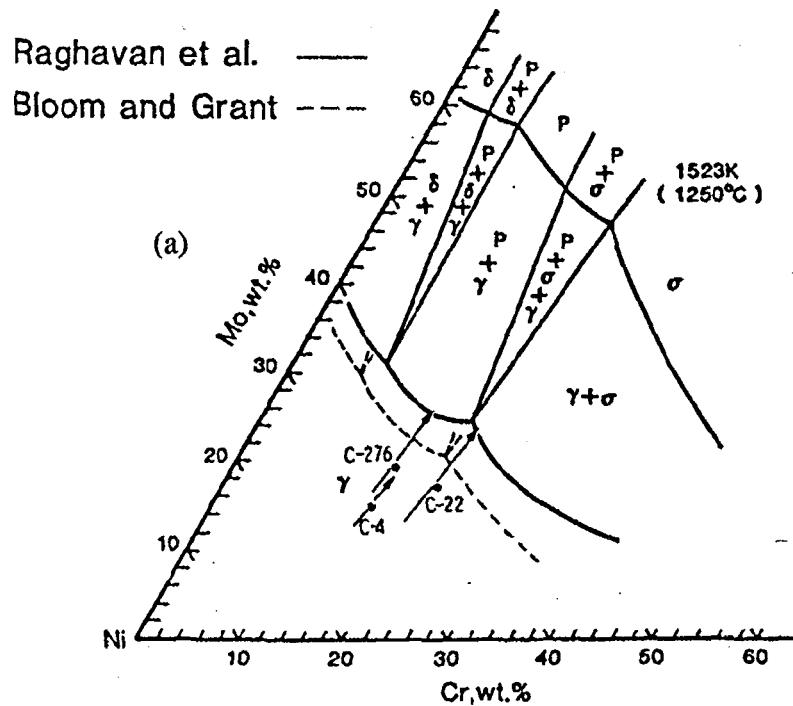


Figure 1—Isothermal sections of the Ni-Cr-Mo system showing nominal equivalent compositions and equivalent solidification profiles (arrows): (a) 1250°C, (b) 850°C.

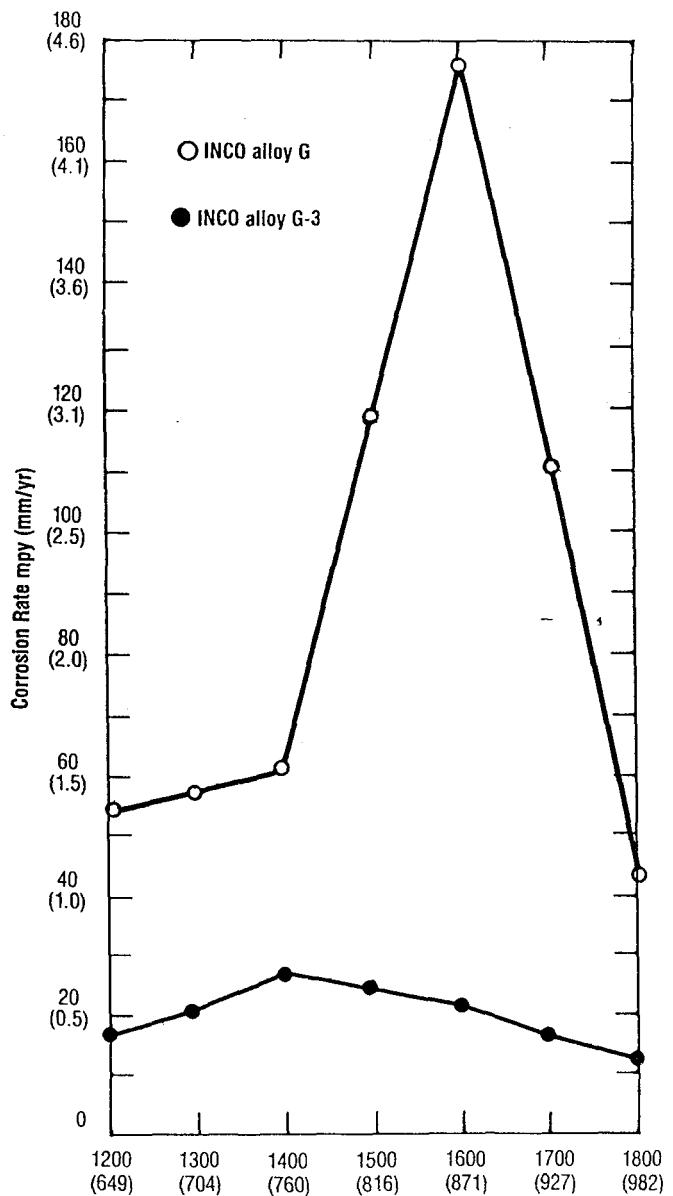


Figure 2—Effect of heat-treatment temperature on the corrosion rate of Alloys G and G-3. Test samples were heated for one hour to indicated temperatures and air cooled. Following heat treatment, samples were exposed to procedure ASTM G-28, Method A (24 hours in boiling 50%  $H_2SO_4$  plus 42 g/l of  $Fe_2(SO_4)_3$ ).

