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A Review of Thermal Aging Embrittlement in Pressurized Water Reactors (MRP-80)

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Technical Report

Materials Reliability Program A Review of Thermal Aging Embrittlement in Pressurized Water Reactors (MRP-80)

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REPORT SUMMARY

Various failures of nuclear steam supply system components could potentially be attributed to thermal aging embrittlement effects. This report documents results of a review of PWR materials summarizing the available data and recommendations for follow-on testing to determine the effects of thermal aging.

Background
Numerous materials used in a pressurized water reactor (PWR) nuclear steam supply system (NSSS) are exposed to elevated temperatures throughout the plant operating period. In most cases, the response of these materials to long-term elevated temperature exposure is unknown. Various failures of NSSS component items—such as valve stems, studs, and bolts—have typically been attributed to improper heat treatment of the material. However, in the majority of these cases, it is now believed that failures could be attributed to thermal aging effects. These failures are both costly and time consuming for nuclear plant operators. While the effects of long-term aging (>200,000 hours) at temperatures below 700ºF for all types of alloys are not well understood, limited studies to date show that some materials will experience significant embrittlement that must be managed as the plant operating period increases.

Objective
To summarize the available thermal aging data, identify materials and components susceptible to thermal aging, and develop recommendations for follow-on testing.

Approach
Investigators reviewed the thermal aging embrittlement potential of low alloy steel plates and forgings widely used in PWRs. Specifically examined were data pertinent to 1) welds and heat-affected zones, 2) high strength low alloy (HSLA) bolting materials, 3) austenitic stainless steels, including welds and castings, 4) Martensitic stainless steels, 5) precipitation hardenable (PH) stainless steels, 6) austenitic PH alloys, 7) nickel-based alloys such as alloys 600 and 690, and 8) weld metal alloys 82/182 and 52/152. For those materials possibly susceptible to thermal aging embrittlement, additional testing is recommended to verify their embrittlement potential and kinetics and to provide guidance for their aging management.

Results
This review concludes that the following materials are not susceptible to thermal aging embrittlement in a PWR environment: 1) austenitic PH alloys X-750, 718, and A-286, 2) alloys 600 and 690, 3) weld metals alloys 82/182 and 52/152, and 4) wrought austenitic stainless steels. Austenitic stainless steel welds and castings are widely recognized as susceptible to thermal aging embrittlement at PWR temperatures, and the phenomenon has been extensively studied. The present review also found data indicating other materials—including HSLA bolting

materials and PH stainless steels—are potentially susceptible to thermal aging embrittlement at PWR temperatures. For these materials, fracture toughness tests and/or multi-temperature Charpy V-notch impact tests and associated criteria are recommended to verify their embrittlement potential and kinetics and to provide guidance for aging management.

EPRI Perspective

Long-term plant life and license renewal require an understanding of thermal aging susceptibility for all PWR materials. Such information—also needed in aging management of plant components—would reduce the risk of component failure by increasing awareness of material behavior over time and possible material failure mechanisms. This white paper serves as a valuable reference document for utility materials engineers, while its recommendations for follow-on testing provide input for obtaining aged materials from decommissioned plants or replaced components. Ultimately, the study of such materials and components will provide data crucial to developing effective aging management guidelines.

Keywords

Thermal aging
Embrittlement
Carbon steels
PWRs

ABSTRACT

This report has reviewed the thermal aging embrittlement potential of materials widely used in Pressurized Water Reactors (PWRs). Data pertinent to thermal aging embrittlement for low alloy steel plates and forging including welds and heat affected zones (HAZ), low alloy high strength bolting materials, austenitic stainless steels including welds and castings, martensitic stainless steels, and PH (precipitation hardenable) stainless steels, austenitic precipitation hardenable alloys, nickel-based alloys such as Alloys 600 and 690 and their weld metals have been examined. The review concludes that austenitic materials Alloys X-750, 718, A-286, Alloys 600 and 690, their weld metals Alloys 82/182 and 52/152, and wrought austenitic stainless steels are not susceptible to thermal aging embrittlement under PWR environment. Currently austenitic stainless steel welds and castings are widely recognized being susceptible to thermal aging embrittlement at PWR temperatures and the phenomenon has been extensively studied. However, the present review has also found data indicating other materials, e.g. high strength low alloy (HSLA) bolting materials and PH stainless steels, being potentially susceptible to thermal aging embrittlement at PWR temperatures. The findings of this review are summarized in the Technical Summary at the end of this report. For these materials potentially susceptible to thermal aging embrittlement, additional testing is recommended to verify their embrittlement potential and kinetics, and / or provide guidance for their aging management.

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1 INTRODUCTION

There are numerous materials utilized in a pressurized water reactor (PWR) nuclear steam supply system (NSSS) that are exposed to elevated temperatures throughout the plant operating period. In most cases, the behavior response of these materials to long-term, elevated temperature exposure is unknown. In all cases, this information was neither available nor required during plant design and construction.

Various failures of NSSS component items, such as valve stems, studs, and bolts have typically been attributed to improper heat treatment of the material. However, in a majority of these cases, it is now believed that failures could be attributed to thermal aging effects. These failures are both costly and time consuming for nuclear plant operators. The effects of long-term aging (>200,000 hours) at temperatures below 700°F for all types of alloys are not well understood. Effects of thermal aging have been studied for a few materials such as precipitation-hardenable (PH) stainless steels, martensitic stainless steels, and duplex cast stainless steels. The results of these studies show that some of the materials are expected to experience significant embrittlement that must be managed as the plant operating period increases. Although this data has been reviewed as part of plant license renewal activities, it has not been compiled in a systematic and comprehensive manner that is convenient and readily accessible to utility engineers.

It is important for long-term plant life assurance and license renewal to develop an understanding of the thermal aging susceptibility for all PWR materials. Such information is needed to aid in aging management of plant components. This information would reduce the risk of component failure, as a result of thermal aging, due to an increased awareness of the material behavior over time and the possible failure mechanisms of these materials. Thermal aging of materials used in PWRs is a time and temperature dependent degradation mechanism that typically results in a decreased toughness of the material. In addition, the hardness of many of these materials increases, which decreases their stress corrosion cracking resistance over time. Therefore, the long-term and elevated-temperature thermal aging potential of carbon and low alloy steels, stainless steels, and nickel-base alloys is a concern for plant life operation and license renewal.

Thermal degradation of cast austenitic stainless steels (885°F embrittlement) can occur at temperatures as low as 500°F to 650°F where a brittle (alpha prime) phase can precipitate from chromium-rich delta ferrite. Because the operating temperature for many primary side component items is generally between 550°F and 650°F, long-term thermal degradation (such as that experienced over a 40 year operating period) could reduce the material fracture toughness. For components expected to be in-service for a long period of time at these temperatures, fracture toughness analysis may be necessary to justify a prolonged-life operation.

PWR operating temperatures for primary side component items range from 550°F to 650°F. At these temperatures, the long-term aging effects of many alloys are not well understood. Although the materials for these components initially have a high toughness and resistance to SCC, exposure at these temperatures for a long term (>200,000 hours or about 23 years) may result in a significant reduction in fracture toughness or SCC resistance.

The objective of this thermal embrittlement white paper for PWR materials is to summarize the available thermal aging data and develop recommendations for follow-on testing. The white paper is a valuable reference document for utility materials engineers and the recommendations for follow-on testing will provide input to obtain aged materials from decommissioned plants or replaced components, which will provide data for effective aging management.

2
CARBON AND LOW ALLOY STEELS

The major PWR reactor coolant system (RCS) pressure boundary components and bolting fabricated from ferritic carbon and low alloy steels include hot leg and cold leg pipings (e.g. stainless steel cladded SA-105 Gr. II and SA-106 Gr. C), the reactor vessel shell & closure head, the steam generator, and the pressurizer (e.g. stainless steel cladded SA302 Gr. B and SA533 Gr. B plate, SA508 Class 2 forging, and SA-515 and SA-516 Grade 70 plate). Other ferritic low alloy steels used in the RSC boundary are high strength low alloy (HSLA) bolting materials, such as SA-193 Gr. B7, SA-320 Gr. L73, and SA-580 Gr. B23 & B24, used for steam generator manway bolting and reactor vessel closure head bolting. Table 2-1 lists the chemical composition requirement of many carbon and low alloy steels, including HSLA bolting materials, used in the RCS of PWRs [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. With the exception of HSLA materials, the nominal chemical compositions of carbon and low alloys steel piping, forging, and plates are similar. Therefore, the thermal aging of HSLA used for bolting in PWRs is discussed separately from plate and forging materials.

2.1 Thermal Aging of Non-Bolting Low Alloy Materials

For PWRs, the operating temperatures of the primary circuit components ranges from 536 to 662^{o}F (280 to 350^{o}C). Because the operating temperatures are less than 0.3 times the absolute melting temperature, creep or other self diffusion controlled embrittlement mechanisms are not of concern. The two possible aging embrittlement mechanisms are temper embrittlement and strain aging embrittlement. Strain aging in low alloy steels result from interactions between dislocations and the interstitial atoms of nitrogen and carbon. Strain aging can cause an increase in yield and flow stress, a decrease in ductility, an increase in DBTT, and reduction in upper shelf energy. The region of plastic strain required for strain aging may arise locally due to welding, which is largely eliminated by PWHT. In addition, reactor vessel steels contain very little nitrogen due to vacuum degassing and aluminum grain refinement. Several studies reported an increase in ductile brittle transition temperature (DBTT) between 10 to 20^{o}C in SA-533 Gr B and SA-508 Gr. B steels due to strain aging [13, 14, 15]. Hence, the potential for strain aging is very moderate and is an unlikely aging concern for carbon steels.

The dominant embrittlement concern for this class of low alloy ferritic steels, hence the primary interest of thermal aging embrittlement has been temper embrittlement. This type of temper embrittlement is also called two-step temper embrittlement to differentiate it from one-step temper embrittlement or tempered martensitic embrittlement (TME) for HSLA bolting materials. In temper embrittlement (also called two-step embrittlement) of low alloys forging and plates, the steel is usually tempered at temperature 1200^{o}F (650^{o}C) producing lower strength and hardness, and embrittlement occurs upon slow cooling or prolonged exposure to temperature range 707-1112^{o}F (375-600^{o}C). For HSLA bolting materials, TME is caused by the as-quenched materials being tempered at relatively low temperature of ~662°F (350°C, hence also known as 350°C embrittlement) causing a sharp drop in room temperature impact fracture energy.

The thermal aging embrittlement of low alloy steels generally refers to this type of temper embrittlement and will be used interchangeably hereafter in this section. Temper embrittlement and the effect of alloying elements, such as chromium, nickel, magnesium, and molybdenum on the temper embrittlement process have been studied extensively [16, 17, 18]. The results show that temper embrittlement does not affect pure Fe-C or Fe-P-C alloy, but it occurs to a marked extent in iron-base alloys containing Cr or Mn, together with P and C. It occurs slightly in alloys containing high Mn or high Cr and carbon, and very minute amount of P. The embrittlement mechanism is diffusion and segregation of impurity elements, such as phosphorous, tin, antimony, and arsenic at the grain boundaries after prolonged exposure to temperatures in the 400-600°C (752-1112°F). The exact temperature range of temper embrittlement and the embrittlement potential are dependent on chemical composition. The generally accepted temper embrittlement temperature range is between 375 and 560°C (707 to 1040°F) [19].

Temper embrittlement is manifested as an increase in DBTT, due to the change from predominantly cleavage fracture to predominantly intergranular fracture along impurity segregation paths. The DBTT is found to be directly related to the grain boundary concentration of the impurities, usually to P in commercial low alloy steels. The segregation of these impurities appears to be an equilibrium phenomenon which can be modeled by an Arrhenius relationship, with peak embrittlement temperature around ~500°C (932°F). At temperature above 600°C (1112°F), the impurities tend toward solution in the ferrite matrix with little or no grain boundary segregation. At temperatures below this range, very long exposure times are necessary for the impurities to diffuse to and segregate at grain boundaries. The presence of carbon tends to accelerate the embrittlement process due to preferential segregation of the impurities at the interface between grain boundary carbides and ferrite grains.

Studies of thermal aging embrittlement of low alloys steels for PWR applications are mostly limited to SA-302 Gr. B and SA-533 Gr. B plate, SA-508 Class 2 forging, their welds and HAZ. This is largely due to studies of neutron irradiation embrittlement in the beltline region and the emphasis given to safety of the reactor pressure vessel steels. Because of their similar nominal chemical compositions, these carbon and low alloy steels used in PWRs are expected have similar temper embrittlement response, e.g., similar embrittlement potential and aging kinetics at the same temperature. SA-533 Gr B plate is essentially a quenched and tempered, nickel modification of SA-302 Gr. B steel. In addition these steels were the most important low alloys steels in the PWRs pressure boundary as they were also used as shell materials for the steam generator and the pressurizer. The thermal aging temperature used is typical of the reactor vessel during operation. Hence the results are applicable except for the pressurizer. The results of the long term thermal aging studies of these materials are summarized below according to product form.

2.1.1 Plate and Forging

In 1970, Serpan and co-workers of Naval Research Laboratory reported thermal aging results obtained from the Big Rock Point Reactor (BRPR). No measurable increase in DBTT of a 6 inch thick A-302 Gr. B plate after 9,726 hours thermal aging. Only ~8°C (15°F) increase in DBTT after 26,000 hours thermal aging at 585°F (307°C) [20, 21]. The chemical composition of the A-302 Gr. B plate and the heat treatment prior to aging are listed in Table 2-2.

In the 1970s and 1980s, Druce and co-workers of AERE Harwell (UK Atomic Energy Authority) performed thermal aging studies on commercially produced PWR pressure vessel steels, their welds and heat affected zone (HAZ) [22, 23, 24, 25]. These materials underwent isothermal heat treatments of up to 20,000 hours duration at temperature between 572 and 1112°F (300 and 600°C). These studies showed that the susceptibility of these low alloy steels to aging embrittlement at PWR operating temperatures is low. One A-533 Gr. B plate and three A-508 Class 3 forgings were included in the aging study. The chemical composition and prior heat treatment are listed in Table 2-3. The Charpy impact properties prior to thermal aging were found to vary significantly in different products and according to position within any one product. Table 2-4 summarizes the DBTT and USE properties before the thermal aging. The DBTT generally increases with distance from the surface due to slower cooling rate with increasing depth beneath surface during quenching. USE is largely dependent on inclusion density with higher toughness associated with lower inclusion densities. The highest inclusion volume tend to be at the mid-thickness for plates and at the inner surface of ring forgings. For the A-533 Gr. B plate, specimen position and orientation are found to have a large influence on DBTT and upper shelf energy (USE), but do not affect the susceptibility to temper embrittlement. Post weld heat treatment had little or no influence on susceptibility temper embrittlement before isothermal aging treatments. A PWHT of 1139°F (615°C) for 25 hours had no significant effect on the impact fracture characteristics or subsequent temper embrittlement susceptibility of the A-533 Gr. B plate. Isothermal heat treatments at 1112°F (600°C) for up to 100 hours had no effect on the impact characteristics of the A-533 Gr. B plate in both quenched and tempered and quenched tempered and PWHT conditions. Longer periods resulted in an increase in transition temperature which is associated with microstructural degradation.

Figure 2-1 and Figure 2-2 illustrate the response to thermal aging at different temperatures on specimens taken from mid-thickness positions of the A-533 Gr. B plate material in the PWHT condition. Similar observations are made of specimens taken from the plate surface. Thermal aging up to 20,000 hours at 572°F (300°C) resulted in no significant changes in tensile properties, hardness, DBTT, USE, tearing resistance at 554°F (290°C), or the amount of low-temperature intergranular fracture. Aging at 752°F (400°C) and 932°F (500°C) increased DBTT up to 25°C and 40°C respectively. Results from the non-PWHT A-533 Gr. B plate and A-508 forgings similarly confirmed low susceptibility to thermal aging at PWR operating temperatures. In the case of A-508 Forging 2, aging for up to 20,000 hours at 572°F (300°C) resulted in no change in either DBTT or USE, and aging at 842°F (450°C) increased the DBTT by 15°C. In the case of A-508 Forging 3, no experimentally significant changes were observed after aging up to 10,000 hours at 572°F (300°C) and 662°F (350°C) and 20,000 hours at 842°F (450°C) (see Table 2-4).

Specimens taken from the inner surface of a ring forging (A-508 Forging 1) were the only material to exhibit some changes in properties following aging at 572°F (300°C). Figure 2-3 shows the DBTT was increased by 30°C after 2,000 hours and then remain constant after more than 10,000 hours. Specimens away from inner surface showed much less increase in DBTT. No changes were observed in yield and tensile stresses following aging at 572°F (300°C) from specimens taken either close to or remote from the inner surface. Grain boundary enrichment of phosphorus was consistently observed following 20,000 hours aging at 752-932°F (400-500°C). However, no grain boundary chemical composition changes were detected following aging at 572°F (300°C).

Lowe and DeVan performed thermal aging studies on the B&WOG reactor vessel steel thermal aging surveillance materials during the 1980s and 1990s. In 1983, Lowe reported no significant changes in Charpy impact properties of SA-302 Gr. B, SA-533 Gr. B, and typical Mn-Mo-Ni weld metal removed from reactor vessel surveillance program after 15,000 hours at 580°F (305°C) [26]. In the 1990s, DeVan and co-workers performed Charpy impact testing and fracture toughness testing on the thermally aged materials removed from reactor vessel surveillance programs [27, 28]. These surveillance specimens were thermally aged on the service structures in the B&WOG PWRs. The material had been kept below the insulation to maintain the aging temperature. The materials, including SA-508B forging, SA-533B plate, and submerged-arc welds fabricated from Mn-Mo-Ni weld wire with Linde 80 flux, are representative of the materials used to fabricate the beltline shell course regions of certain commercial PWRs. The chemical composition and heat treatment prior to aging is listed in Table 2-5. In addition, specimens from each aged material were subjected to anneal heat treatment at 650°F (343°C) and 850°F (454°C) for 168 hours.