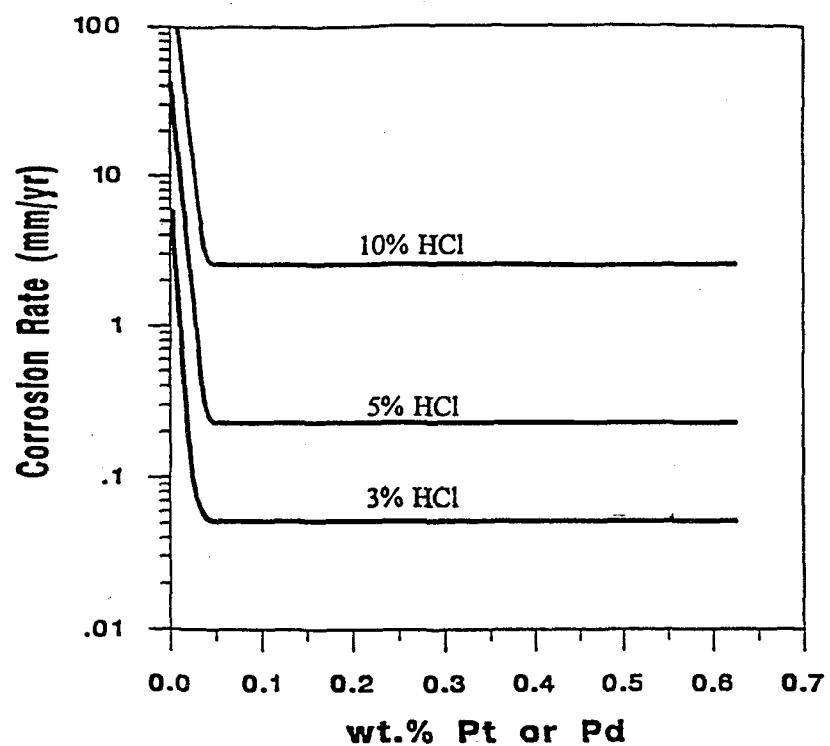


Figure 3. Effect of palladium or platinum content in titanium on the corrosion rate in boiling HCl solutions.

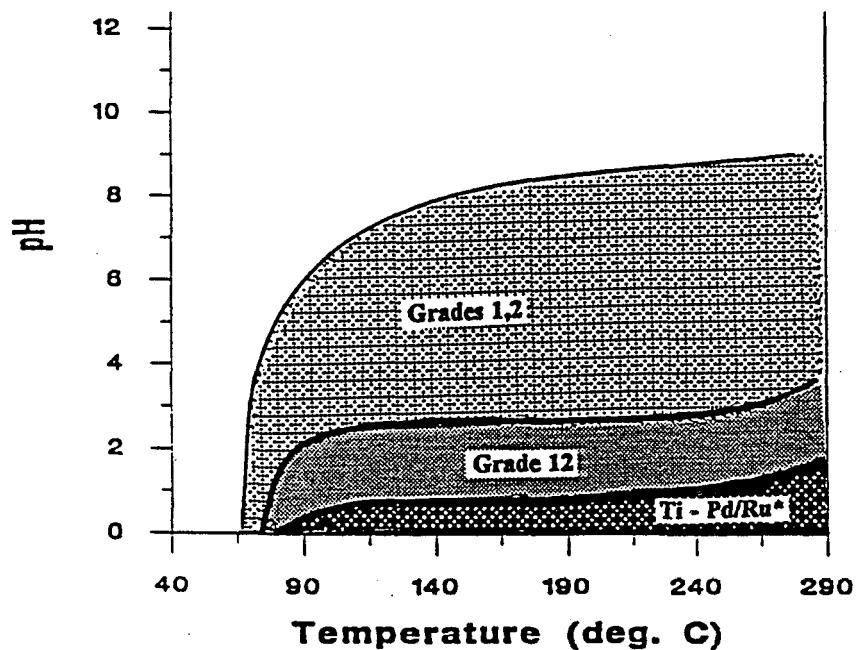


Figure 4. Temperature-pH limits for crevice corrosion of various titanium alloys in naturally aerated saturated-NaCl brine. Shaded areas are regions of alloy susceptibility to crevice attack.

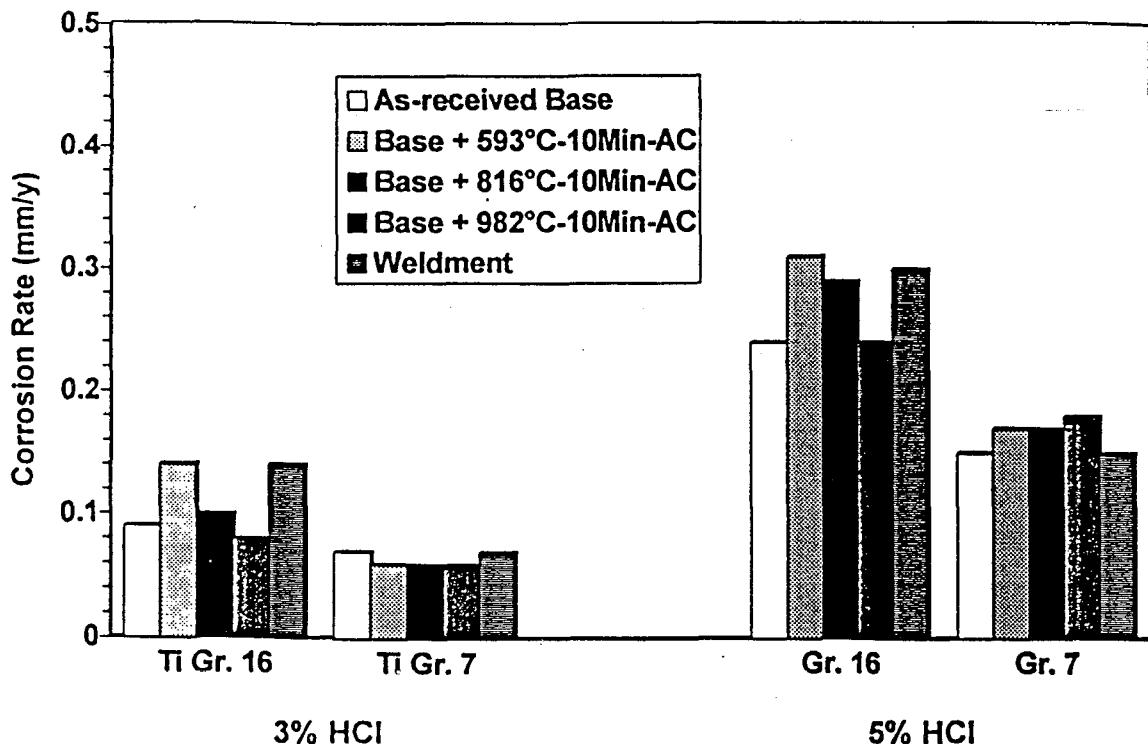


Figure 5. Effect of thermal treatments on corrosion resistance of Ti-Grades 7 and 16 in boiling HCl.

## APPENDIX

### 1. Corrosion of Superaustenitic Stainless Alloys and Ni-Cr-Mo Alloys

The superaustenitic stainless alloys and the Ni-Cr-Mo alloys are used predominantly to resist aqueous corrosion. The following comments related to the corrosion resistance of these alloys are extracted from a publication by Stephenson.<sup>28</sup> The high chromium level in these alloys provides resistance to oxidizing acids. Chromium and molybdenum, together with tungsten if present, promote resistance to pitting and crevice corrosion in halide environments. High nickel and chromium contents impart resistance to halide-ion stress-corrosion cracking and, together with molybdenum (plus tungsten), diminish the susceptibility to sulfide stress-corrosion cracking. Copper, when present, tends to inhibit depassivation under less oxidizing conditions and reinforces molybdenum in enhancing resistance to reducing acids. The carbon content is kept low to diminish the risk of sensitization during fabrication/welding. Alternatively or in addition, titanium or niobium may be used in small amounts to stabilize carbon, and in larger amounts to impart additional strength.

These alloys usually have a high resistance to uniform corrosion. The main concern is their susceptibility to localized corrosion. A relative measure of the pitting resistance equivalent (PRE) of these alloys is given in terms of composition as follows<sup>53</sup>:

$$\text{PRE} = \% \text{Cr} + 3.3 \times \% \text{Mo} + 30 \times \% \text{N}.$$

Based on this expression, the PRE values for Alloys 825, 625, C-22, C-4, C-276, and 59 are 32, 54, 65, 69, 69, and 76, respectively.<sup>53</sup> Corresponding value estimated for Alloy G-3 is 46, being considerably below the values for the high molybdenum-bearing alloys, but significantly above the value for Alloy 825.

Some of these alloys were exposed to various corrosive solutions, namely, ASTM G-28A, ASTM G-28B and "Green Death" (11.5% H<sub>2</sub>SO<sub>4</sub>-1.2% HCl-1% FeCl<sub>3</sub>-1% CuCl<sub>2</sub>) at several temperatures up to their boiling points.<sup>53</sup> The results verified the high value of PRE calculated for Alloy 59. Critical temperatures for pitting and crevice corrosion, pit and crevice depths, and uniform corrosion rates were measured. Of significance, is the superior resistance of Alloy 59 to the "Green Death" solution which attempts to simulate

severe oxidizing chloride-acid conditions. The critical temperatures in this solution were greater than 120, 120, and 110°C for pitting corrosion and 110, 110, and 105°C for crevice corrosion for Alloys 59, C-22, and C-276, respectively.<sup>53</sup> In an oxidizing solution of NaCl-HCl-Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (pH 2 and 24,300 ppm Cl<sup>-</sup>) the critical temperatures were reported as above 150 and as 150°C for pitting corrosion and as 102 and 80°C for crevice corrosion for Alloys C-22 and C-276, respectively. The corresponding critical temperatures for Alloy 825 were 25 and equal to or less than minus 5°C.<sup>41</sup>

Corrosion rates were reported for Alloys C-276, C-22, and 59, which had been exposed to 34 different environments consisting of different concentrations of either H<sub>2</sub>SO<sub>4</sub>, HCl, or mixtures of the two acids at several different temperatures.<sup>16</sup> Alloy 59 generally showed the lowest rates for the more dilute solutions of HCl and H<sub>2</sub>SO<sub>4</sub>—HCl mixtures, while Alloy C-276 generally showed the lowest rates for the more concentrated of these two types of solutions and for all concentrations of H<sub>2</sub>SO<sub>4</sub>. The range of concentrations were 1 to 10% for HCl and 10 to 96% for H<sub>2</sub>SO<sub>4</sub>. Temperatures listed ranged from 52 to 107°C, with boiling also being listed for some of the solutions. In contrast to these results, when the corrosion rates were obtained following exposure in accordance with ASTM-28 A and B, the materials in decreasing order of performance for method A were Alloys 59, C-22, C-4, and C-276; for method B, they were Alloys 59, C-22, C-276, and C-4.<sup>16</sup>