Results of the Charpy V-notch impact testing of aged, unaged control materials, and aged and annealed are listed in Table 2-6, which showed essentially no change in DBTT after aging at ~280°C (536°F) for ~100,000 hours for SA-533 Gr. B plate, SA-508 Class 2 forging, and submerged arc weld metals. The effect of post-aging annealing for 168 hours at 649°F (343°C) and 850°F (454°C) is also limited, either elevating or lowering the DBTT by •15°C. Fracture toughness tests were conducted at 250°F (121°C) and 550°F (288°C) per ASTM E 813-87 on plate A, the forging, and the weld metals. After the testing, J_{Ic} and J_Q values were obtained following ASTE E 1152-87. Aging at ~536°F (280°C) for 93,000 hours resulted in 15% drop in J_{Ic} and J_Q values in the SA-533 Gr. B plate. Post-aging annealing at 850°F (454°C) for 168 hours had no effect on the fracture toughness. In addition to Charpy V-notch impact and fracture tests, the microstructure of the unaged and aged materials were investigated by atom probe field ion microscopy (APFIM) [29]. APFIM showed no significant evolution of the structure of the materials. The unaged and the thermal-aged materials have a similar ferritic matrix chemistry and carbide compositions. The same matrix copper level was found before and after the long term thermal aging. The copper remains in solid solution with a concentration following the solubility of copper in iron for unaged specimens, which confirms that the thermal mobility of copper in iron at 536°F (280°C).

In 1993, Hawthorne reported virtually no DBTT changes after thermal aging at 600°F (316°C) for 5,000 hours of one A-533 Gr. B plate and four submerged arc welds (two Linde 80 welds, one Linde 0091 weld, and one Linde 124 weld) [30]. The 30 ft-lb (41J) DBTT is listed in Table 2-7 and chemical composition and heat treatment prior to thermal aging of the plate and welds are listed in Table 2-8.

2.1.2 Weld Metal

Druce and co-workers performed thermal aging studies on weldment typical of commercially produced PWR pressure vessel steels [22, 23]. The chemical analysis of weld metal taken from a 235mm (9 ¼ in.) PWR submerged arc weldment is given in Table 2-3. The samples was given a simulated PWHT of 24 hours at 605-622°C (1121-1152°F). The Charpy V-notch specimens were machined in the TS orientation and aged at 300°C and 450°C for up to 10,000 hours. The test, results are shown in Figure 2-4, which can be seen that all the data from aged specimens lie within the scatter band observed prior to aging. In addition, no changes in the predominantly cleavage low-temperature fracture mode of hardness were detected. This demonstrates that this weldment was not susceptible to thermal aging.

Lowe and DeVan performed thermal aging studies on the B&WOG reactor vessel steel thermal aging surveillance materials. The submerged-arc welds fabricated from Mn-Mo-Ni weld wire with Linde 80 flux are representative of the materials used to fabricate the beltline shell course regions of certain commercial PWRs. The chemical composition and heat treatment prior to aging is listed in Table 2-5. Results of the Charpy V-notch impact testing of aged, unaged control materials, and aged and annealed are listed in Table 2-6, which showed essentially no change in DBTT after aging at ~536°F (280°C) for ~100,000 hours for the submerged arc weld metals. Fracture toughness tests showed no significant changes in J_{Ic} and J_Q in the weld metals after aging at ~536°F (280°C) for ~100,000 hours. Post-aging annealing at 850°F (454°C) for 168 hours resulted in a slight increase in toughness values.

However, Charpy impact test results of the Doel I and II reactor vessel surveillance specimens indicate that a small thermal aging effect on the weld metal is possible [31]. Gérard et al. reported an increase of 30°C (54°F) in DBTT and a 14 J decrease in USE after approximately 63,000 hours at 287°C (549°F) of thermal aging for the submerged-arc weld (see Figure 2-5). The reactor vessels were fabricated from a steel similar to A-508, Cl.3 and the chemical compositions of the weld metal and base metal are listed in Table 2-9. Analysis by scanning transmission electron microscopy detected segregation of Mn, Mo, P to the grain boundary, although the difference between the as-received and aged samples is insignificant.

2.1.3 Heat Affected Zone (HAZ)

Druce and co-workers performed thermal aging studies on simulated HAZ from reactor vessel weldment [24, 25]. Thermal cycling was used to simulate the various thermal histories and microstructures of materials adjacent to multi-pass welds, a coarse grained simulation with a peak temperature of 2372°F (1300°C); a fine-grained simulation with a peak temperature of 2012°F (1100°C); and a refined grained simulation comprising two thermal cycles, the first at 2372°F (1300°C) and the second at 1652°F (900°C). In addition, two coarse grained intercritical microstructures were simulated using furnace heating, i.e., after an initial oil quench from 2372°F (1300°C), material was reheated to 1337°F (725°C) or 1490°F (810°C), held for ½ hour and re-quenched. All simulated HAZ materials were given a simulated PWHT of 25 hours at 1139°F (615°C) prior to thermal aging.

The aging behavior of simulated fine and coarse grained HAZ of A533B plate is illustrated in Figure 2-6 and Figure 2-7. Prior to aging, the DBTT values of simulated fine or coarse grained

HAZ are lower than that of mid-thickness position of the quenched and tempered plate. Aging at 572°F (300°C) produced no detectable changes in mechanical and Charpy impact properties in both the coarse or fine grained HAZ up to 20,000 hours. Aging at 752°F (400°C) for 20,000 hours caused DBTT of the coarse grained HAZ to increase to 212°F (100°C) from –58°F (–50°C) with no indication of saturation, but with little changes in USE and the mechanical properties. Similar observations were made in case of the fine grained HAZ, although aging at 752°F (400°C) for 20,000 hours produced much less DBTT increase. The embrittlement is generally accompanied by an increase in the proportion of low-temperature intergranular failure from impact testing. The simulated refined grained HAZ exhibited considerable variation in DBTT prior to aging with fracture appearance entirely transgranular cleavage. Aging at 572°F (300°C) and 752°F (400°C) produced no detectable changes in the refined grained HAZ. The simulated intercritical HAZ microstructures had DBTT values similar to those of the coarse and fine grained HAZ. Because aging at 842°F (450°C) produced an increase of 35-40°C in its DBTT, the simulated intercritical HAZ is considered to be more resistant to thermal aging embrittlement than coarse grained HAZ.

Previous studies of such low alloy steels indicated temper embrittlement susceptibility to be markedly dependent on prior austenite grain size and impurity content, increasing with increasing grain size and the presence of specific impurities, in particular P, but also As, Sb, Sn. Results of the observed embrittlement behavior in simulated HAZ are consistent with the degree of segregation occurring during isothermal heat treatments. Phosphorus was detected on the intergranular fracture surface of specimens aged at 752, 842, and 932°F (400, 450, and 500°C). The level of grain boundary segregation of phosphorus was found to be a function of aging temperature and time.

Hence, the coarse grained region of the HAZ resulting from welding is considerably more susceptible to temper embrittlement than the parent materials. Significant increases in transition temperature induced by slow cooling from PWHT are conceivable in pressure vessel steels when aged at temperatures at 752°F (400°C). Based on the experimental data, a temper embrittlement model based on the phosphorus segregation was developed. This model is based on McLean's model of equilibrium segregation. The aging kinetics of this model at different temperatures is illustrated in Figure 2-8. From this model, the increases in DBTT of the A533B plate (containing 55ppm P) from aging at 617°F (325°C) for 40 year end-of-life (40 design life denotes 32 EFPYs or ~$3x10^5$ hours) embrittlement were estimated below.

Material	**Estimated Increase in DBTT**
Simulated coarse grained HAZ	75-100°C
Base materials	≤ 10°C
Simulated fine grained HAZ	~30°C
Simulated refined grained HAZ	≤ 10°C
Simulated Intercritical HAZ	~ 30°C
Actual HAZ	~ 30°C
Actual weld metal	≤ 10°C

It needs to be noted that the embrittlement kinetics are affected by factors such as bulk phosphorus and other impurity element content, grain sizes, and product forms. Although the exact lower cut-off temper embrittlement temperature is difficult to define, the above aging data indicate that the thermal aging embrittlement is rather insignificant at temperatures 617°F (325°C) or lower.

In 2001, Nanstad and co-workers reported short term thermal aging results for reactor vessel steels [32]. Typical reactor pressure vessel steels such as A-302 Gr. B, A-533 Gr. B and A-508 Class 2 were heat treated to introduce coarse grain HAZ from typical weld pass. These materials were annealed at 750, 842, and 900°F (399, 450, and 482°C) for 168 hours to simulate an reactor pressure vessel annealing procedure. Aging at 399°C (750°F) for 168 hours resulted in changes in DBTT of all four material tested. However, aging at 450 and 482°C caused a noticeable increase in DBTT in the coarse grained HAZ. Nanstad et al. suggested 900°F (399°C) as a lower-bound aging temperature for temper embrittlement in coarse grain regions of HAZ in reactor pressure vessel steels. However, a duration of 168 hours is considered too short to establish the 900°F as a lower-bound embrittlement temperature during the PWR lifetime.

For domestic commercial PWRs, the highest operating temperature in the RCS would be ~650°F (~343°C) for the pressurizer. Hence, the most susceptible region to thermal aging embrittlement is expected to be the HAZ in the low alloy shell material next to the weldment. However, there is little long term aging data at 650°F, especially of HAZ. An embrittlement model (see Figure 2-8) based on thermally activated equilibrium segregation of phosphorus indicated significantly higher thermal aging embrittlement at 662°F (350°C) than 572°F (300°C). Although the lower end of temper embrittlement temperature range for low alloy steels has been generally estimated to be 707 to 752°F (375 to 400°C), it appears that an increase in DBTT exceeding 75-100°C is possible for a coarse grained HAZ with impurities near the higher end of allowable range, and operating at temperatures around 650°F.

2.2 Thermal Aging of Low Alloy Bolting Materials

High strength low alloy (HSLA) bolting materials such as SA-193 Gr. B7, SA-320 Gr. L43, and SA-540 Gr. B23 and B24 have been used for reactor vessel closure studs and steam generator manway studs in domestic PWRs [33]. The required chemical composition is listed in Table 2-10. The chemical composition of SA-193 Gr B7 and SA-320 Gr. L43. are equivalent to AISI 4140, 4340, 4340-H, and 4340-Mod respectively. The required mechanical properties are listed in Table 2-1. AISI 4140 is classified as a Cr-Mn steel and AISI 4340, 4340-H, and 4340 mod are classified as Ni-Cr-Mo steel. Compared to carbon and low alloy steel plate and forging used for the reactor vessel, these bolting materials contain higher amounts of carbon, nickel, and chromium. The additional carbon, chromium, and nickel contents in these alloys further increase their hardenability, strength, and wear resistance. This allows them to be oil-quenched to form martensite instead of water quenching. The slower oil quench reduces temperature gradients and internal stresses, distortion, and cracking tendencies. However, the addition of Cr to low alloys steels tend to increase its susceptibility to temper embrittlement under certain conditions. The general heat treatment procedures for these materials are austenizing, followed by liquid-quenching and tempering. Typical austenizing temperature for these alloys is ~1562°F (850°C). The microstructures following oil quenching is martensitic with some possible retained austenite.

The temper embrittlement afflicting such high-strength low alloy steels is called tempered martensitic embrittlement (TME), also called the one-step temper embrittlement. In the temper embrittlement discussed above to low alloys forging and plates, the steel is usually tempered at relatively higher temperature of 1200°F (650°C) producing lower strength and hardness, and embrittlement occurs upon slow cooling or prolonged exposure to (707-1112°F) 375-600°C (two-step embrittlement). In TME, the as-quenched material is improperly tempered at relatively low temperature of ~662°F (350°C, hence also known as 350°C embrittlement) which could result in sharp drop in room temperature impact fracture energy. The exact mechanisms of TME is not completely understood. The requisite of segregation of impurities, such as phosphorus, sulfur, and nitrogen to prior austenite grain boundaries for TME and higher susceptibility for the coarse grained microstructure are very similar to the two-step temper embrittlement. However, TME has been traditionally characterized by a drop in room temperature Charpy impact energy instead of using the multi-temperature transition curve, i.e., decrease in DBTT and USE. Experiments show that the susceptibility of impact energy for high purity AISI 4340 is much less than that for commercial purity AISI 4340 (see Figure 2-9) [34]. A feature unique to TME is embrittlement coinciding with the beginning cementite precipitation. The presence of undissolved carbides at the prior austenite grain accentuates the intergranular fracture. Figure 2-10 illustrates the influence of tempering temperature (for 1 hour) on the mechanical and impact properties of a AISI 4340 steel that was oil quenched [34]. Embrittlement failures of HSLA have been routinely attributed to TME (improper heat treatment during fabrication). In 1973, NRC issued Regulatory Guide 1.65 which stated the SA-320 Gr. L43 and SA-193 Gr. B7 reactor vessel closure studs become increasing susceptible to SCC if they are heat treated to a tensile strength above 170 ksi. The purpose of the regulatory guide was to prevent improper tempering at lower than the required tempering temperatures, not in-service degradation.

The specified minimum tempering temperature is 1100°F for SA-193 Gr. B7 and 800°F for SA-540 Gr. B23 and B24. The exact tempering temperatures varies according to the required final tensile strength level and could be higher than the minimum. Because of the minimum tempering temperature required to prevent TME, it should not be a concern for the low alloy bolting materials. On the other hand, should thermal aging embrittlement develop during service at ~500°F, it would not be considered the "one-step temper embrittlement", i.e., TME. Regardless of the nomenclature, the long term thermal aging embrittlement of these bolting materials at elevated temperatures in PWRs has not been studied and there is little data. However, the reported embrittlement findings in the two cracked reactor head closure studs at a BWR in 1989 indicate that the potential for thermal aging embrittlement during service exists. The failure mechanism was attributed to stress corrosion cracking (SCC). The SCC is postulated to have developed due to exposure to oxygenated water during an outage in the ~2 weeks prior to heat-up while the studs were in tension.

The cracked 6 inch dia. studs in that BWR were fabricated to the requirements of SA-320, Gr. L43 (AISI 4340) [35]. The chemical analysis of the two cracked studs is listed in Table 2-11. The operating temperature of stud at the reactor flange was estimated to be 500°F. The two studs had accumulated approximately 120,000 hours before being removed. The fabrication records indicate that the studs were quenched from 1550°F and tempered at 1020°F. The mechanical test results of the studs in the as-received condition are listed in Table 2-10, which show that the tensile and yield strengths increased by 15-17 ksi, and the Charpy impact energy (+10°F) dropped by 25 ft-lb during service. A re-heat treatment, quenching from 1600°F and tempered at 1200°F restored the impact toughness and tensile properties to approximately the CMTR levels. However, subsequent aging at 500°F for up to 5,000 hours did not cause any change in the tensile properties, except a small (4 to 5 ft-lb) drop in impact energy. This apparent lack of aging degradation was postulated due to insufficient aging time and/or a more severe quenching of the re-heat treatment which resulted in less retained austenite (hence less potential to form untempered martensite). The cause of the embrittlement in the failed stud is believed to be derived from two sources, the precipitation and coarsening of cementite, and the transformation of some retained austenite into untempered martensite during prolonged exposure to 500°F. Research indicates that the lowering of carbon content from precipitation of interlath carbides at 500°F promotes the transformation of retained austenite into untempered martensite.

2.3 Conclusions

The thermal aging embrittlement potential of carbon and low alloy steels in PWRs can be divided into two separate categories based on the composition and usage: (a) plate, forging, welds, and HAZ for reactor vessel, pressurizer, and steam generator shells; (b) high strength low alloy bolting materials. The following conclusions and recommendation are reached for the two categories:

2.3.1 Low alloy steel plate, forging, welds, and HAZ

1. For low alloy steel plate, forging, welds, and HAZ, the two possible thermal aging mechanisms are temper embrittlement and strain aging embrittlement. Temper embrittlement, also being called two-step temper embrittlement, is due to diffusion and segregation of impurity elements, such as phosphorous, tin, antimony, and arsenic into grain boundaries after prolonged exposure to temperatures in the 707-1112°F (375-600°C) temperature range. Strain aging in low alloy steels result from interactions between dislocations and the interstitial atoms of nitrogen and carbon. Strain aging embrittlement is insignificant for carbon and low alloys steels used in PWRs. This leaves temper embrittlement as the only long term thermal degradation mechanism.
2. Studies of thermal aging embrittlement of carbon and low alloys steels have been limited to reactor vessel steels, welds, and HAZ. Results of these studies show that the long term thermal aging embrittlement of reactor vessel steels and welds at PWR temperatures at 572°F (300°C) is very modest, 0-50°C. Thermal aging embrittlement is most pronounced in the coarse grained HAZ. For a A-533 Gr. B plate containing high amount of 55ppm phosphorus and exposed to 617°F (325°C), the end-of-40year-life increase in DBTT has been estimated to be 75-100°C. A shift of 75-100°C in DBTT, which remains considerably below the PWR operating temperatures, is not considered a concern. Hence, for the vast majority of low alloy steel components, welds and HAZ, their susceptibility to long term thermal aging embrittlement is not expected to be a concern.
3. For domestic commercial PWRs, the highest operating temperature in the RCS would be ~650°F (343°C) for the pressurizer. Hence, the most susceptible place to thermal aging embrittlement is expected to be the HAZ in the low alloy shell material next to the weldment. However, there is little long term aging data at 650°F, especially of HAZ. Embrittlement models based on thermally activated equilibrium segregation of phosphorus indicated long term thermal aging embrittlement may be significantly higher at 350°C than 300°C at the end of the 40-year design life, although the lower end of temper embrittlement temperature range for low alloy steels has been estimated to be 707 to 752°F (375 to 400°C). It appears that an increase in DBTT exceeding 75-100°C is possible for a coarse grained HAZ with impurities near the higher end of allowable range, and operating at temperatures around 650°F.