A comprehensive review of the susceptibility of the superaustenitic stainless alloys and the Ni-Cr-Mo alloys to the various forms of corrosion in different chloride media and in hydrogen environments was presented by Gdowski.<sup>18</sup> Resistance to stress-corrosion cracking in boiling 42% MgCl<sub>2</sub> and 45% MgCl<sub>2</sub> solutions was greatly enhanced by increasing the nickel content relative to that present in conventional austenitic stainless steels. In the boiling 45% solution, Alloys 625, C-276, C-22 did not show any cracking in 1000-hour tests, while Alloy 825 with lower nickel and molybdenum contents cracked in 46 hours. This compared to failure in less than two hours for the conventional stainless steels (316 and 316L). The stress-corrosion-cracking studies quoted for a 42% solution of boiling MgCl<sub>2</sub> performed by Copson supported these results in that no failure occurred in the testing period of 1000 hours for nickel contents above 45%. A number of alloys (304, 304L, 316, 316L, 20Cb-3, 825, 20-Mod, G, and C-276) were tested in various NaCl

solutions for stress-corrosion cracking and localized corrosion. U-bend samples were exposed for one month at 141°C. All of the conventional stainless steels exhibited stress-corrosion cracking as well as crevice corrosion and/or pitting. None of the high-nickel alloys showed any cracking, while pitting and crevice corrosion developed in Alloys 20Cb-3 and 825 in one of the solutions, namely, 0.8% NaCl-0.2% H<sub>3</sub>PO<sub>4</sub>. The other solutions consisted of 4% NaCl-1% H<sub>3</sub>PO<sub>4</sub>, 0.8% NaCl-0.5% CH<sub>3</sub>COOH, 2% NaCl (825 and 20Cb-3 were not tested). Alloy 825 was reported as being subjected to uniform thinning in a 0.8% NaCl-HCl solution with a pH of 2.2. following a 10-day exposure at 141°C.

Anodic polarization<sup>m</sup> tests indicated that the Ni-Cr-Mo alloys (as well as titanium alloys) are susceptible to both crevice and pitting corrosion in aqueous halide solutions.<sup>41</sup> A review of several studies on the susceptibility to crevice corrosion in various chloride media showed that Alloys C-22, C-276, and, to a lesser extent, C-4 are considerably less susceptible than other alloys (255, 316L, 904L, 625, 20 Cb-3, and 825) tested. For example, a ten-day exposure of Alloy 825 in 10% FeCl<sub>3</sub> at 25°C resulted in a crevice penetration of 3175  $\mu\text{m}$ ; by contrast, no crevices developed in either Alloys C-22 or C-276. In the same test, Alloy 625 showed a penetration of 76  $\mu\text{m}$ .

Very limited reference is made to pitting in chlorides.<sup>18</sup> Smooth samples of Alloys C-276 and 625 were exposed for 24 hours to a 7% H<sub>2</sub>SO<sub>4</sub>-3% HCl-1% FeCl<sub>3</sub>-1% CuCl<sub>2</sub> solution. Exposure at 25°C gave a corrosion rate of 7.6  $\mu\text{m}$  per year with no pitting for both alloys. At 102°C, the two alloys exhibited a considerable difference in their resistance to corrosion, namely, corrosion rates of 610 and 48,060  $\mu\text{m}$  per year for Alloys C-276 and 625, respectively, with pitting only in the latter alloy (which has a much lower Mo content). Similar tests on cold-worked materials (up to 50% cold work) did not result in any pitting for Alloy C-276. The critical pitting and crevice-corrosion temperatures, as measured both in a FeCl<sub>3</sub> and in an oxidizing NaCl-HCl solution, indicate that Alloys C-22 and C-276 both have a much higher resistance to pitting and crevice corrosion relative to that of Alloy 825. For example, the critical pitting

<sup>m</sup> The term polarization refers to the displacement of an electrode potential from its equilibrium potential resulting in a net current. Anodic polarization measurements allows identifying the passive region and the critical pitting potential of a metal in a given medium.

temperatures on exposure to 6% $\text{FeCl}_3$  for 24 hours are about 70, 60, 38, 38, and 0°C for Alloys C-22, C-276, 625, C-4, and 825, respectively. Potentiostatic polarization tests, whereby induced galvanic currents are obtained by applied constant voltages, showed a direct correlation between an increase in the resistance to localized attack and an increase in the molybdenum content.<sup>18</sup>

Using potentiodynamic polarization curves, which measures corrosion current as a function of a continuously increasing or decreasing applied voltage, and potentiostatic polarization curves, Caruso evaluated the relative susceptibility to pitting corrosion of 316L, and Alloys 625, 825, and C-22 in simulated J-13 well water heated to 95°C and containing a 1000-fold increase in chloride content.<sup>54</sup> Only Alloys 625 and C-22 showed extended ranges of passive behavior, indicating immunity in these two alloys to localized corrosion in the test environment. Visual examination of the test samples showed no localized attack on Alloy C-22, slight crevice corrosion on Alloy 625, and both pitting and crevice corrosion for Alloy 825 and 316L. In adding a cementitious material simulating a backfill, the pitting potentials of both 316L and Alloy 825 was significantly raised, thereby indicating an increase in the passive range, and with no evidence of localized corrosion. The author suggested that this was due to the formation of a  $\text{CaCO}_3$  protective film and to the resulting high pH value.

Lukezich and Ahluwalia performed similar tests in simulated J-13 well water at its nominal composition and at a 1000-fold increase in chloride content(6.4 ppm and 6400 ppm Cl).<sup>22</sup> Tests were performed at 100°C. Alloys C-22, H-9M, 825, and 316L were evaluated. In the nominal water, 316L showed unstable behavior, while the other three materials exhibited stable passivity. A current peak formed in the passive region in each of the three potentiodynamic polarization curves, which is attributed to the oxidation of Mo to  $\text{Mo}^{+6}$  with no visible damage to the samples. In the chloride-enriched water, both 316L and Alloy 825 exhibited abrupt breakdown of passivity at relatively low potentials (below which oxygen evolution is expected) as well as crevice corrosion and deep pits. Alloy H-9M showed less susceptibility to localized corrosion than the above two alloys. Alloy C-22 did not exhibit any physical change in the chloride-enriched water other than a discoloration appearing on the sample and in the liquid when the breakdown potential was exceeded. The authors state that, Alloy C-

22 appeared to be virtually unaffected by the increase in the chloride content from 6.4 to 6400 ppm. Potentiostatic tests were made in both solutions, also at 100°C, for Alloys C-22 and 825 and 316L. The results obtained corroborated those obtained with the potentiodynamic tests.

In his report, Gdowski presented a review on the corrosion of a number of alloys in marine environments.<sup>18</sup> Sea water is much more aggressive than J-13 well water. Many of the same constituents are present in both environments, but, at much higher concentrations in the sea water. In addition to the high chloride contents, magnesium, which is believed to be the most aggressive cation, is present in sea water in concentrations of about two orders of magnitude greater than in J-13 well water. A pH of 8.1, which is slightly more alkaline than that of J-13 well water, was quoted for a representative sea water. Among the Ni-Cr-Mo alloys included in the review are Alloys 825, 625, and C. In offshore marine atmospheres, these alloys did not fail in ongoing stress-corrosion-cracking tests that lasted for up to 28 years. In sea-water tests of two-year duration, none of the three alloys showed any stress-corrosion cracking; however, Alloy 825 exhibited pitting and crevice corrosion, both of which were absent on Alloys 625 and C. In a ten-year sea-water test, Alloy C suffered no detectable weight loss or pitting. In Alloy 625, localized corrosion was detected only following seven years of exposure to sea water. Crevice-corrosion tests in filtered sea water at 30°C for 30 days were made on a number of alloys including Alloys C-276, 625, and 825. Of the alloys tested, only Alloys 625 and C-276 were free from attack.

In a separate investigation,<sup>18</sup> crevice corrosion and corrosion rates of Alloy C-276 were measured in sea-water over a range of temperatures. Crevice-corrosion tests (with excess dissolved oxygen) were performed at temperatures ranging from 35 to 107°C for approximately 100 days, while tests for uniform corrosion measurements were performed at temperatures from 10 to 288°C with times from 15 to 150 days. In these tests, crevice attack was undetected and corrosion rates were very low, between 2.5 and 5.1  $\mu\text{m}$  per year.

One of the more recent developments in the Ni-Cr-Mo family of alloys is a tungsten-free, low-iron 59% Ni-23% Cr-16% Mo material, referred to as Alloy 59. This alloy showed a higher resistance to corrosion than did Alloys C-22, C-4, and C-276 when tested

according to both ASTM G-28A (120-hour exposure) and G-28B (24-hour exposure).<sup>16</sup> Alloy 59 also showed a relatively high resistance to sensitization. For example, using ASTM G-28, procedure B, following an exposure of one hour at 871°C, Alloy C-22 was heavily attacked and showed a corrosion rate of 8.5 mm per year, while Alloy 59 corroded at a rate of only 0.10 mm per year. After a pre-treatment of five hours at 871°C, the rates were 40.2 and 0.43 mm per year, respectively. Intergranular penetration of Alloy 59 was also considerably less than that observed for the other Ni-Cr-Mo alloys. The time-temperature-precipitation diagram for the onset of precipitation at grain boundaries and within the grains for Alloy 59<sup>16</sup> can be superimposed on the diagram reported for Alloy C-22.<sup>18</sup> This is seen by comparing the curves in Figure A-1a with those in Figure A-1b. Microprobe analysis following an exposure of 100 hours at 900°C, corresponding to the maximum precipitation rate, indicated the precipitate in Alloy 59 to be the Mu phase.<sup>16</sup> In a recent review article on nickel-based alloys, Agarwal and Herda indicated that Alloy 59, in having the highest pitting resistance equivalent and the lowest iron content has improved corrosion resistance over Alloys C-22 and C-276 as well as over many other alloys. The elimination of tungsten and the reduction of iron to about 1% gives the alloy superior thermal stability. With the combination of high chromium (23% Cr) and high molybdenum (16% Mo) contents, the authors claim that Alloy 59 exhibits one of the highest critical pitting and crevice-corrosion temperatures.<sup>55</sup>

## **2. Failure of Ni-Cr-Mo Alloys in Hydrogen Environments**

In the annealed condition, the Ni-Cr-Mo alloys are not susceptible to hydrogen embrittlement (HE). The cold-worked alloys are also not susceptible to HE unless either galvanically coupled to a less noble material or cathodically charged with hydrogen.<sup>56</sup> Failure by HE is distinguished from failure by stress-corrosion cracking in that the former involves the absorption of atomic hydrogen at the cathode, while the latter involves anodic dissolution. It is possible, that at some point in time the highly corrosion-resistant barrier wall would come in contact with the corrosion-allowance alloy. In a wet environment, under sufficient stress, and with the evolution of hydrogen at the cathodic barrier, HE of the corrosion-resistant alloy could occur if it were in the cold-worked condition or if part of the structure had experienced local plastic deformation. Gdowski points out that studies on HE in the Ni-Cr-Mo alloys were focused primarily

on the cold-worked and/or aged conditions that provided the high strength levels required for oil-field operations.<sup>18</sup> The strength levels of these alloys in the mill-annealed condition, however, are sufficient to meet the design requirements for the proposed waste containers.