2.3.2 For HSLA bolting materials

1. High strength low alloy bolting materials AISI 4340 and 4140 (SA-193 Gr. B7, SA-320 Gr. L43, and SA-540 Gr. B23 and B24) have been used for reactor vessel closure studs and steam generator manway studs in domestic PWRs. Compared to carbon and low alloy steel forgings and plates used in PWRs, these bolting materials contain higher amount of carbon, nickel, and chromium, which increase their hardenability, strength, and wear resistance. The embrittlement due to improper heat treatment for HSLA materials is called tempered martensitic embrittlement (TME) or the one-step temper embrittlement. Embrittlement failures of HSLA studs have usually been attributed to TME. Because of the minimum tempering temperature required to prevent TME, it should not be a major concern for the low alloy bolting materials. By definition, TME is not an aging embrittlement mechanism.

2. The long term aging effect of low alloy bolting materials at their exposure temperatures in PWRs has not been studied and there is little aging degradation data in the open literatures. However, the finding of two cracked reactor head closure studs at a BWR in 1989 indicates that the potential thermal aging embrittlement during service exists. The embrittlement is believed deriving from two mechanisms, the precipitation and coarsening of cementite and the transformation of some retained austenite into untempered martensite during prolonged exposure to 500°F. Research indicates that the lowering of carbon content from precipitation of interlath carbides at 500°F promotes the transformation of retained austenite into untempered martensite.

2.4 Recommendations

2.4.1 Low alloy steel plate, forging, welds, and HAZ

The effect of thermal aging embrittlement on the shell materials of PWR pressurizers can be evaluated in the same fashion as the reactor vessel embrittlement due to neutron irradiation. The effect of embrittlement due to neutron irradiation is well studied and currently is evaluated in accordance with Reg. Guide 1.99, Rev. 2 [36]. Since the ASME Code fracture toughness is indexed by the material parameter RTNDT, Reg. Guide 1.99, Rev. 2 provides a formula to include this irradiation embrittlement effect in the following form:

$$\text{Adjusted } RT_{NDT} = \text{Initial (unirradiated) } RT_{NDT} + \Delta RT_{NDT} + \text{Margin}$$

The term ΔRT_{NDT} is the additional shift term due to irradiation induced embrittlement, which can be as high as approximately 140°F for the end of extended life of 60 years for the beltline of reactor pressure vessel materials, based on the following:

Adjusted RT_{NDT} = 270°F (PTS screening criteria)
Initial (unirradiated) RT_{NDT} = 60°F (approximately the worst heat being observed)
Margin = 65°F

For the long-term thermal aging of pressurizer shell materials with no appreciable embrittlement due to neutron irradiation, the shift (ΔRT_{NDT}) due to thermal aging can be accommodated is therefore approximately 140°F. Hence, the following tests is recommended on a section of pressurizer shell that have seen the highest temperature i.e. 650°F from a decommissioned pressurizer.

Most direct measurement of long-term aging embrittlement can be made by comparing transition range fracture toughness of an aged material to that of un-aged material. This can simply be accomplished by comparing T_0 values from the Master Curve method in accordance with ASTM E1921-02 standard. Actual theoretical background and applications are documented in PWRMRP-26 [37].

The testing requires about 10 Charpy sized specimens with EDM notches with fatigue pre-cracking per product form (base metal, HAZ, and weld). Three point bending tests will be performed using these specimens with the resulting K_{Jc} values used for determining T_0 value of the material. Another set of 10 Charpy sized specimens are needed to establish a T_0 value for a un-aged material. This can be done by cutting another section from the same shell that has not been exposed to long-term thermal aging. If this is not feasible, a T_0 from a similar material can be used from the literature. The T_0 shift between aged and un-aged material is very good indicator for thermal aging embrittlement, better than a Charpy shift value because T_0 shift is a direct measurement of fracture toughness in the ductile-to-brittle transition range. If the shift (ΔRT_{NDT}) is less than 140°F, then thermal aging embrittlement is not a concern for PWR pressurizers and similar low alloy steels in the PWRs. It is also desirable to perform multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact testing to verify thermal aging embrittlement or the lack of it.

2.4.2 For HSLA bolting materials

It is recommended that multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact tests on HSLA bolting materials removed from PWRs or BWRs. The selected components should have operating temperature among the highest for this class of materials and should have accumulated substantial operating time, e.g., more than 100,000 hours. One possible specimen source is stuck reactor vessel head closure studs from units whose closure head operating temperatures is near 600°F. The test results will either show lack of thermal aging embrittlement or establish the extent of the thermal aging embrittlement from long-term exposure to the operating temperature. It is important that, in case of results indicating thermal aging embrittlement, the possibility of embrittlement due to the initial mis-heattreatment can be ruled out. Hence, specimens should be removed from HSLA bolting materials with known initial mechanical and impact properties. If the DBTT transition temperature exceeds the room temperature and/or the loss of room temperature impact energy exceeds 50%, the material could be considered susceptible to thermal aging embrittlement.

However, unlike the reactor vessel materials, there is no criteria or guidelines regarding how much embrittlement in terms of transition temperature shift or loss of fracture toughness can be tolerated for HSLA bolting materials without undermining the safety. Hence, in case the material is susceptible to thermal aging embrittlement, a thermal aging program will be needed to establish the screening criteria based on operating temperature and time and to develop guidelines for safety assessment. One approach is to perform fracture toughness tests (K_{Ic} or J_{Ic}) and evaluate the critical flaw size for these components based on fracture mechanics. Because HSLA bolting components are typical outside the pressure boundary, it is possible that replacement would be preferable to safety analysis based on fracture mechanics.

Table 2-1
Chemical Requirements of Carbon and Low Alloy Steels Used in PWRs [1-12]

Material Type	C	Mn	P	S	Si	Mo	Ni	Cr	V
SA-105 Gr. I & II Pipe flange & Fitting	0.35 max	0.90 max	0.05 max	0.05 max	--	--	--	--	--
SA-106 Gr. B & C Seamless pipe	Gr. B 0.30 max Gr. C 0.35 max	0.29-1.06	0.048 max	0.058 max	0.10 max	--	--	--	--
SA-194 Gr. 2H Bolting	0.40 min	--	0.040 max	0.050 max	--	--	--	--	--
SA-212 Gr. B Plate	0.31 max, up to 1 in. thick 0.33 max, 1 to 2 in. thick 0.35 max, 2 to 8 in. thick	0.90 max	0.035 max	0.04 max	0.15-0.30	--	--	--	--
SA-216 Gr. WCB Casting	0.30 max	1.00 max	0.05 max	0.06 max	0.60 max	0.25 max	0.50 max	0.50 max	Cu 0.50 max
A-234 Gr. WPB Fitting	0.30 max	0.29-1.06	0.050 max	0.058 max	0.10 min	--	--	--	--
SA-515 Gr. 70 Plate	0.31 max, up to 1 in. thick 0.33 max, 1 to 2 in. thick 0.35 max, 2 to 8 in. thick	1.20 max	0.035 max	0.035 max	0.15-0.40	--	--	--	--
SA-516 Gr. 70 Plate	0.27 max, up to ½ in thick 0.28 max, ½ to 2 in. thick 0.30 max, 2 to 4 in. thick 0.31 max, over 2 in. thick	085-1.20	0.035 max	0.035 max	0.15-0.40	--	--	--	--
SA-508, Class 2 Forging	0.27 max	0.50-0.80	0.025 max	0.025 max	0.15-0.35	0.55-0.70	0.50-0.90	0.25-0.45	0.05 max
SA-302, Gr. B Plate	0.20 max, up to 1 in. thick 0.23 max, 1 to 2 in. thick 0.25 max, over 2 in. thick	1.15-1.50	0.035 max	0.040 max	0.15-0.30	0.45-0.60	--	--	--
SA-533, Gr. B Plate	0.25 max	1.15-1.50	0.035 max	0.040 max	0.15-0.30	0.45-0.60	0.40-0.70	--	--
SA-320 Gr. L43 ***Bolting (AISI 4340)***	0.38-0.43	0.60-0.85	0.04 max	0.04 max	0.20-0.35	0.20-0.30	1.65-2.00	0.70-0.90	--
SA-193 Gr. B7 (AISI 4140) Bolting	0.38-0.48	0.75-1.00	0.04 max	0.04 max	0.20-0.35	0.15-0.25	--	0.80-1.10	--
SA-540 Gr. B23, Bolting (AISI 4340H)	0.37-0.44	0.60-0.95	0.025 max	0.025 max	0.20-0.35	0.20-0.30	1.55-2.00	0.65-0.95	--
SA-540 Gr. B24, Bolting (4340 Mod)	0.37-0.44	0.70-0.95	0.025 max	0.025 max	0.20-0.35	0.30-0.40	1.65-2.00	0.70-0.95	--

Table 2-2
Chemical Composition and Heat Treatment of A302 Gr. B Plate [20]

C	Mn	Si	P	S	Ni	Cr	Mo	Al	V	Cu	Ti
0.20	1.31	0.25	0.012	0.023	0.20	0.17	0.47	0.02	0.03	0.20	--
Austenitized 1650°F (899°C) for 2h, Water quench, Tempered 1200°F (649°C) for 6h, Furnace cool to below 600°F (316°C).											

Table 2-3
Chemical Composition of PWR RV Steels and Weld Metal [25]

		C	Mn	Mo	Ni	Si	Cr	P	S	Cu	V	As	Sb	Sn	W	Co	Ti	Al	N
A533B Plate	0T	0.18	1.43	0.48	0.57	0.30	0.11	0.005	0.005	0.11	<0.01	0.02	<0.01	0.02	<0.01	0.02	<0.01	0.03	0.012
	0.5T	0.21	1.43	0.48	0.57	0.22	0.11	0.005	0.005	0.11	<0.01	0.02	<0.01	0.02	<0.01	0.02	<0.01	0.03	0.013
A508 Forging 1	0.91W	0.23	1.49	0.49	0.79	0.30	0.08	0.008	0.004	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.02	0.011
	0.7W	0.20	1.42	0.46	0.75	0.28	0.08	0.007	0.004	0.05	<0.01	<0.01	<0.01	<0.01	NA	0.01	<0.01	0.02	0.008
A508 Forging 2	0.5T	0.22	1.36	0.49	0.71	0.24	0.11	0.006	0.004	0.06	<0.01	<0.01	<0.01	0.02	<0.01	0.01	<0.02	0.03	0.0086
A508 Forging 3	0.95W	0.19	1.38	0.52	0.73	0.25	0.24	0.006	0.009	0.07	0.04	0.02	<0.005	0.03	0.02	0.02	<0.01	0.03	0.0096
	0.5W	0.16	1.36	0.51	0.71	0.25	0.24	0.007	0.008	0.07	0.04	0.02	<0.005	0.01	0.02	0.01	<0.01	0.03	0.0096
Weld Metal		0.13	1.41	0.56	0.05	0.47	0.03	<0.003	0.016	0.04	<0.01	<0.02	<0.005	<0.005	<0.01	<0.01	0.09	<0.005	0.003
Real HAZ																			
-Forging		0.17	1.54	0.53	0.78	0.26	0.22	<0.003	0.012	0.06	<0.01	<0.02	<0.005	<0.005	<0.01	0.02	0.01	0.04	0.009
-Adjacent weld metal		0.057	1.59	0.60	0.47	0.40	0.03	0.006	0.013	0.08	<0.01	0.04	<0.005	<0.005	<0.01	0.03	0.01	0.01	0.010

Table 2-4
Charpy V-Notch Impact Properties Prior to Thermal Aging [25]

	150mm (5.9 in) A533B Plate				545mm (21.5 in) A508 Forging 1*			510mm (20 in) A508 Forging 2	235mm (9¼ in) A508 Forging 3	
	PWHT		Non-PWHT							
	0T	0.5T	0T	0.5T	1W	0.9W	0.7W	0.5W	1W	0.5W
DBTT, °C	-52	-5	-40	-26	-44	-34	-13	10	5	-2
USE, J/cm^2	280	189	230	185	228	249	256	202	161	207

* Results from ½ size Charpy specimens

Prior to aging, Forging 1 and 3 were given PWHT at 112-1148°F (600-620°C); Forging 2 was studied both with and without a PWHT at 1112-1148°F (600-620°C).

Table 2-5
Chemical Composition and Heat Treatment of Thermal-Aged Surveillance Materials [27, 28]

	C	Mn	P	S	Si	Ni	Cr	Mo	Cu
SA-533B, Plate A	0.21	1.32	0.010	0.016	0.20	0.52	0.19	0.57	0.15
SA-533B, Plate B	0.23	1.39	0.013	0.013	0.21	0.64	--	0.50	0.17
SA-508B, Forging	0.24	0.72	0.014	0.012	0.21	0.76	0.34	0.62	0.02
Submerged Arc Weld, A	0.09	1.49	0.016	0.016	0.51	0.59	0.06	0.39	0.28
Submerged Arc Weld, B	0.08	1.63	0.017	0.012	0.61	0.58	0.10	0.39	0.30

	Heat Treatment Prior to Aging
SA-533B, Plate A	Austenitized 899-927°C (1650-1700°F) for 1h/in, Water quench, Tempered 649°C (1200°F) for 1h/in, Air cool, Stress-relieved 593-621°C (1100-1150°F) for 29 h, Furnace cool
SA-533B, Plate B	Austenitized 829-913°C (1525-1675°F) for 4h, Water quench, Tempered 649-677°C (1200-1250°F) for 4h, Furnace cool, Stress-relieved 593-621°C (1100-1150°F) for 40h, Furnace cool
SA-508B, Forging	Austenitized 854-877°C (1570-1610°F) for 4h, Water quench, Tempered 666-688°C (1230-1270°F) for 10h, Water quench, Stress-relieved 593-621°C (1100-1150°F) for 30h, Furnace cool
Submerged Arc Weld, A	Stress-relieved 593-621°C (1100-1150°F) for 29h, Furnace cool
Submerged Arc Weld, B	Stress-relieved 593-621°C (1100-1150°F) for 30h, Furnace cool

Table 2-6
Charpy V-notch Impact Test Results of Thermal Aging Surveillance Materials [27, 28].

Material	Thermal Aging Condition	41J (30ft-lb) Transition Temperature °C (°F)	Upper-Shelf Energy J (ft-lb)
SA-533B, Plate A	Unaged	-2 (+29)	110 (81)
	Aged 93,000 hours at 280°C (536°F)	-6 (+22)	114 (84)
	Aged + Anneal 343°C (650°F) for 168 hours	-7 (+20)	103 (76)
	Aged + Anneal 454°C (850°F) for 168 hours	-8 (+17)	111 (82)
SA-533B, Plate B	Unaged	-1 (+30)	136 (100)
	Aged 93,000 hours at 280°C (536°F)	+9 (+48)	130 (96)
	Aged + Anneal 343°C (650°F) for 168 hours	+7 (+45)	130 (96)
	Aged + Anneal 454°C (850°F) for 168 hours	-7 (+20	111 (82)
SA-508B, Forging	Unaged	-34 (-29)	198 (146)
	Aged 103,000 hours at 282°C (540°F)	-33 (-28)	187 (138)
	Aged + Anneal 343°C (650°F) for 168 hours	-8 (+17)	187 (138)
	Aged + Anneal 454°C (850°F) for 168 hours	-10 (+14)	179 (132)
Submerged Arc Weld, A	Unaged	-3 (+26)	88 (65)
	Aged 93,000 hours at 280°C (536°F)	-11 (+12)	98 (72)
	Aged + Anneal 343°C (650°F) for 168 hours	-6 (+21)	108 (80)
	Aged + Anneal 454°C (850°F) for 168 hours	-12 (+10)	99 (77)
Submerged Arc Weld, B	Unaged	+4 (+40)	84 (62)
	Aged 103,000 hours at 282°C (540°F)	+4 (+39)	81 (60)
	Aged + Anneal 343°C (650°F) for 168 hours	-7 (+19)	90 (66)
	Aged + Anneal 454°C (850°F) for 168 hours	+10 (+50)	84 (62)

Table 2-7
Chemical Composition and Heat Treatment of Thermal-Aged Plates and Welds [30].

	Code	Cu	P	Ni	C	Mn	Si	S	Mo	Cr
SA-533 Gr. B, Plate	24G	0.20	0.017	0.63	0.22	1.4	0.19	0.008	0.54	0.19
Linde 80 Weld	WBA	0.37 min 0.42 max	0.010 0.017	0.55 0.68	0.079 0.096	1.27 1.36	0.71 0.79	0.012 0.019	0.42 0.50	0.10 0.13
Linde 0091 Weld	W9B	0.30 min 0.39 max	0.008 0.009	0.62 0.65	0.15 0.16	1.08 1.14	0.28 0.30	0.008 0.008	0.47 0.47	0.12 0.13
Linde 80 Weld	WW7	0.35	0.013	0.10	0.08	1.56	0.60	0.008	0.54	0.12
Linde 124 Weld	73W	0.31	0.005	0.60	0.098	1.56	0.45	0.005	0.58	0.25
		Heat Treatment Prior to Aging								
SA-533 Gr. B, Plate	24G	Austenitized 899°C (1650°F) for 1h/in min., Water quench, Tempered 671°C (1240°F) for 1h/in min., Water quench, Stress-relieved 621°C (1150°F) for 24 h, Furnace cool (56°C/h max.)								
Linde 80 Weld	WBA	Stress-relieved 621°C (1150°F) for 24h, Furnace cool (56°C/h max.)								
Linde 0091 Weld	W9B	Stress-relieved 621°C (1150°F) for 24h, Furnace cool (56°C/h max.)								
Linde 80 Weld	WW7	Stress-relieved 621°C (1150°F) for 24h, Furnace cool (56°C/h max.)								
Linde 124 Weld	73W	Stress-relieved 607°C (1125°F) for 40h, Furnace								

Table 2-8
Charpy V-notch Impact Test Results [30]

		41J (30ft-lb) Transition Temperature °C ()	
		Unaged,	Thermal-Aged at 316°C (600°F) for 5,000 hours
SA-533 Gr. B, Plate	24G	-23°C (-10°F)	-23°C (-10°F)
Linde 80 Weld	W8A	-1°C (30°F)	-1°C (30°F)
Linde 0091 Weld	W9B	-54°C (-65°F)	-48°C (-55°F)
Linde 80 Weld	WW7	-15°C (5°F)	-15°C (5°F)
Linde 124 Weld	73W	-32°C (-25°F)	-32°C (-25°F)

Table 2-9
Chemical Composition of Doel-I and II Thermal-Aged Surveillance Materials [31].