The degree of cold work, the temperature and time of aging, the stress level, the direction of stressing, alloy composition, and the environmental composition all effect the susceptibility to HE. Gdowski presents the results of a number of studies showing the effects of these factors on HE in Alloys C-276, C-4, and 625.<sup>18</sup> Samples were stressed close to their yield strengths. The tests were conducted in the NACE Solution (aqueous solution of 5% NaCl-0.5% acetic acid saturated with 100% H<sub>2</sub>S gas) recommended for testing the susceptibility to HE. Tests were performed either under hydrogen charging or galvanic coupling. By galvanic coupling the test metal to a less noble metal, the test metal becomes cathodic to the less noble metal with the evolution of hydrogen at its surface. This is corrosion-resistant alloy coming in contact with the corrosion-allowance alloy with hydrogen being generated at the surface of the former alloy.

Of the three alloys, Alloy C-276 generally appeared to exhibit the greatest resistance to HE and Alloy C-4 the least. The effect of impurities is unclear, although it is suggested that impurities will adversely affect HE.<sup>18</sup> Phosphorus appears to have a detrimental affect by segregating at grain boundaries during aging. The susceptibility to HE increased with the degree of cold work. Samples stressed parallel to the rolling direction were shown to be more resistant to HE than were those stressed transversely. An increase in either aging time or aging temperature of cold-worked materials resulted in a decrease in the time to failure. Based on limited information, it appears that with an increase in test temperature the alloys become less susceptible to HE. The effect of temperature (25 to 149°C) is attributed to the hydrogen becoming more dispersed throughout the lattice with an increase in temperature in contrast to their concentration at defect sites at the lower temperatures. The presence of H<sub>2</sub>S in the test solution increases the susceptibility to HE. It is suggested that H<sub>2</sub>S promotes the absorption of atomic hydrogen into the lattice.

### 3. ADDITIONAL COMMENTS ON CORROSION OF TITANIUM AND ITS ALLOYS

Gdowski and Ahluwalia recently published a review on the physical metallurgy, mechanical and physical properties, and corrosion characteristics of titanium and of slightly alloyed titanium alloys.<sup>45</sup> The extensive amount of data available on Ti-Grade 12 indicates that this material is not susceptible to stress-corrosion cracking at naturally occurring potentials in various brines. The alloy is particularly well suited to service in the chemical industry where the environment is either mildly reducing or varying between oxidizing and reducing.

Ti-Grade 12 is claimed to possess superior resistance to sweet and sour chloride brines at high temperatures.<sup>46</sup> It is commonly used in a number of applications where crevice corrosion is of some concern. It is resistant to crevice corrosion and pitting in concentrated NaCl brines up to at least 260°C for pH values equal to or greater than three. It is fully resistant to sulfides, H<sub>2</sub>S, and elemental sulfur to at least 260°C. Its critical pitting and crevice corrosion temperatures, determined by ASTM G-48, method B, are above 120°C. It is fully resistant to cracking and localized attack on testing according to ASTM G-44. Crevice corrosion, however, can occur in very restricted crevices at low pH values in sodium chloride solutions at elevated temperatures. The susceptibility to crevice corrosion in NaCl solutions increases with increasing temperature, increasing chloride-ion concentration, decreasing dissolved oxygen, and decreasing pH values. In chloride solutions with a neutral pH, crevice corrosion of titanium has not been observed below 120°C. In saturated NaCl brines, the substitution of Ti-Grade 12 for Ti-Grade 2 greatly extends the resistance to crevice corrosion to higher temperatures and lower pH values. The use of Ti-Grade 7 will allow exposures to still lower pH values and /or higher temperatures for the same corrosion rates in these brines (Fig. A-2).<sup>57</sup>

In Ti-Grade 12, there is no significant difference in the corrosion-rest potentials between base metal, weld metal, and the heat-affected-zone metal and, therefore, there should be no intergalvanic effects in weldments of this alloy.<sup>46</sup> However, under marginal or active corrosion conditions, the weldment can experience an accelerated corrosive attack depending on alloy composition. The increase in impurity content (iron, sulfur, and oxygen) associated with the coarse

transformed beta microstructures weldments is a factor in this acceleration. Generally, weldments of Ti-Grade 12 exhibit corrosion resistance similar to the unwelded metal.