	C	Co	Cr	Mn	Ni	P	S	Si	Mo	Cu
Base	0.147	0.012	0.58	0.96	0.79	0.01	0.01	0.25	0.35	0.085
Submerged Arc Weld	0.066	--	0.08	1.31	0.125	0.016	0.013	0.33	0.484	0.12-0.35

Table 2-10
Requirement of Mechanical Properties, High-Strength Low Alloy Bolting Materials [35]

Heat Treatment	Diameter inch	Charpy	Tensile Strength	Yield Strength	Elong. (2 in)	Red. of Area	Hardness
			ksi, min	ksi, min	%, min	%, min	min.-max.
SA-193, B7 AISI 4140	2 ½ and under 2 ½ to 4 4 to 7	--	125 115 100	105 95 75	16 16 18	50 50 50	--
SA-320, L43 AISI 4340	4 and under	15 ft-lb min, Avg. of 3 (at –150°F or lower)	125	105	16	50	--
SA-540, Gr. B23 & B24* (4340-H & 4340-Mod.)	Up to 6 6 to 8 8 to 9 ½	35 ft-lb min, Avg. of 3 min.(at +10°F)	115	100	15	50	HB 248-298 HB 255-321 HB 262-321
BWR RV Closure Stud CMTR	--	45 avg (at +10°F)	156.8 avg	140.8 avg	18.7 avg	57.8 avg	HRC 31-38
BWR, RV Closure Stud #47 (as removed)	6 in	20.5 avg (at +10°F)	173.0 avg	155.2 avg	18.0 avg	56.5 avg	HRC 34-35
BWR, RV Closure Stud #70 (as removed)	6 in	19 avg (at +10°F)	172.7 avg	157.5 avg	17.0 avg.	57.6 avg	HRC 35-37

* Only the 100 ksi yield strength level is listed in this table.

Table 2-11
Chemical Analysis Results of a BWR Reactor Vessel Closure Stud [35]

Material Type	C	Mn	P	S	Si	Mo	Ni	Cr	V
SA-193 Gr. B7 (AISI 4140) Bolting	0.38-0.48	0.75-1.00	0.04 max	0.04 max	0.20-0.35	0.15-0.25	--	0.80-1.10	--
SA-540 Gr. B23, Bolting (AISI 4340H)	0.37-0.44	0.60-0.95	0.025 max	0.025 max	0.20-0.35	0.20-0.30	1.55-2.00	0.65-0.95	--
SA-540 Gr. B24, Bolting (4340 Mod)	0.37-0.44	0.70-0.95	0.025 max	0.025 max	0.20-0.35	0.30-0.40	1.65-2.00	0.70-0.95	--
SA-320 Gr. L43 Bolting (AISI 4340)	0.38-0.43	0.60-0.85	0.04 max	0.04 max	0.20-0.35	0.20-0.30	1.65-2.00	0.70-0.90	--
CMTR	0.43	0.72	0.010	0.014	0.29	0.26	1.75	0.80	--
Stud 47, as received	0.44	0.65	0.005	0.015	0.27	0.21	1.66	0.75	--
Stud 70, as received	0.44	0.67	0.007	0.012	0.27	0.23	1.69	0.78	--

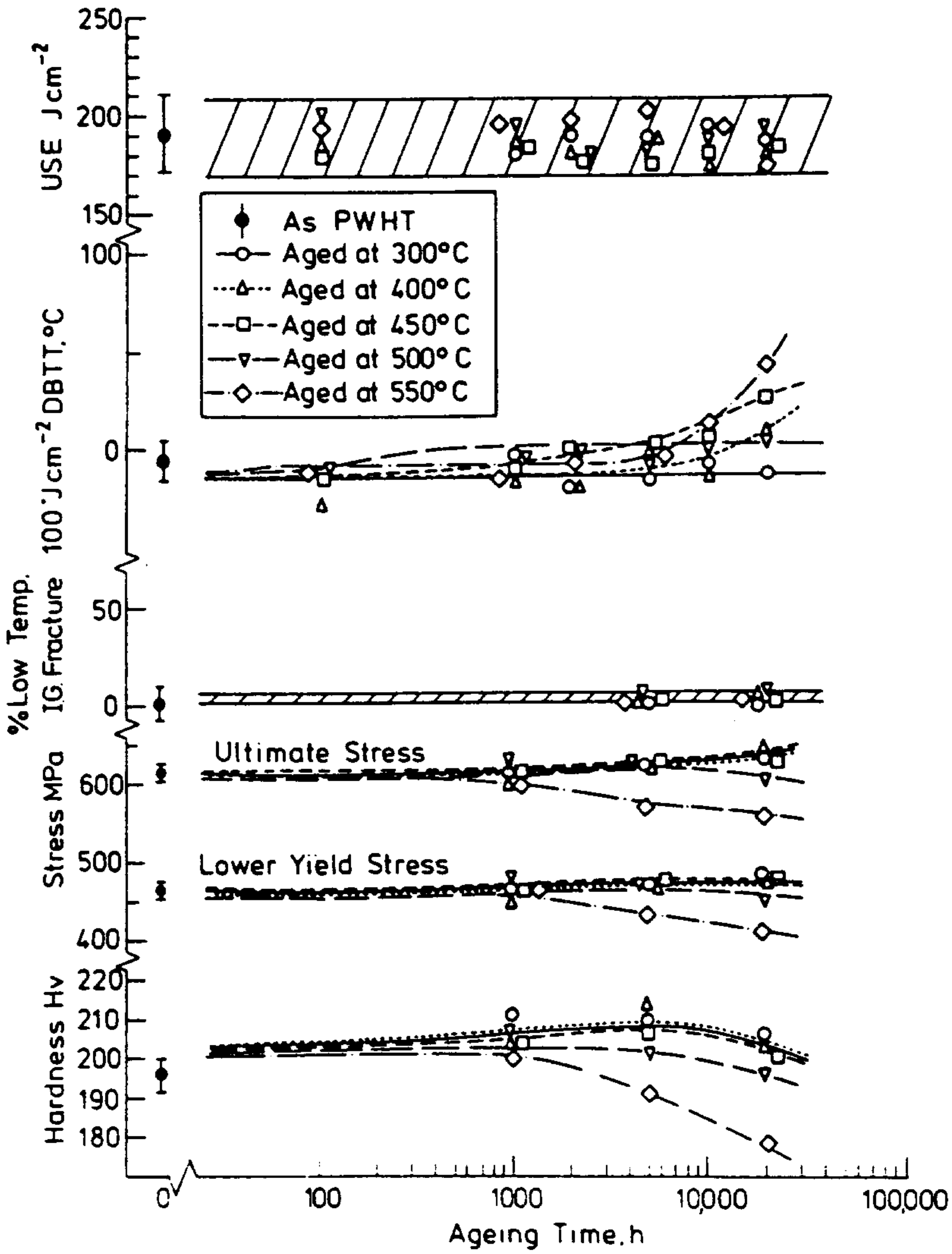


Figure 2-1
Effect of thermal aging at 300°C (572°F) on mechanical properties of A-533 Gr. B plate (Mid thickness position, PWHT) [25].

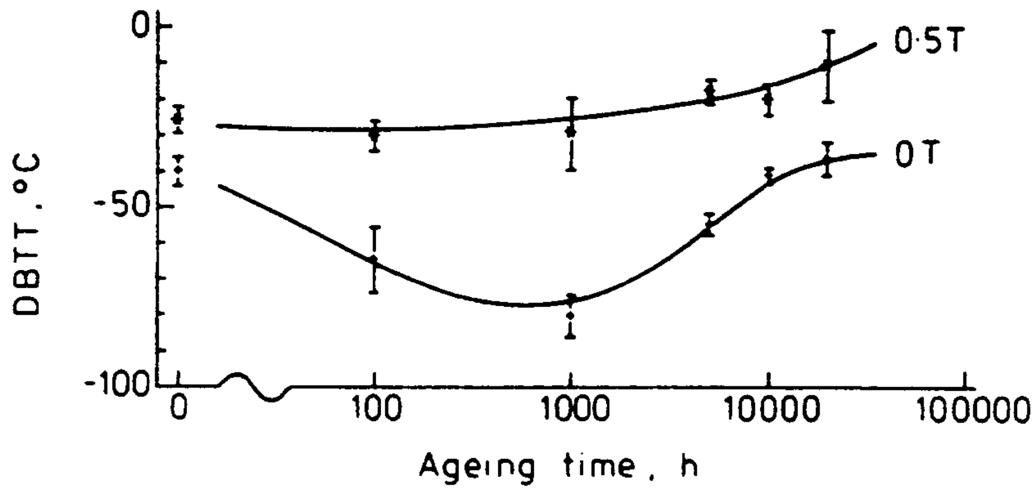


Figure 2-2
Effect of thermal aging at 400°C (752°F) on DBTT of non-PWHT A-533 Gr. B plate at Surface (0T) and Mid-thickness (0.5T) position [25].

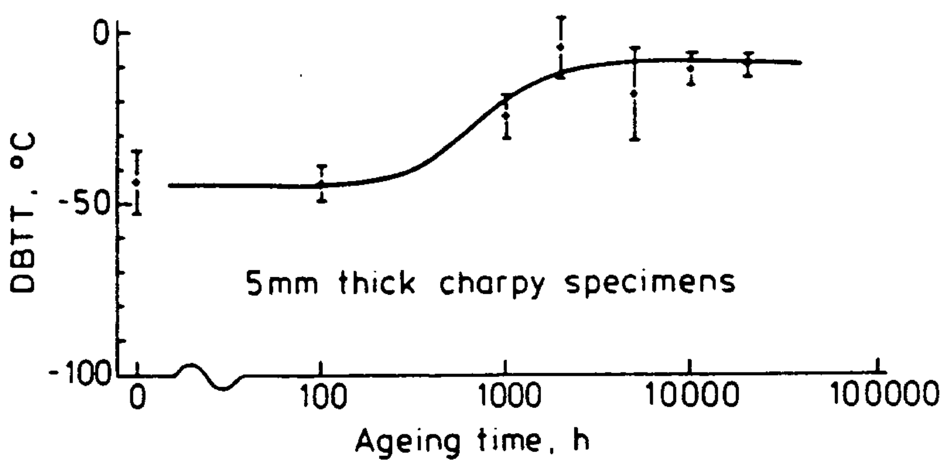


Figure 2-3
Effect of thermal aging at 300°C (572°F) on DBTT of non-PWHT A-508 Class 3 forging [25].

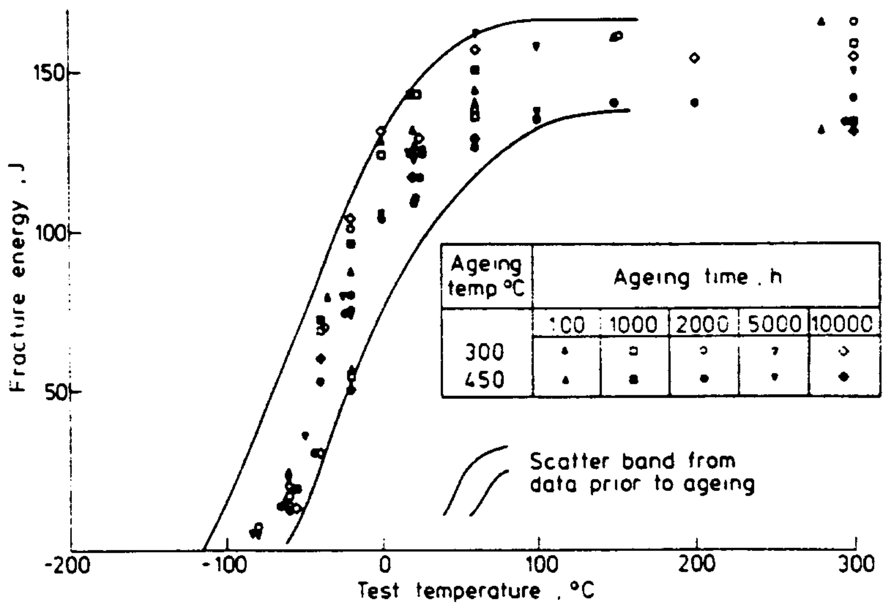


Figure 2-4
Effect of thermal aging at 300°C (572°F) and 450°C (842°F) on Charpy fracture energy of reactor vessel steel weldment [25].

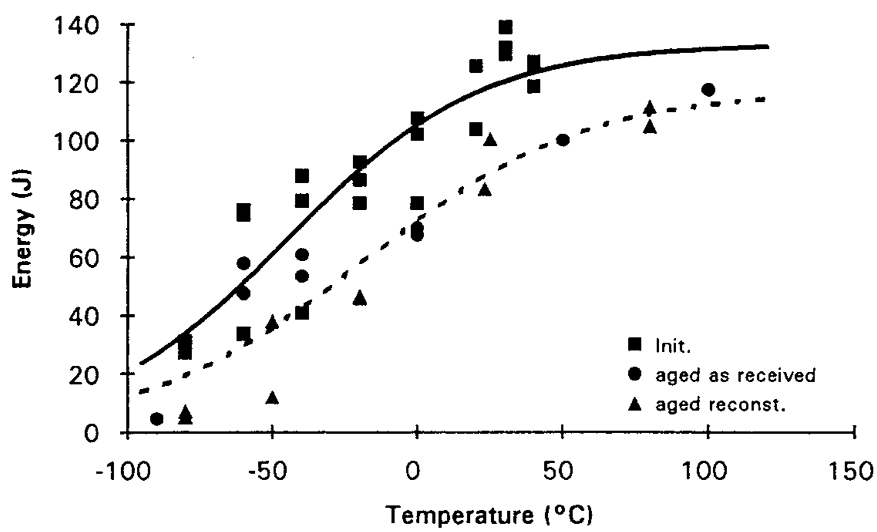


Figure 2-5
Effect of thermal aging at 287°C (549°F) for 63,000 hours on Charpy fracture energy of reactor vessel steel weldment [31].

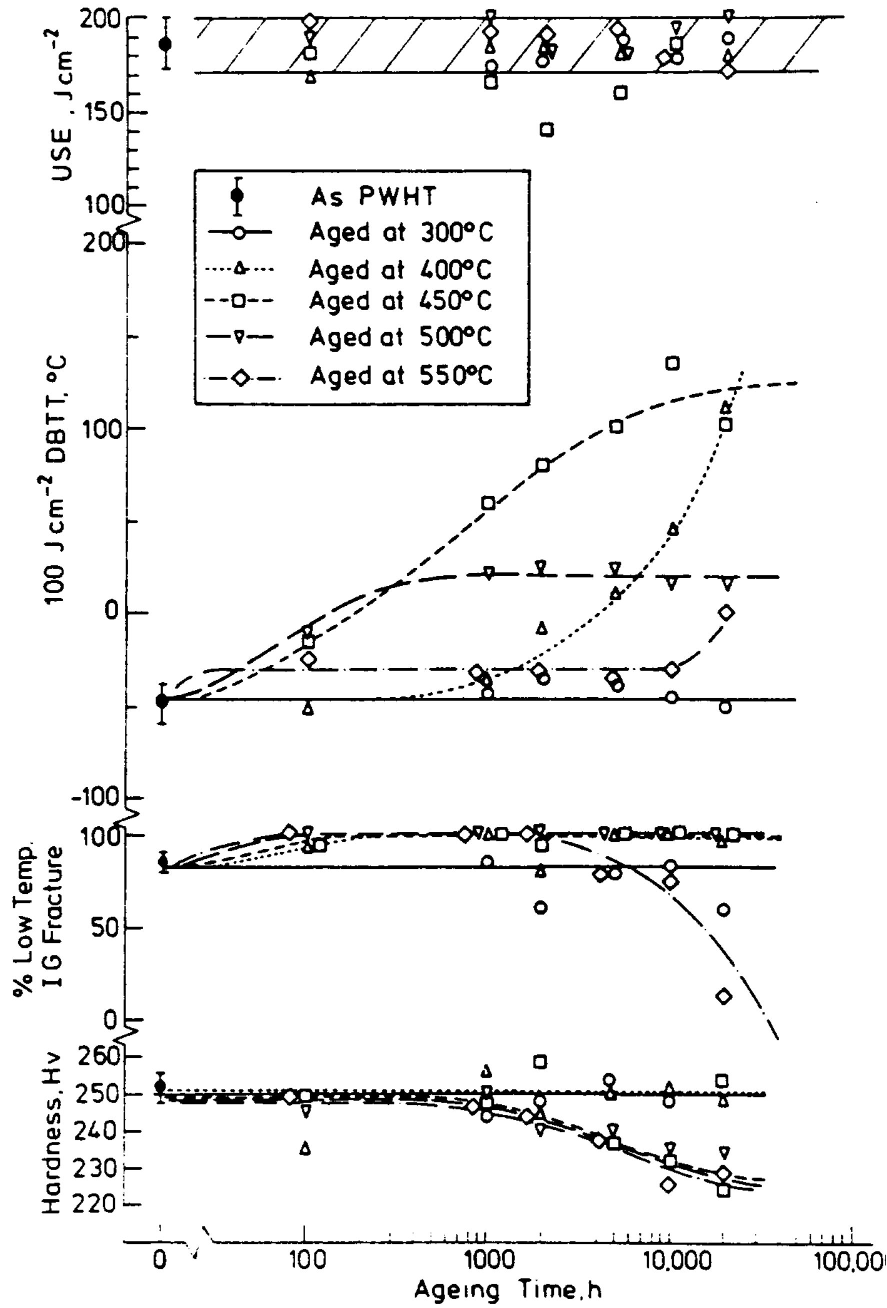


Figure 2-6
Effect of thermal aging on the properties of A-533 Gr. B simulated coarse grained HAZ at various temperatures [25].