Schutz and Xiao compared the corrosion resistance of Ti-Grade 16 with that of several other titanium grades including Ti-Grades 7 and 12.<sup>42</sup> They obtained nearly equivalent results for Ti-Grades 7 and 16 with respect to corrosion resistance to dilute reducing acids and to resistance to acidic halide crevice attack. The corrosion rate on exposure to a number of different acids, both reducing and oxidizing, were evaluated as a function of acid concentration. For example (Fig. A-3), at low concentrations of boiling HCl solutions, Ti-Grades 12 (0% Pd) and 16 (.05% Pd) exhibited essentially the same resistance to general corrosion as did Ti-Grade 7 (0.15% Pd). At about 1.5% HCl, the corrosion rate of Ti-Grade 12 rises above that of Ti-Grade 7, while the corrosion of Ti-Grade 16 only begins to rise above that of Ti-Grade 7 at about 3.5 wt% HCl. At the higher concentrations, however, Ti-Grade 16 becomes only slightly more subject to attack relative to Ti-Grade 7. The corrosion rates at 2 wt% HCl are 0.06, 0.06 and 0.75 mm per year for Grades 7, 16, and 12, respectively; at 6 wt% HCl, the rates are 0.23 and 0.4 mm per year for Ti-Grades 7 and 16, respectively.

Crevice corrosion tests in both chlorinated and non-chlorinated oxidizing brines, which included pH levels as low as 1.0, did not reveal any attack of either Ti-Grades 7 or 16. Samples were exposed for 30 days at temperatures up to 260°C. Ti-Grade 12 was not evaluated. In a separate crevice-corrosion investigation quoted by the authors,<sup>42</sup> samples were exposed at 100 and 200°C for up to 1000 hours. No incidence of crevice attack was reported for both Ti-Grades 7 and 16, whereas, all samples of Ti-Grade 12 were attacked.

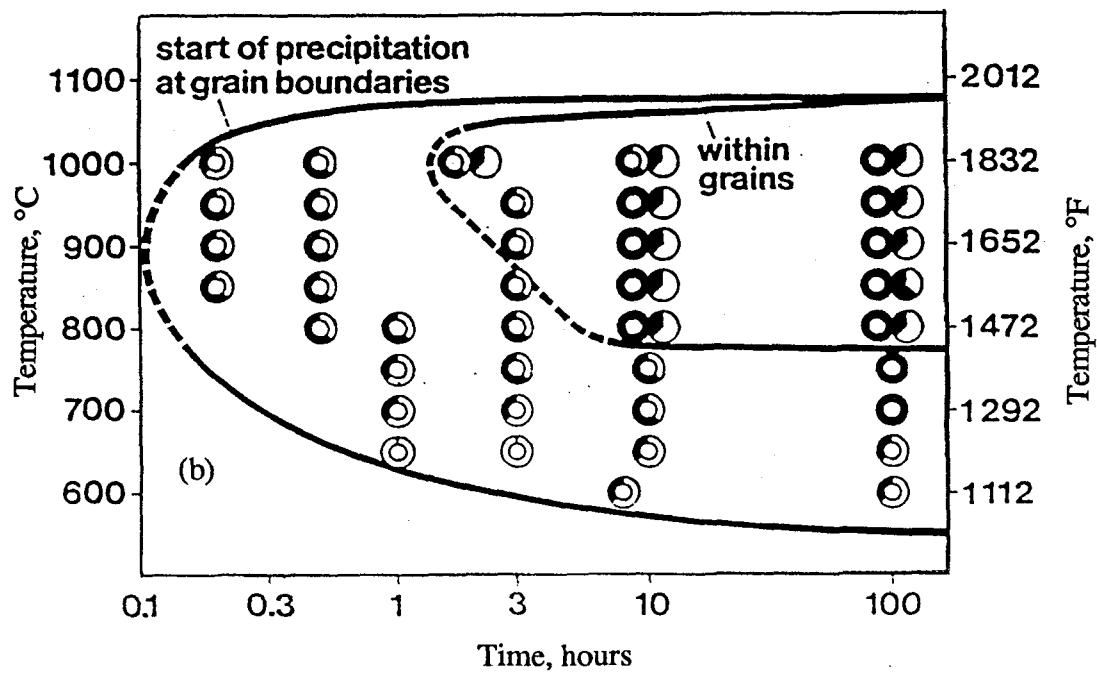
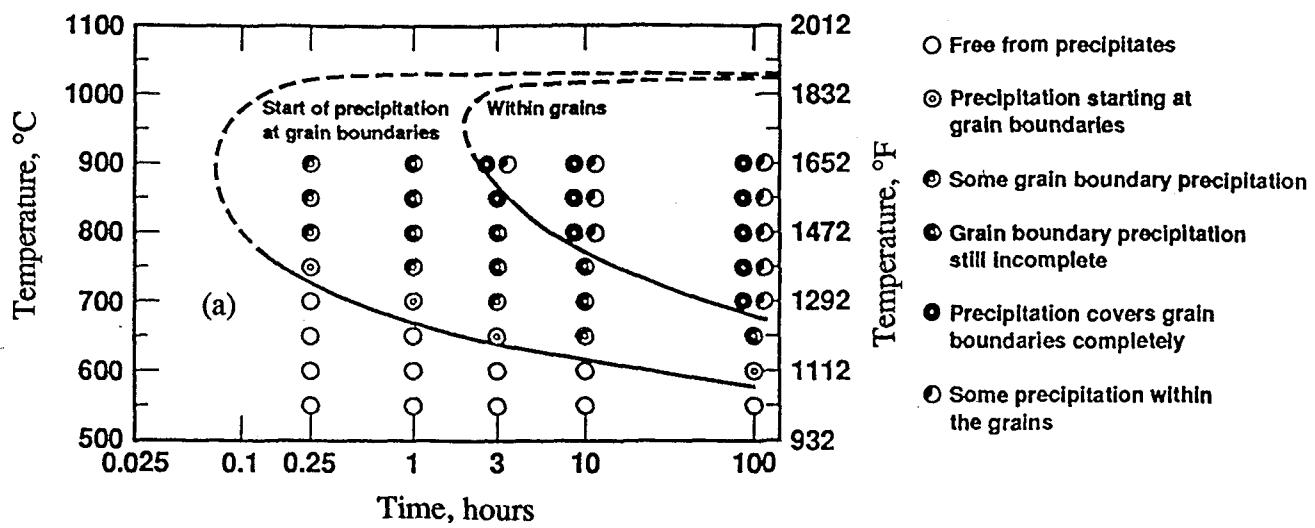