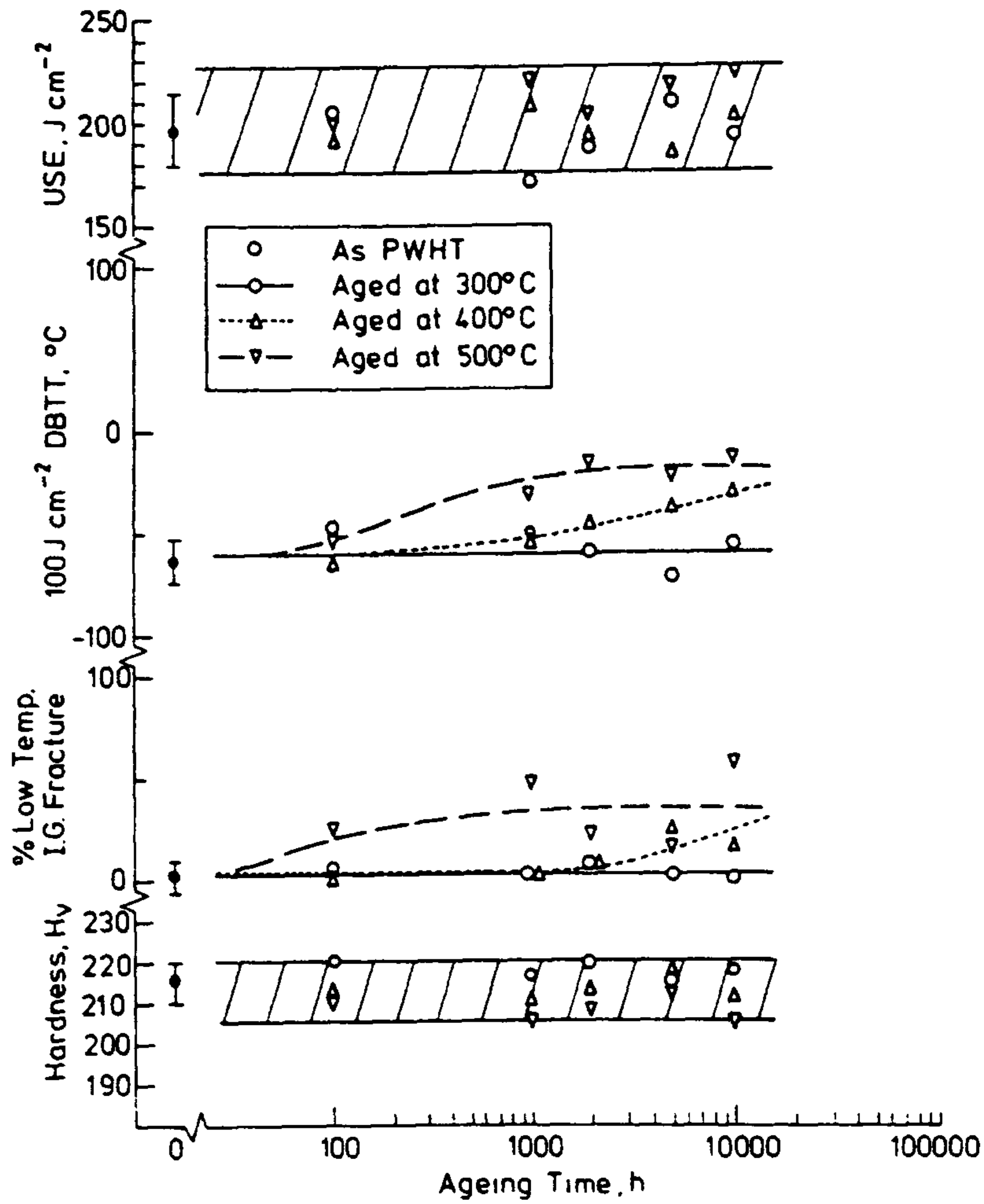


Figure 2-7
Effect of thermal aging on the properties of A-533 Gr. B simulated fine grained HAZ at various temperatures [25].

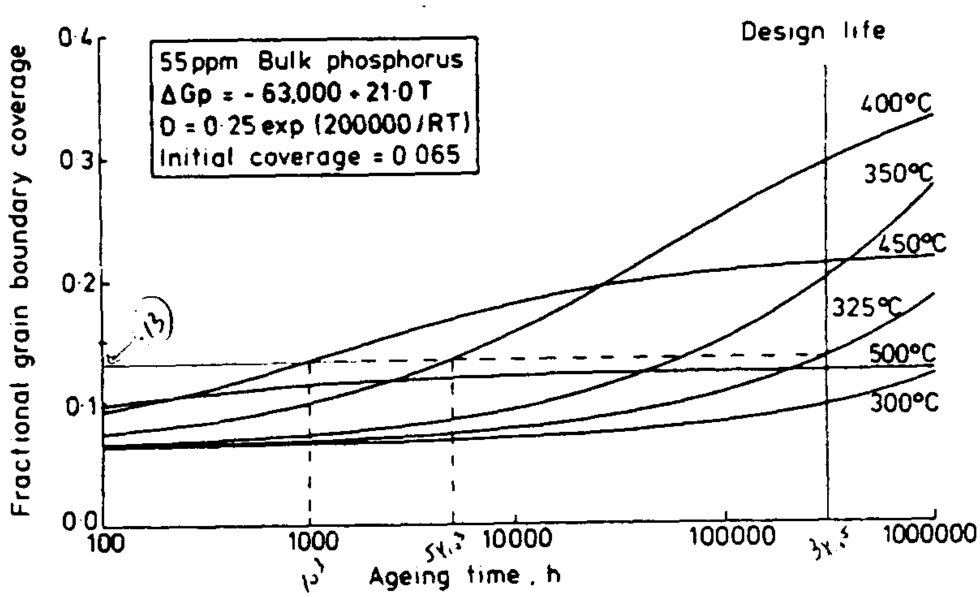


Figure 2-8
Predicted kinetics of phosphorus grain boundary segregation for thermal aging of a coarse grained HAZ containing 55ppm phosphorus between 300 and 500°C. Design life denotes 32 EFPYs or ~3x10^5 hours [25].

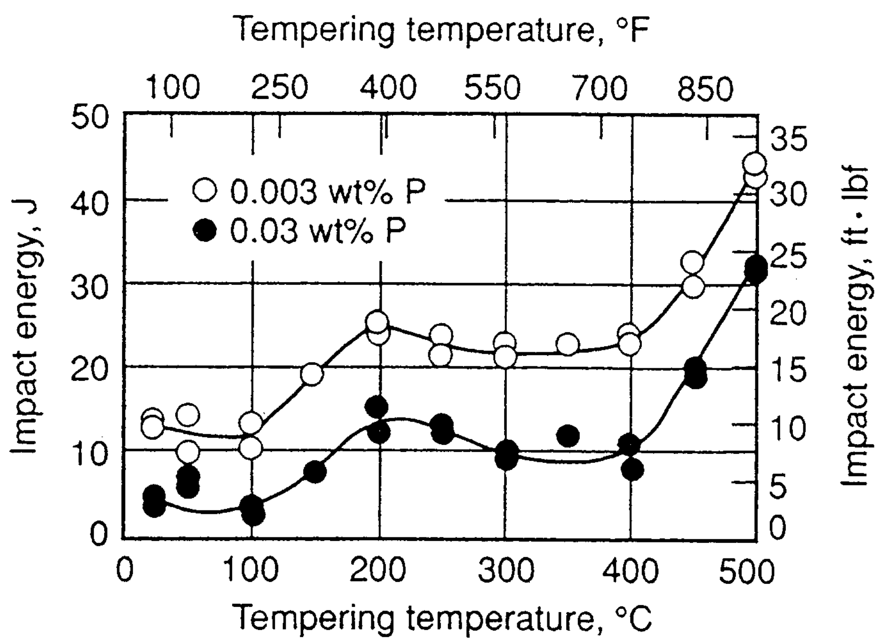


Figure 2-9
The influence of phosphorus on the room-temperature Charpy V-notch impact energy of AISI 4340 steel as a function of tempering temperature [34].

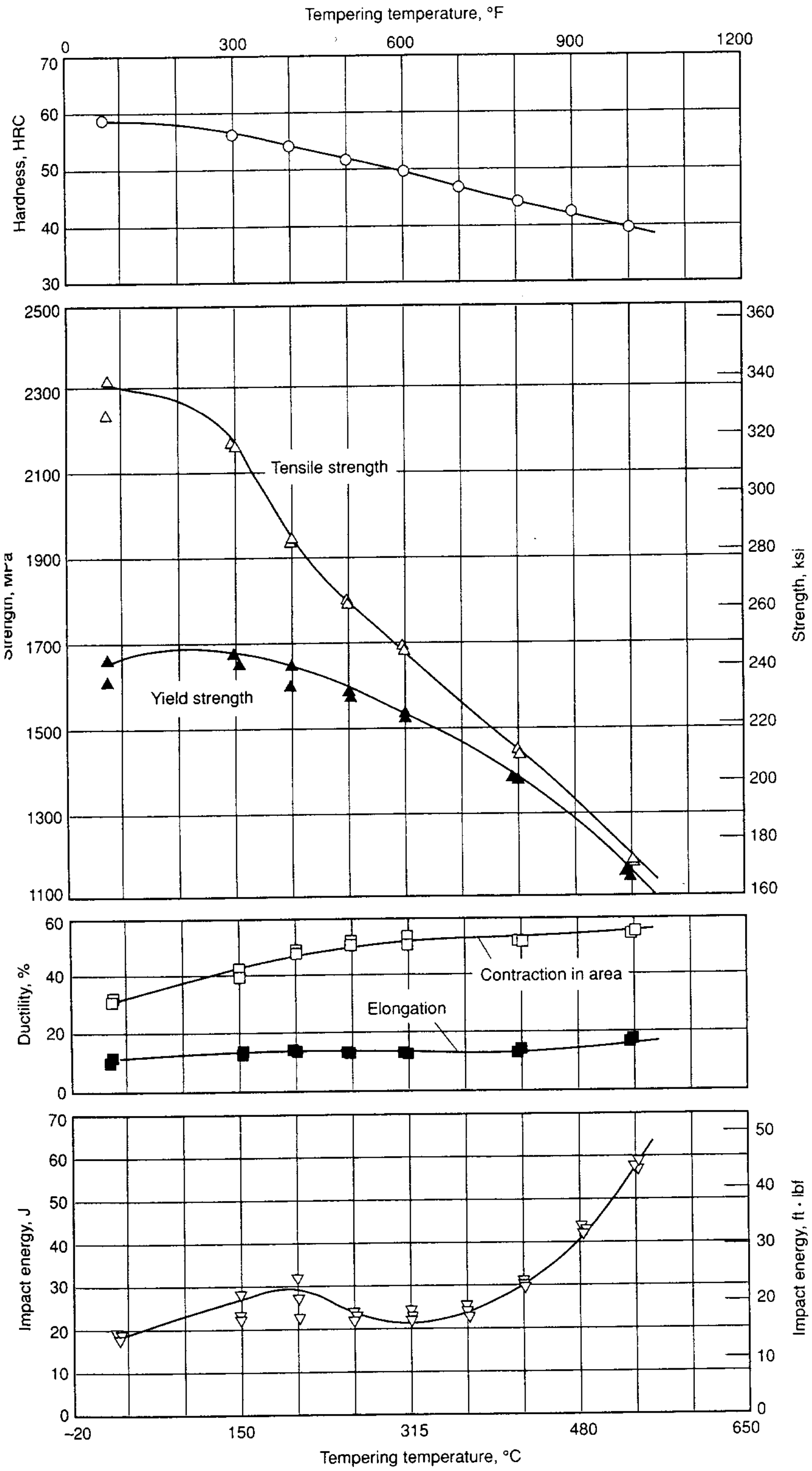


Figure 2-10
Influence of tempering (for 1 hour) at different temperature on the properties of AISI 4340 that was oil quenched [34].

3 PRECIPITATION HARDENABLE STAINLESS STEELS

For applications requiring high strength, precipitation hardenable (PH) stainless steels offer an alternative to cold worked austenitic and martensitic stainless steels. Intricate components can be fabricated easily in the annealed condition and subsequently hardened by heat treatment. Compared to martensitic stainless steels, the higher chromium contents provide PH stainless steels with higher corrosion resistance. In PWRs, failed Type 410 martensitic stainless steel pump shafts and valve stems were often replaced by those fabricated from Type 17-4 PH stainless steels.

The PH stainless steels can be divided into three groups, martensitic, semi-austenitic, and austenitic. The PH stainless steel used in domestic PWRs include the martensitic Type 17-4 PH, the semi-austenitic Alloy A286, and Type 17-7 PH stainless steel. Aging behavior of Alloy A286 is discussed with the two nickel-based precipitation hardenable alloys also used in PWRs, Alloy X-750 and X-718, due to their similar microstructures, mechanical properties, and applications as high strength bolting materials.

3.1 Martensitic 17-4 PH stainless steels

Type 17-4 PH (AISI 630) is often used in domestic PWRs and BWRs. Its mechanical properties are controlled by two metallurgical phenomena, the transformation of austenite to martensite and precipitation hardening. The heat treatment of Type 17-4 PH consists of the following two steps

1. Solution treatment at 1900^{oF} for 0.5-1 hours, followed by air or oil-quench (condition A).

2. Precipitation treatment at 900-1150°F for 1-4 hours.

At the solution heat treatment temperature of 1900°F, the microstructure is austenite interspersed with islands of δ ferrite. The solution heat treatment dissolves the main precipitation phases. Upon cooling, the austenite transforms to martensite starting (M_s) at 270°F and finish (M_f) at 90°F. The microstructure of Type 17-4 PH in condition A is untempered martensite matrix supersaturated with copper and interspersed with delta (δ) ferrite stringers. Due to the lower carbon content and the carbon tied up as columbium carbides, the as-quenched Type 17-4 PH has a much lower hardness than the as-quenched Type 410 martensitic stainless steel.

The precipitation treatment has the effects of tempering the martensitic matrix and precipitation of copper rich precipitates. This increases the yield strength and hardness and increases the ductility at the same time. The precipitation heat treatment temperatures are typically between 900 and 1150°F (H900, H1100, H1150 etc.). The H900 condition has the maximum hardness, but reduced ductility and fracture toughness. For higher ductility and SCC resistance, Type 17-4 PH is normally used in the over-aged H1100 condition in PWRs. The microstructure of H1100 condition is tempered martensite matrix with fine copper-rich particles and 1-8% δ ferrite. The chemical compositions and typical mechanical properties of Type 17-4 PH are listed in Table 3-1 and Table 3-2, respectively [38, 39]. Even though condition A and condition H1100 may have comparable tensile strength and hardness levels, Type 17-4 PH is not used in condition A because untempered martensite results in lower ductility and SCC resistance.

3.2 Thermal aging embrittlement of Type 17-4 PH (H1100)

The secondary thermal aging of Type 17-4 PH at temperatures above 600°F was recognized by Armco Steel Corporation (Armco), the original developer of this alloy. For the Type 17-4 PH material aged to H-1100 condition, Armco reported the following values of room temperature Izod impact (ft-lb.) after being aged at 700, 800 and 900°F for 1000 or 2000 hours as listed in Table 3-3 [38]. This indicates that, for the three temperatures investigated, the secondary aging kinetics for Type 17-4 PH (H-1100) are the fastest around 800°F. This was reflected in Armco's recommendation for parts requiring corrosion resistance and high strength at service temperatures not higher than 600°F. As the aging rate has an inverse exponential dependency on temperature, the time required to achieve significant embrittlement would take longer than a few thousand hours. Hence, these short-term low temperature aging data could not settle the question of long-term aging effect of Type 17-4 PH (H-1100) at or near 600°F. The 1989 ASME Boiler and Pressure Vessel Code Section III mentioned that Type 17-4 PH in the H-1100 condition has reduced toughness at room temperature after exposure for about 5000 hours (~7 months) at 600°F and after shorter exposure above 650°F [40]. All these observations and test results indicate the significant loss of ductility and impact strength of Type 17-4 PH (H-1100) from relatively short term exposure at 600°F.

The potential secondary aging of Type 17-4 PH (H-1100) for BWR applications at 550°F was a concern in the early 1960s [41]. The metallurgical basis of thermal aging embrittlement of Type 17-4 PH (H-1100) was studied in the early 1960s [42]. The thermal aging embrittlement at 800°F was accompanied by increases in hardness and tensile strengths. The low temperature aging embrittlement and hardening was a surprise at the time from the following three considerations: little additional decrease in copper solubility below 1100°F to allow additional precipitation hardening, diminishing precipitation hardening from continued overaging of copper precipitates, and continued tempering of the martensitic matrix. Hence, it was reasoned that the age embrittlement of Type 17-4 PH (H-1100) must be caused by precipitation of a second phase, not related to the primary Cu-rich precipitates. Due to their similar embrittlement characteristics, the secondary aging embrittlement of Type 17-4 PH (H-1100) was linked to the 885°F embrittlement of ferritic stainless steels. The generally accepted mechanism for the 885°F embrittlement of ferritic stainless steels is associated with the precipitation of a alpha prime phase (α'), which is a very fine, coherent, chromium-rich body centered cubic phase. With X-ray diffraction and X-ray fluorescence analysis, Antony identified the existence of α' in the aged Type 17-4 PH (H-1100) [42].

Clarke later showed that variation in Type 17-4 PH chemical composition has a significant influence on the initial room temperature Charpy impact properties and the embrittlement kinetics (see Figure 3-1 and Figure 3-2) [43]. The α' precipitation cause of thermal aging embrittlement of Type 17-4 PH is also supported by studies of embrittlement of cast austenitic stainless steels (CASS) in a similar temperature range. CASS such as CF-3, CF-8, CF-3M and CF-8M (similar to wrought grades Types 304L, 304, 316L, and 316 except CASS typically contains 5 to 25 percent ferrite) have been used in LWRs. Exposure of CASS to temperatures between 482 and 662^{o}F leads to an increase in hardness and tensile strength with a corresponding decrease in ductility and impact strength and a shift of the Charpy transition curve (DBTT) to higher temperature. The primary cause of embrittlement is attributed to formation of the Cr-rich α' phase in the ferrite phase by spinodal decomposition with a secondary contribution from precipitation and growth of grain boundary carbides [44].