Figure A-1—Isothermal time-temperature-precipitation (TTP) diagrams for (a) Alloy C-22 and (b) Alloy 59.

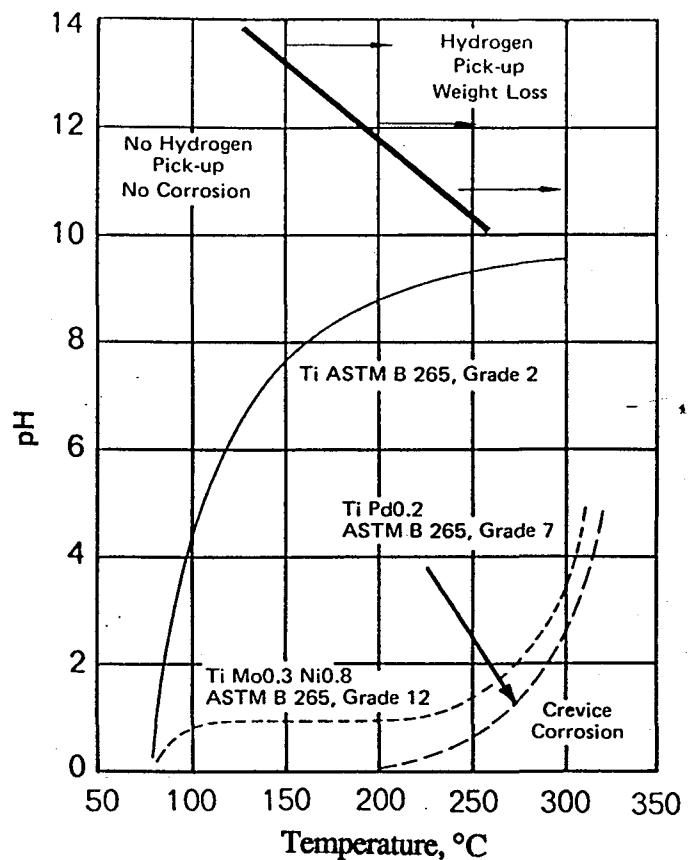


Figure A-2—Corrosion resistance of titanium and titanium alloys in saturated NaCl brines.

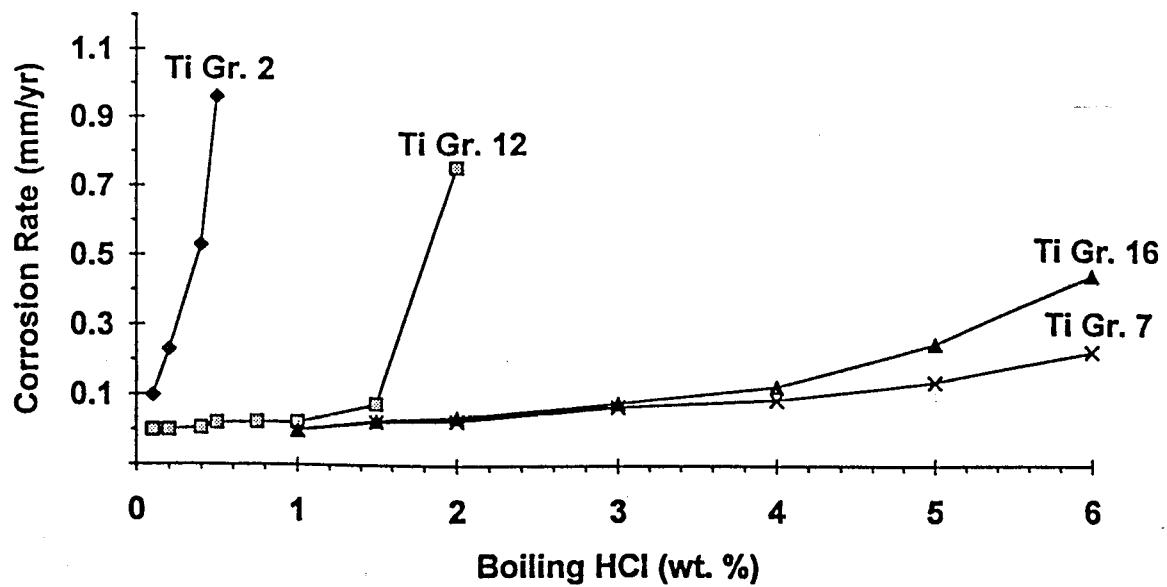


Figure A-3. Corrosion-rate profiles for Ti-Grade 7 and Ti-Grade 16 in boiling HCl solutions.