Compared to martensitic stainless steels such as Type 403 and 410, Type 17-4 PH is more susceptible to thermal aging embrittlement due to its higher contents of chromium and other alloying elements. The effect of thermal aging on Charpy impact properties is shown in Figure 3-3 [43]. The ductile-brittle transition temperature (DBTT) of unaged Type 17-4 PH (H-1100) is similar to unaged Type 410 martensitic stainless steel, i.e., around room temperature [45]. The transition temperature of aged Type 17-4 PH (H-1100) can approach ~500^{o}F as compared to 75-200^{o}F for Type 410 from comparable exposure to elevated temperature [46]. In addition, thermal aging embrittlement of Type 17-4 PH (H-1100) is accompanied by a severe decrease in upper shelf energy (USE), unlike Type 410 steel whose USE is only moderately decreased by aging at similar temperatures.

Because thermal aging embrittlement of CASS and martensitic PH stainless steels is accompanied by an increase in hardness, embrittlement is often characterized by hardness increase. Yrieix et al. found that the decline in Charpy impact properties is linearly correlated with hardening [47]. Empirical correlations were also made to link hardness increase with exposure temperature and time based experimental test results [47, 48]. Based on these studies, an embrittlement model for Type 17-4 PH (H-1100) in the PWRs has been developed by Xu et al. [49]. The hardness increase of Type 17-4 PH (H-1100) components removed from service was found in good agreement with the model. Based on the model, Figure 3-4 shows the increase in the fracture appearance transition temperature ($FATT_{50}$) and decrease in USE as a function of exposure time at 600^{o}F. The increase in DBTT and loss of USE is in agreement with studies by Clarke and Meyzaud et al. Although the embrittlement kinetics is sensitive to heat-to-heat differences in composition, severe thermal hardening and embrittlement would be reached for Type 17-4 PH (H-1100) near 600^{o}F during PWR lifetime.

3.3 Semi-Austenitic PH Stainless Steel (Type 17-7 PH)

The semi-austenitic PH stainless steel Type 17-7 PH has been used for CRDM leaf springs in certain domestic PWRs [50]. The chemical composition requirement of Type 17-7 PH is listed in Table 3-1. The microstructure of semi-austenitic PH stainless steels after cooling from the solution treatment temperature (condition A) is austenite, instead of martensite for Type 17-4 PH. However, martensite is eventually formed (1) by a conditioning heat treatment which raises the martensite transformation temperature to above room temperature, (2) or by cooling to subzero temperature (3) or by cold-rolling. Type 17-7 PH is most widely used in the TH1050 condition for optimum ductility and SCC resistance. The complete TH 1050 heat treatment consists of the following steps:

1. Solution anneal at 1900 ± 25 °F to place carbon and other alloying elements into solution. Upon cooling to room temperature the microstructure consists of austenite matrix with delta ferrite stringers (condition A). Parts are easily fabricated in this condition.
2. Conditioning heat treatment at 1400 ± 25°F for 90 minutes. The austenite matrix becomes unstable as carbon is removed in the form of chromium carbide ($Cr_{23}C_6$). The material is air cooled to 32-60°F within 1 hour and held for 30 minutes. The microstructure consists of an acicular martensitic matrix with chromium carbides precipitated at regions of high lattice energy such as grain boundaries, slip lines, and ferrite stringers (condition T).
3. Precipitation heat treatment at 1050 ± 10°F for 90 minutes followed by air cool (condition TH1050). This provides additional strengthening from coherent NiAl and Ni_3Al precipitates and additional tempering to the martensitic matrix. The microstructure, after the TH1050 heat treatment consists of a tempered martensitic matrix with ferrite stringers and chromium carbide precipitates at grain boundaries and other regions of high energy. However, the NiAl and Ni_3Al precipitates can not be observed with an optical microscope.

Type 17-7 PH in the TH1050 condition is somewhat softer and more ductile compared to two other commonly used heat treatments RH950 and CH900. The RH950 heat treatment consists solution heat treated at 1750°F, transformed to martensite by cooling to –100°F, and precipitation at 950°F for 1 hour. Type 17-7 PH in the CH900 has the maximum strength but limited fabricability. The material is solution annealed at 1950°F and cold-rolled by 60%, which transforms the austenite to martensite (condition C). This is followed by precipitation hardening at 900°F for 60 minutes (CH900). The typical mechanical properties of Type 17-7 PH in TH1050, RH950, and CH900 conditions are listed in Table 3-2.

Failures of Type 17-7 PH (CH900) springs in solenoid valves in the PWR primary water environment were reported in the 1980s [51]. The failures were reported to be by relatively straight intergranular cracks without branching or any ductility. As noted above, Type 17-7 PH in the CH900 condition has the highest yield strength and hardness possible for Type 17-7 PH material. The investigation of these failures remained inconclusive although hydrogen cracking was suspected. The failed springs also had a higher level of tin which was known to cause embrittlement by its segregation to the grain boundaries.

Failures of Type 17-7 PH (TH1050) CRDM leadscrew leaf springs were also observed in the 1980s and 1990s [50, 52]. These failures of leaf springs have been by brittle intergranular cracks with either shallow branching or no branching at all. Fracture morphology of failed Type 17-7 PH (TH1050) leaf springs appears to be similar to that of the failed Type 17-7 PH(CH900) solenoid valve springs. SAM analysis revealed the presence of boron and titanium only on the grain facets of the brittle fracture surfaces. Higher amounts of sulfur and carbon were also observed on the brittle fracture surfaces. These finding indicated the spring failures were due to grain boundary embrittlement from detrimental phases such as borides, sulfides, and carbides. Because the failed the leaf springs were limited to one heat, the embrittlement may have been produced by abnormal heat treatment during fabrication.

3.4 Thermal aging embrittlement of Type 17-7 PH

Unlike Type 17-4 PH, there has been a lack aging studies regarding Type 17-7 PH. Armco literatures showed that aging at 700 and 800°F for 500 hours increases the yield and tensile strengths, decreases the ductility, but resulted only in minor changes at 600°F [39]. Such aging responses of Type 17-7 PH (TH1050) at 600, 700, and 800°F are very similar to these of Type 17-4 PH (H-1100). Similar to Type 17-4 PH (H-1100), the 800°F embrittlement of Type 17-7 PH (TH1050) can be reversed by heating up to the precipitation treatment temperature of 1050°F. Considering their similar chemical composition and microstructures, one would expect similar embrittlement kinetics for Type 17-7 PH (TH1050) as Type 17-4 PH (H-1100).

A review of the literature has revealed little past research effort on the long term aging behavior of semi-austenitic PH stainless steels such as Type 17-7 PH. This may be due to the fact that Type 17-7 PH sees only very limited uses in LWR applications and is never used for pressure boundary or structural components. Test data indicates that Charpy impact energy of unaged Type 17-7 PH (TH1050) is ~4 ft-lb at room temperature and ~5 ft-lb at 212°F [53]. Such a low level of impact toughness is comparable to that of thermally embrittled Type 17-4 PH (H-1100). This suggests that the transition temperature of unaged Type 17-7 PH (TH1050) is already above The room temperature and the upper shelf energy is lower than that of unaged Type 17-4 PH (H-1100). The transition temperature of Type 17-4 PH (H-1100) and martensitic stainless steel Type 410 is around room temperature. The inferior impact toughness of unaged Type 17-7 PH (TH1050) is in line with its very high hardness but low level of ductility. Charpy impact test data of aged Type 17-7 PH have not been found. However, the effect of long term exposure to elevated temperature could be more of a concern for Type 17-7 PH (TH1050), which has very low impact toughness even in the unaged state.

3.5 Conclusions

1. The martensitic Type 17-4 PH (H-1100) and semi-austenitic Type 17-7 PH (TH1050) stainless steels are used in domestic PWRs. Past failure investigations showed that long term exposure to elevated temperature can lead to severe embrittlement. Compared to martensitic stainless steels such as Type 403 and 410, Type 17-4 PH and 17-7 PH are more susceptible to thermal aging embrittlement due to the higher content of chromium, nickel, and other alloying elements.

2. Thermal aging embrittlement of Type 17-4 PH is accompanied by an increase in hardness. Exposure of Type 17-4 PH (H-1100) to 500-600°F can causes the DBTT to shift to well above room temperature and a severe decrease in USE. Although the embrittlement kinetics are sensitive to heat-to-heat differences in composition, significant thermal hardening and embrittlement would be reached for Type 17-4 PH (H-1100) near 600°F during PWR lifetime.

3. Very limited information is available on the long-term thermal aging embrittlement of Type 17-7 PH (TH1050). Based on the limited data, the thermal aging embrittlement kinetics of Type 17-7 PH (TH1050) could be similar to that of Type 17-4 PH (H-1100). Because of the very low impact toughness of the unaged Type 17-7 PH (TH1050) compared to Type 17-4 PH (H-1100), any embrittlement effect due to long term exposure to elevated temperatures could be more of a concern for Type 17-7 PH (TH1050).

3.6 Recommendations

A thermal aging management program is recommended for PH stainless steels. The program will identify the PH stainless steels used in PWRs at elevated temperatures. However, unlike the reactor vessel materials, there is no criteria or guidelines regarding how much embrittlement in terms of transition temperature shift or loss of fracture toughness can be tolerated. To establish the embrittlement kinetics, which can be used for establishing a thermal aging screening criteria, multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact should be performed. Therefore, the program also needs to establish criteria for safety assessment.

One approach is to perform fracture toughness tests (K_{Ic} or J_{Ic}) for thermally embrittled materials and evaluate the critical flaw size for these components based on fracture mechanics. A possible source of test specimens is the Type 17-4 PH CRDM leadscrew couplings used in the CRDMs of Babcock & Wilcox (B&W) PWRs. However, the program should also investigate suitable replacement materials if it is needed or more economical than performing fracture toughness tests and analysis. One possible source of testing materials for Type 17-4 PH is the thermal aging specimens (hardness, tensile, and impact) of EBR-II reactor materials surveillance program. These Type 17-4 PH specimens have been thermally aged at 371°C (700°F) in a helium atmosphere for approximated 156,000 hours, although the aging temperature is a somewhat higher than PWR temperatures [54, 55].

Table 3-1
Chemical Composition of Type 17-4 PH and 17-7 PH Stainless Steels [38, 39]
(wt%, maximum unless range or minimum is indicated)

	C	Mn	Si	P	S	Cr	Ni	Cb+Ta	Cu	Al
17-4 PH	0.07	1.00	1.00	0.040	0.030	15.50-17.50	3.00-5.00	5xC-0.45	3.00-5.00	--
17-7 PH	0.09	1.00	1.00	0.040	0.030	16.00-18.00	6.50-7.75	--	--	0.75-1.50

Table 3-2
Typical Room Temperature Mechanical Properties of Type 17-4 PH by Precipitation Heat Treatment at Different Temperature [38]

Heat Treatment	Hardness		Tensile Strength	Yield Strength	Elong. (2 in)	Red. of Area	Charpy V-notch
	Brinell	Rockwell	ksi	ksi	%	%	ft-lbs
17-4 PH (H1100)	332	HRC34	150	135	17.0	58	45
17-4 PH (H1025)	352	HRC38	170	165	15.0	56	35
17-4 PH (H900)	429	HRC44	200	185	14.0	52	15
17-7 PH (TH1050)	--	HRC43	200	185	9	--	~4
17-7 PH (RH950)	--	HRC48	240	225	6	--	--
17-7 PH (CH900)	--	HRC49	265	260	2.0	--	--

Table 3-3
Temperature Izod Impact Values of Type 17-4 PH (H-1100) [38].
The initial room temperature Izod impact value is 56 ft-lbs

Aging Temperature	1000 hours Exposure time	2000 hours Exposure time
700 oF	7 ft-lb.	4 ft-lb.
800 oF	3 ft-lb.	2 ft-lb.
900 oF	6 ft-lb.	11 ft-lb.

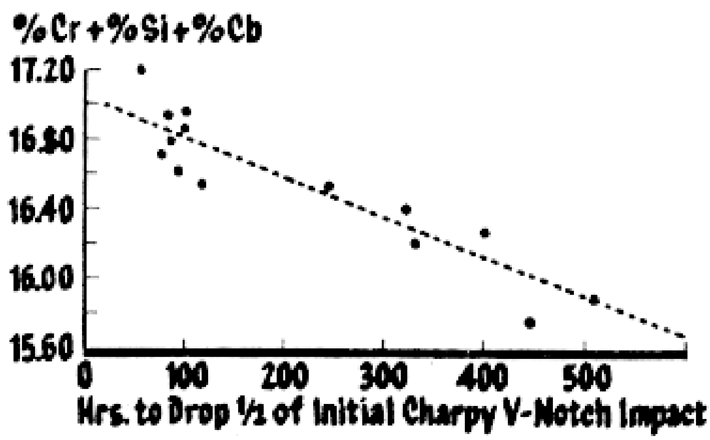


Figure 3-1
Type 17-4 PH (H-1100), effect of %Cr + %Si + %Cb on exposure time at 800 °F to cause a 50% drop in initial room temperature Charpy impact energy [43].

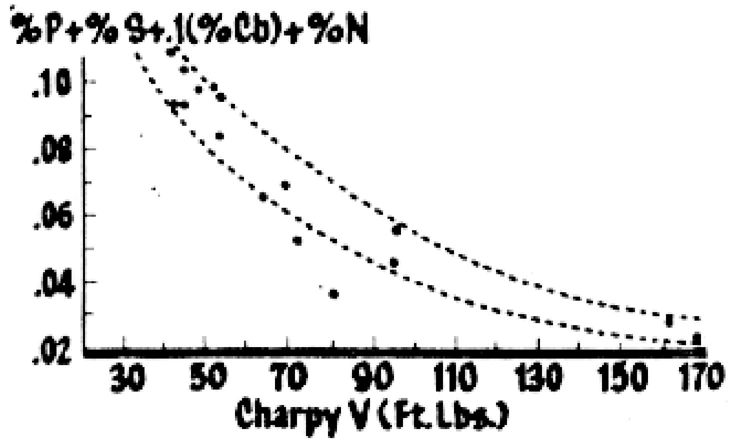


Figure 3-2
Type 17-4 PH (H-1100), effect of %P + %S + 0.1%Cb + %N on the initial room temperature Charpy impact energy [43].

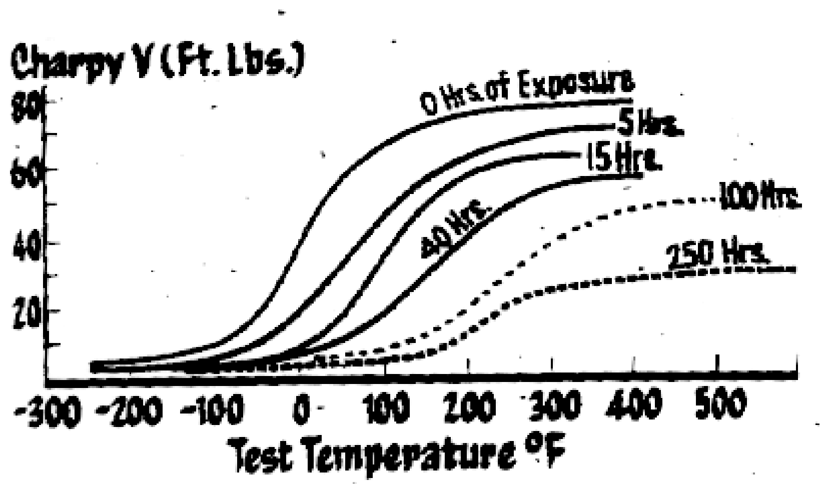


Figure 3-3
Effect of Exposure on Charpy V-notch Impact Properties at 800°F for Type 17-4 PH (H-1100) [43].

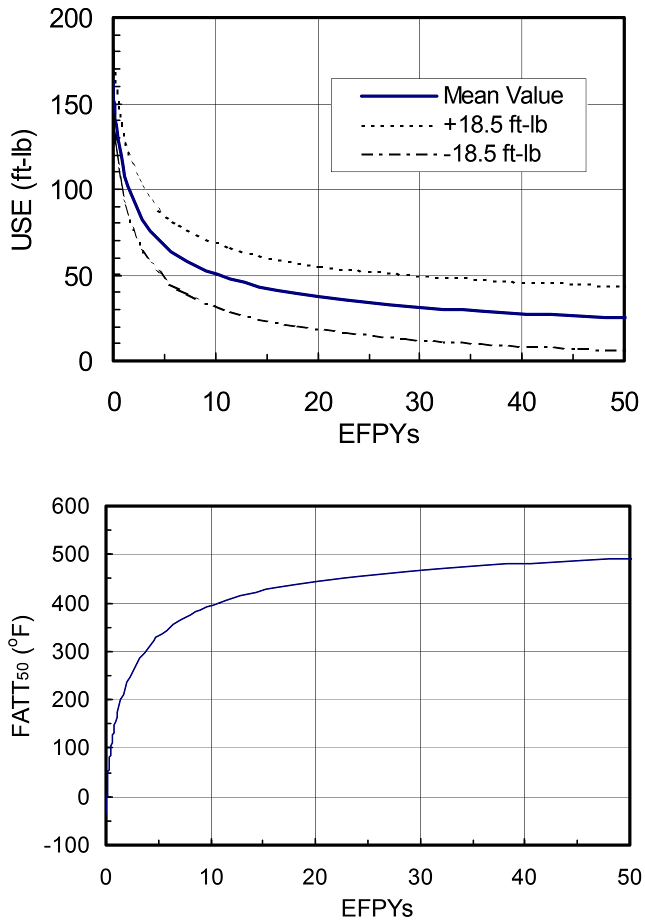


Figure 3-4
Predicted embrittlement of Type 17-4 PH (H-110) FATT50-vs.-EFPYs and USE-vs.-EFPYs as a function of exposure time at 600°F [49].

4
TYPE 410 MARTENSITIC STAINLESS STEELS

The low carbon grade (containing 0.15% or less carbon) martensitic stainless steels, Type 403, 410, and 416, have been used in domestic PWRs [56, 57, 58]. These martensitic stainless steels are used in PWR primary coolant systems, such as for hold-down spring, CRDM motor tube center section and internal components. These types of martensitic stainless steels are also used in the secondary side for valve stems, pump shafts, and fasteners. The chemical compositions for the various types of 400 series stainless steels are listed in Table 4-1[59, 60, 61, 62, 63, 64]. As can be noted, Types 403 and 416 of martensitic stainless steels have nearly identical composition with Type 410, their progenitor. Their heat treatment and mechanical properties are also the same. Type 403 is known as the "turbine quality" grade of the general purpose Type 410. Type 403 has a slightly lower range of chromium to reduce the propensity of forming δ ferrite. Compared to Type 410, Type 403 also has lower maximum for silicon and phosphorus. Compared to Type 410, Type 416 has a higher sulfur content to improve machinability.

The microstructures of martensitic stainless steels depend on chromium and carbon contents and heat treatment. For the low carbon grade with ~0.10% C, the chromium content is limited to 13% in order to achieve full hardening. In the annealed condition, the microstructures of Type 410 consists of a matrix of equiaxed ferrite grains with randomly dispersed carbides. In the quenched and tempered condition, the microstructure consists of martensite matrix with a dispersion of carbide precipitates. The required room temperature mechanical properties are summarized in Table 4-2. These alloys can be used in hardened and stress relieved, tempered, or annealed conditions with typical heat treatment steps listed below. The quench and temper condition is used for most PWR applications.

1. Austenizing at 1800°F for 1 hour per inch thickness (austenite).

2. Quenching by air cooling or oil quench to room temperature (martensitic).

3. Stress-relieved at 300-800°F for 3 hours and air cool;
   or tempered at 1100-1400°F for 4 hours and air cool;
   or fully annealed at 1550-1650°F for 1-3 hours + furnace cool to 1100°F + air cool to room temperature; or process annealed at 1350-1450°F for 1-3 hours and air cool.

The mechanical properties of martensitic stainless steels depend on the heat treatment temperature. The general trend of hardness, toughness, and general corrosion rate as a function of heat treatment temperature is illustrated in Figure 4-1[65]. The typical mechanical properties are summarized in Table 4-3[66]. Heat treatment between 800-1050°F is not usually used for martensitic stainless steels due to temper embrittlement and loss of corrosion resistance.

4.1 Temper Embrittlement of Type 410

The reported failures of martensitic stainless in PWRs are limited to valve stems, studs, or pump shafts fabricated from Type 410 and heat treated to the quenched and tempered condition [57, 67]. So far, there has been no reported failures of martensitic stainless steels in the reactor coolant system of PWRs, where components are mainly inside the control rod drive assembly. The failure mechanism of Type 410 valve stems was intergranular stress corrosion cracking (IGSCC) along the prior austenite grain boundaries [67]. In most cases, the failed components exhibited hardness levels significantly exceeding the specified range for tempered Type 410. These failures were commonly attributed to high hardness due to improper heat treatment during fabrication, which elevated the materials susceptibility to IGSCC. However, thermal aging embrittlement during service or aging was not suspected or investigated. Results of several Type 410 valve component failure investigations in PWRs are summarized below.

In 1984, three main steam isolation valve (MSIV) shafts in Farley Unit 1 and one MSIV shaft in Ginna were found cracked [67]. These shafts were fabricated from tempered Type 410. The chemical compositions of these failed Type 410 shafts are listed in Table 4-1 and are within the ASTM A 276 specification limits. During the fabrication, the failed Farley Unit 1 shafts were austenizing at 1775°F+/–25°F, air or oil quench, and tempered at 950°F to a hardness of Brinell 345-370 (HRC 37-39.8). The measured Rockwell hardness value in the failed shafts averaged HRC 41.3. The measured 500-gram Knoop microhardness averaged 444, which is equivalent to HRC 43.4. A sample from the Farley shaft was re-austenized at 1700°F and tempered at 850, 900, 950, and 1000°F and exhibited Charpy impact energy between 8 and 12 ft.-lb.[68].

The microstructure of Farley MSIV shaft was reported to be tempered martensite. Although heat treatment information were unavailable, the failed Ginna shaft should have received the same quenching and tempering heat treatment since it was from the same valve manufacturer. The measured Rockwell hardness value in the failed Ginna shaft averaged 44.8 and 44 for the uncracked shaft also removed from Ginna. The observed microstructure is untempered martensite, which indicates insufficient tempering temperature or time. In addition, the specified tempering temperature of 950°F is known to result in lower fracture toughness and SCC resistance. In 1991, a river water pump shaft coupling was found cracked at the Beaver Valley nuclear power plant [68]. The impact energy was only 8-15 ft.-lb. and hardness and ductility were below the expected value for tempering at 1000°F. The root cause of the failure was determined to be temper embrittlement due to improper heat treatment. After a corrective heat treatment (exact tempering temperature not stated), the material's impact value was increased to 100-120 ft.-lb.

The improper tempering ~900°F was considered to be a significant factor to the failures of Type 410 valve and pump components in the nuclear power industry. Czajkowski et al. used the ethereal picral etchant, a non-destructive etchant (50-gram picric acid, 250-ml purified ethyl ether, 10-ml 12.8% zephiren chloride solution, 240-ml water) to identify temper embrittlement of Type 410 martensitic stainless steel [68]. Only specimens which were tempered at 900-1200°F had their prior austenite grain boundaries and martensitic structure highly defined. Hardness tests indicated that, within the tempering temperature range having a marked response to etching, hardness declines precipitously with increasing temperature.

The etching method developed by Czajkowski et al. was reported to be effective way of non-destructively determining temper embrittlement of Type 410 stainless steel. However, the study did not perform impact tests of material tempered between 1000-1200°F to demonstrate conclusively the link between etching responsiveness and temper embrittlement. Embrittlement is usually characterized by shifting in transition temperature by performing multi-temperature Charpy impact test. The decline or increase in hardness value itself is insufficient to prove embrittlement unless a correlation has been established. In addition, the etching method suggests temper embrittlement at 1200°F, which is significantly above the 800-1050°F range typically associated with temper embrittlement of martensitic stainless steels. Therefore, it is argued that the unexpectedly high hardness levels of many failed Type 410 pump shafts and valve stems are not due to temper embrittlement at ~950°F, but rather due to a lack of tempering, i.e., lower temperature and/or insufficient tempering time. Hence, evidences of linking temper embrittlement to the past IGSCC of Type 410 are rather inconclusive at best. Incidentally, the failed Type 410 components were usually replaced by 17-4PH, which was known to undergo thermal aging embrittlement at temperatures ~600°F.

4.2 Thermal aging embrittlement of Type 410

It is interesting to note that thermal aging embrittlement of Type 410 during service was not investigated or even suspected as a possible cause for past failures in PWRs. This may be due to the fact that embrittlement of martensitic stainless steels is less pronounced than austenitic stainless steel welds and PH stainless steels and, in part, due to the misconception that thermal aging embrittlement is accompanied by a hardness increase. Meyzaud et al., investigated thermal aging embrittlement of martensitic stainless steels PH steels [46, 69]. The heat chemical compositions are listed in Table 4-4. The chemical composition of 13%Cr heat is the same as Type 410 and the 13-1 (13%Cr-1%Ni) heat is similar to Type 410 except for its slightly higher Ni content. The materials were austenized at 1805°F for 1 hour followed by oil-quenching, and tempering at 1112°F for 4 hours and then air cooled. These two heats along with many other production heats of PH stainless steels were aged at 572, 662, 752, and 842°F (or 300, 350, 400, and 450°C, respectively) from 1000 hours up to 10,000 hours. As shown in, there is no significant effect from aging on the measured hardness of the 13%Cr and the 13-1, except some softening at 842°F for 10,000 hours [46].

Despite a lack of hardening, aging has produced noticeable embrittlement in the tempered Type 410 stainless steel. Meyzaud et. al., performed Charpy impact tests on the un-aged, aged materials at 752°F (400°C) for 5000 and 10,000 hours [69]. As shown in Figure 4-3, aging produced noticeable embrittlement effect on 13%Cr, where those ductile-brittle transition temperature (DBTT) shifted toward higher temperature. The embrittlement effect is more pronounced for the 13-1,whose DBTT shifted by ~135°F (75°C) after 10,000 hours at 752°F. The upper-shelf and lower-shelf are not greatly affected by aging. It is possible the low fracture toughness of the failed Beaver Valley Type 410 was the result of DBTT shifting to above room temperature. Figure 4-4 shows the typical Charpy impact energy curves of unaged Type 410 tempered at 1100, 1225, and 1450°F [70]. Figure 4-5 shows the Izod impact data of Type 410 quenched from 1800°F and tempered at 1150°F to HB 228 [71]. The transition temperatures range from –100 to 200°F. Because the transition temperature of unaged Type 410 is near the room temperature, the room temperature fracture toughness can be sensitive to thermal aging. Meyzaud et al. performed fracture toughness testes at room temperature for materials aged at

752°F (400°C) for 5,000 hours. For 13%Cr, J_{Ic} decreased from ~265 to ~230 kJ/m^2 and dJ/da from ~400 to ~250. No valid values were obtained for the 13-1 alloy due to brittle fracture of test specimens.

The aging embrittlement of ferritic stainless steels at 885°F and austenitic stainless steel castings and weld metal has been accepted to be associated with the precipitation of a very fine, coherent, chromium-rich body-centered cubic alpha prime (α') phase. Studies have also showed similar association of α' with thermal aging embrittlement of martensitic precipitation hardenable (PH) stainless steels at, such as 17-4PH and 15-5PH at ~800°F [42, 46]. The embrittlement due to α' in ferritic and PH stainless steels correlates with a significant increase in hardness level. However, the hardness of thermally aged or embrittled Type 410 is about the same or lower with increasing aging time. Such behavior is similar to temper embrittlement of Type 410 whose hardness is also about the same or lower than stress relieved at temperatures below 800°F. Hence, thermal aging embrittlement of Type 410 is not linked to α'. Therefore, many empirical relations correlating hardness increase (ΔHRC, etc.) with increase in transition temperature (ΔT_{DBTT}) for PH or austenitic weld metals are not suitable for Type 410.

Although temper embrittlement is believed due to grain boundary segregation of impurities such as antimony, phosphorous, tin, arsenic to the prior austenite, a review of literature has not revealed any definitive underlying causes of ~950°F temper embrittlement of martensitic stainless steels. The embrittlement of Type 410 is likely linked to grain boundary segregation of impurities while hardness is controlled by post quench heat treatment temperature. The aging at PWR temperatures for 32 or 48 effective full power years (EFPYs) could cause significant grain boundary segregation of impurities. Even minor increase in DBTT can manifest in drastic deterioration in room temperature impact energy because the initial unaged transition temperature of Type 410 is near the room temperature.

4.3 Conclusions

1. The low carbon grade martensitic stainless steel of Type 403, 410, Type 416 have been used in PWRs, mainly for internal components of CRDM and motor tubes in the RCS, and for value stems and pump shafts on the secondary side. They are most commonly used in the quenched and tempered (950-1250°F) condition. Available embrittlement data are mostly related to Type 410. Thermal aging embrittlement of Type 403 is expected be similar to or bounded by Type 410. The aging effect is expected to be more pronounced for the free machining Type 416 due to its higher sulfur content.

2. Thermal aging embrittlement of Type 410 due to long term aging at 500-600°F is probable, but expected to be less likely with decreasing temperature below that range. The embrittlement is manifested in the DBTT from Charpy impact curves shifting to higher temperature. The transition temperature of unaged Type 410 is around room temperatures. Due to variations in chemical composition and heat treatment, long term aging at 500-600°F can cause Type 410 DBTT above room temperature, but expected to be below 500-600°F. The upper-shelf and lower-shelf are not greatly affected by thermal aging.

3. Thermal aging embrittlement of Type 410 are less pronounced than thermal aging embrittlement of austenitic stainless steels welds and PH stainless steels exposed to the same

temperature. However, thermal aging embrittlement of Type 410 is not accompanied by an increase in hardness. Therefore, empirical relations correlating hardness increase (ΔHRC or ΔHB, etc.) with increase in transition temperature (ΔT_{DBTT}) for austenitic stainless steel welds or martensitic PH stainless steels are not suitable for Type 410.

4. Thermal aging embrittlement could be accompanied by an increase in susceptibility to SCC. Temper embrittlement at ~950°F is shown to decrease the corrosion resistance of Type 410. However, there were no SCC and aging studies of martensitic stainless steels, possibly due to the fact that thermal aging embrittlement of Type 410 was not previously recognized in the literatures.

4.4 Recommendation

It is recommended that multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact tests on martensitic stainless steels removed from PWRs or BWRs. The selected components should have operating temperature among the highest for this class of materials and should have accumulated substantial operating time, e.g., more than 100,000 hours. The test result will either confirm the lack of thermal embrittlement or establish the extent of the thermal aging embrittlement from long-term exposure to the operating temperature. It is important that, in case of results indicating thermal aging embrittlement, the possibility of embrittlement due to the initial mis-heattreatment can be ruled out. Hence, test specimens should be removed from materials with known initial mechanical, impact properties, and heat treatment records during fabrication. If the DBTT transition temperature exceeds the room temperature and/or the loss of room temperature impact energy exceeds 50%, the material could be considered susceptible to significant thermal aging embrittlement.

However, unlike the reactor vessel materials, there is no criteria or guidelines regarding how much embrittlement in terms of transition temperature shift or loss of fracture toughness can be tolerated. If the materials are determined to be susceptible to thermal aging embrittlement, an aging management program is needed to establish the aging kinetics for screening based on operating temperature and time and to develop guidelines to safety assessment. One approach is to perform fracture toughness tests (K_{Ic} or J_{Ic}) for the thermally embrittled materials and evaluate the critical flaw size for these components based on fracture mechanics. However, the program should also investigate suitable replacement materials if it is needed or more economical than performing fracture toughness tests and analysis.

Table 4-1
Nominal Chemical Composition of Martensitic Stainless Steels [59-64]
(wt%, maximum unless range or minimum is indicated)

Type	Specification	C	Mn	P	S	Cr	Ni	Si	Mo
403	ASTM A276-00a	0.15	1.00	0.040	0.030	11.5-13.0	--	0.50	--
403 Modified	Code Case N-4-11 (1337)	0.06-0.13	0.25-0.80	0.03	0.03	11.50-13.00	0.50	0.50	--
403	A511-96	0.15	1.00	0.040	0.030	11.5-13.0	0.50	0.50	0.60
410	ASTM A276-00a	0.15	1.00	0.040	0.030	11.5-13.5	--	1.00	--
410	ASTM A182-96 (F6a)	0.15	1.00	0.040	0.030	11.5-13.5	0.50	1.00	--
410	ASME SA193-65	0.15	1.00	0.040	0.030	11.5-13.5	--	1.00	--
416	ASME SA193-65	0.15	1.25	0.06	0.15 min	12.0-14.00	--	1.00	0.60
410	1984 Farley Unit 1, Cracked MSIV Shafts, HT62687	0.030	0.420	0.002	0.015	11.800	0.250	0.350	0.030
410	1984 Ginna, Cracked MSIV shafts	0.14	0.35	0.005	0.025	11.5	0.23	0.65	0.02
440A	ASTM A276-00a	0.60-0.75	1.00	0.040	0.030	16.0-18.0	--	1.00	0.75

Table 4-2
Room Temperature Mechanical Requirement for Type 403, 410, and 416 [59-64].

<table>
<tr><th rowspan="2">Type and Spec.</th><th rowspan="2">Condition</th><th colspan="2">Hardness</th><th>Tensile Strength</th><th>Yield Strength</th><th>Elong. (2 in)</th><th>Reduction of Area</th></tr>
<tr><th>Brinell</th><th>Rockwell</th><th>ksi</th><th>ksi</th><th>%</th><th>%</th></tr>
<tr><td>Type 403
ASTM A 176-99</td><td>----</td><td>217 max</td><td>96B max</td><td>70 min</td><td>30 min</td><td>25.0 min</td><td>--</td></tr>
<tr><td rowspan="6">Type 403 and 410
ASTM A 276-00a</td><td>Condition A[1] (hot finished)</td><td>--</td><td>--</td><td>70 min</td><td>40 min</td><td>20 min</td><td>45 min</td></tr>
<tr><td>Condition A (cold finished)</td><td>--</td><td>--</td><td>70 min</td><td>40 min</td><td>16 min</td><td>45 min</td></tr>
<tr><td>Condition T (hot finished)</td><td>--</td><td>--</td><td>100 min</td><td>80 min</td><td>15 min</td><td>45 min</td></tr>
<tr><td>Condition T (cold finished)</td><td>--</td><td>--</td><td>100 min</td><td>80 min</td><td>12 min</td><td>40 min</td></tr>
<tr><td>Condition H (hot finished)</td><td>--</td><td>--</td><td>120 min</td><td>90 min</td><td>12 min</td><td>40 min</td></tr>
<tr><td>Condition H (cold finished)</td><td>--</td><td>--</td><td>120 min</td><td>90 min</td><td>12 min</td><td>40 min</td></tr>
<tr><td rowspan="2">Type 403 modified, Code Case 1337 or N-4-11</td><td>Annealed</td><td>--</td><td>--</td><td>70 min</td><td>40 min</td><td>22.0 min</td><td>50.0 min</td></tr>
<tr><td>Hardened & tempered 1200°F</td><td colspan="2">235 (or 226) to 277 Brinell or equivalent</td><td>110 min</td><td>90 min</td><td>16.0 min</td><td>50.0 min</td></tr>
<tr><td>MT 403,
ASTM A 511-96[2]</td><td>Annealed</td><td>207 max</td><td>95B max</td><td>60 min</td><td>30 min</td><td>20 min</td><td>--</td></tr>
</table>

1. ASTM A276-00a, Condition A – annealed, T – hardened and tempered as a relatively higher temperature, H – hardened and tempered at a relatively low temperature.

2. Mechanical properties are supplementary requirement of ASTM A 511-96 for annealed condition. Not applicable when cold-worked or special thermal treatment is ordered.

Table 4-3
Typical Room Temperature Mechanical Properties of Type 403, 410, and 416 [66]
(1” Diameter bars)

Heat Treatment	**Note**	**Hardness**		**Tensile Strength**	**Yield Strength**	**Elong. (2 in)**	**Red. of Area**	**Izod Impact**	
		Brinell	**Rockwell**	**ksi**	**ksi**	**%**	**%**	**ft-lbs.**	
Fully annealed	403, 410	137-159	B75-83	78	40	35	73	95-115	
	416	137-159	B75-83	78	40	31	62	80-95	
Process annealed	403, 410	170-197	B86-92	90	65	27	67	95-115	
	416	170-197	B86-92	90	65	25	60	50-70	
Stress relieved Type 403 and 410	400°F	390	C41	190	145	15	55	--	
	600°F	375	C40	180	140	15	55	20-50	
	800°F	390	C41	195	150	17	55	30	
Tempered Type 403 and 410	1100°F	258	C23	120	100	21	63	80	
	1200°F	235	B99	110	90	22	65	91	
	1300°F	223	B97	105	80	24	68	100	
	1400°F	202	B93	95	65	26	67	105	

Table 4-4
Chemical Composition of Martensitic and PH Stainless Steels [46]

Heat	C	Si	S	P	Mn	Ni	Cr	Mo	Cu	Nb	N	Al
13%Cr	0.114	0.32	0.005	0.009	0.37	0.03	12.57	0.01	0.05	<0.01	0.0211	<0.005
13-1	0.142	0.18	0.001	0.006	0.45	0.76	11.92	0.01	0.06	<0.01	0.0210	<0.005
13-4	0.037	0.21	0.001	0.007	0.53	4.19	12.71	0.66	0.01	<0.01	0.0233	<0.005
16-4	0.049	0.18	0.001	0.008	0.63	4.89	15.22	0.79	0.01	<0.01	0.0280	<0.005
17-4 PH	0.055	0.25	0.002	0.013	0.51	4.56	15.79	0.07	3.27	0.17	0.0235	0.011

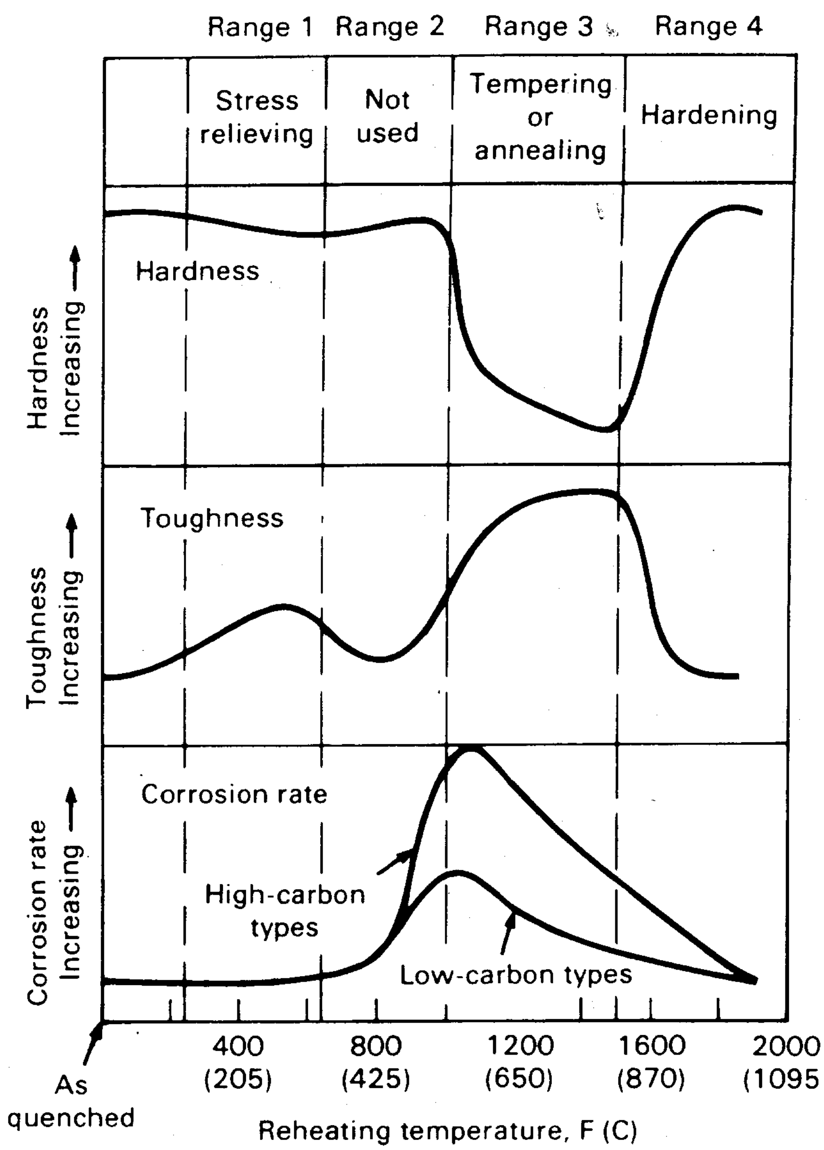


Figure 4-1
General trend of hardness, toughness, and corrosion rate as a function of heat treatment temperature for martensitic stainless steels. Type 403 and 410 are the low-carbon types. [65]

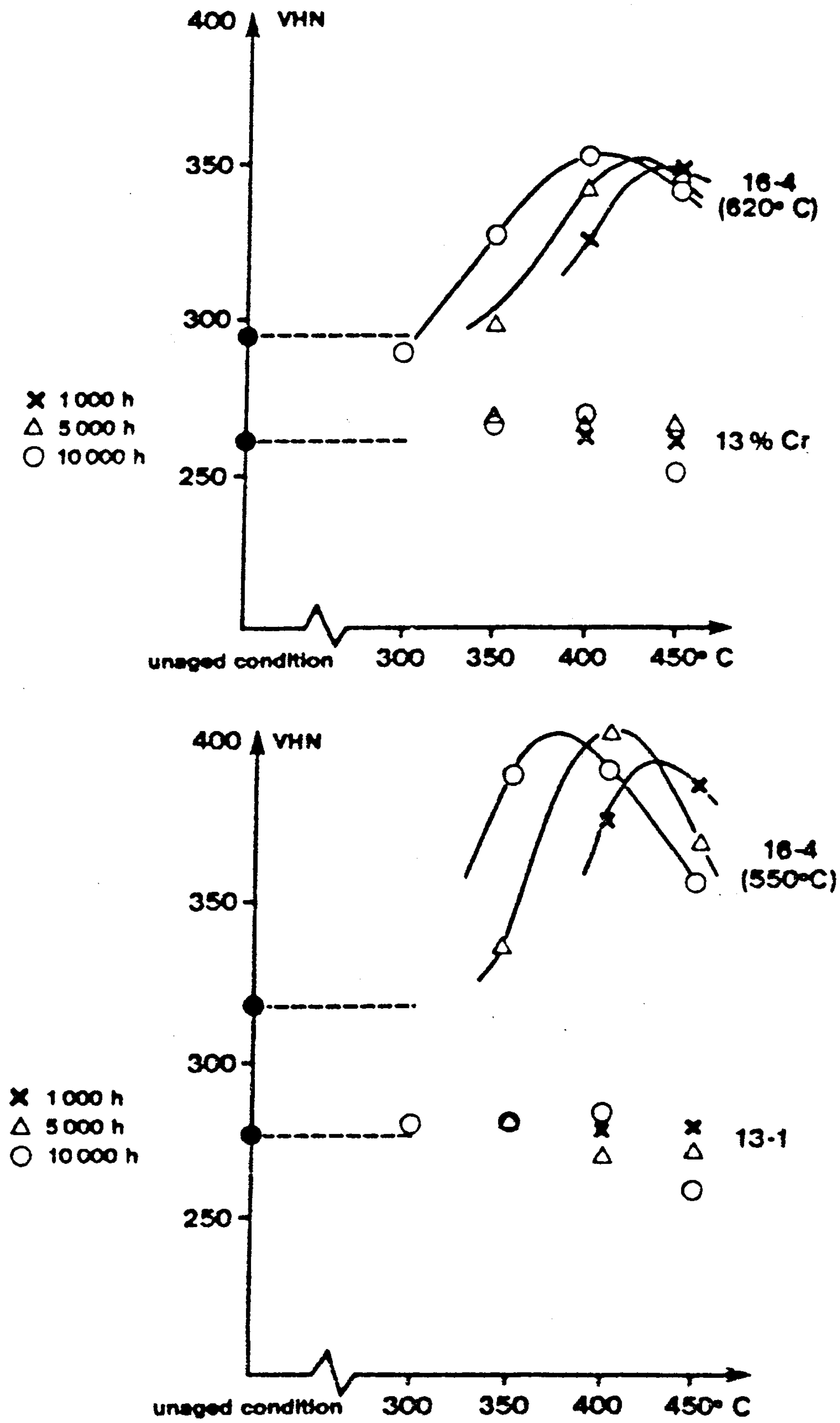
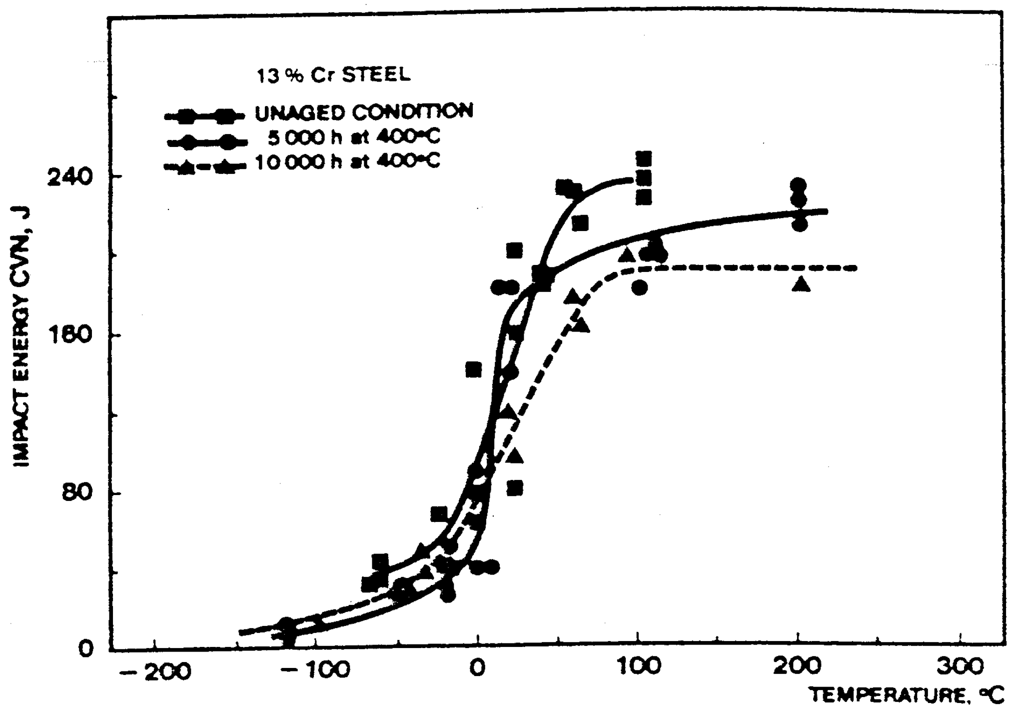
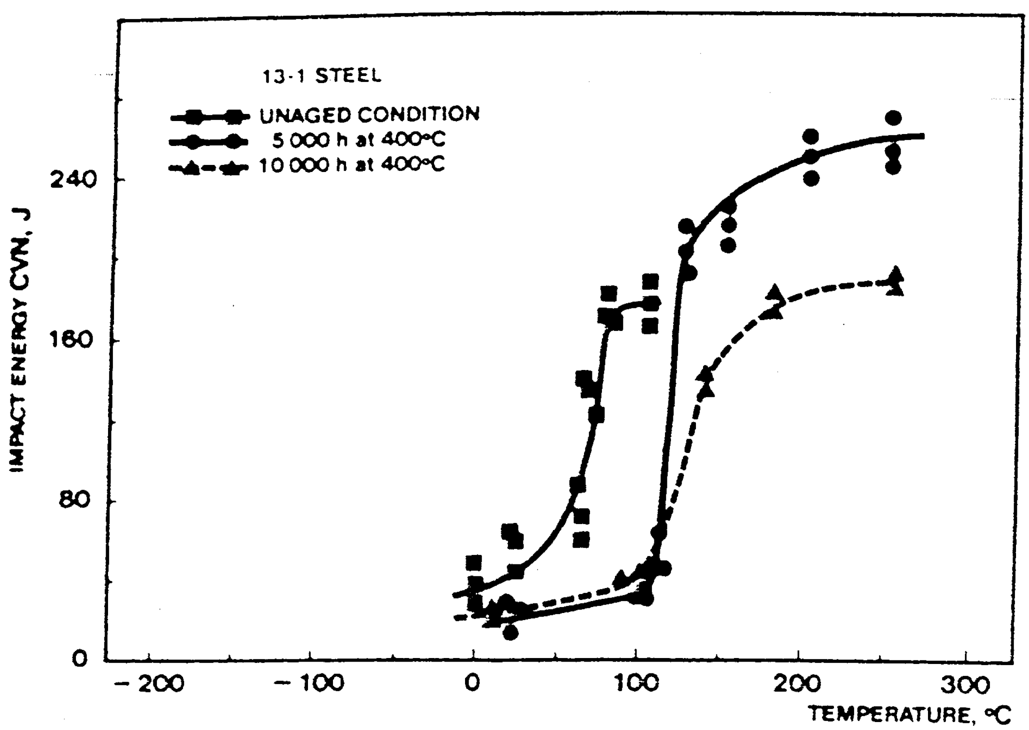


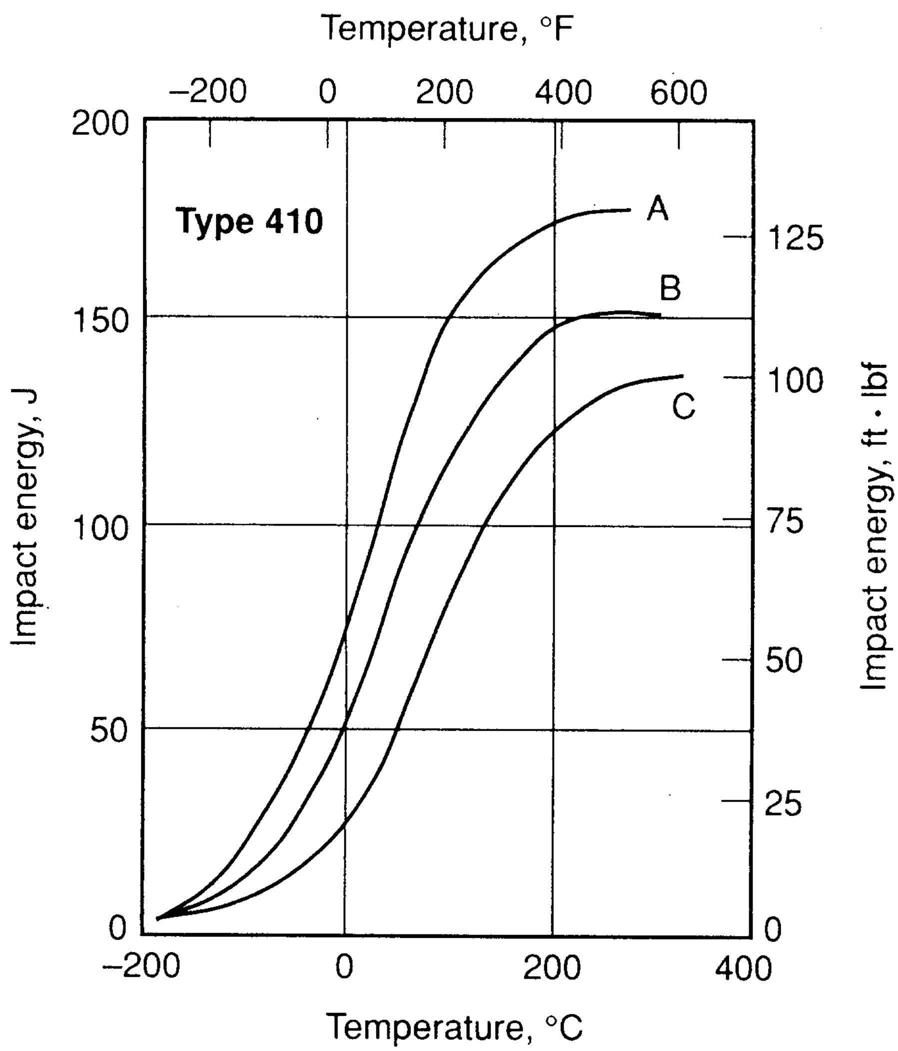
Figure 4-2
Variation in hardness as a function of aging time and temperature for 13%Cr (Type 410), 13%Cr-1%Ni, and 16%Cr-4%Ni. [46]





(1J = 0.738 ft-lb)

Figure 4-3
Charpy V-notch impact energy transition curves in the unaged and aged conditions of 13%Cr (Type 410) and 13%Cr-1%Ni (longitudinal orientation). [69]



(1J = 0.738 ft-lb)

Figure 4-4
Typical Charpy V-notch transition behavior of unaged Type 410 martensitic stainless steel. A is tempered at 1450°F with final hardness 95 HRB; B is tempered at 1225°F with final hardness 24 HRC; and C is tempered at 1100°F with final hardness 30 HRC. [70]

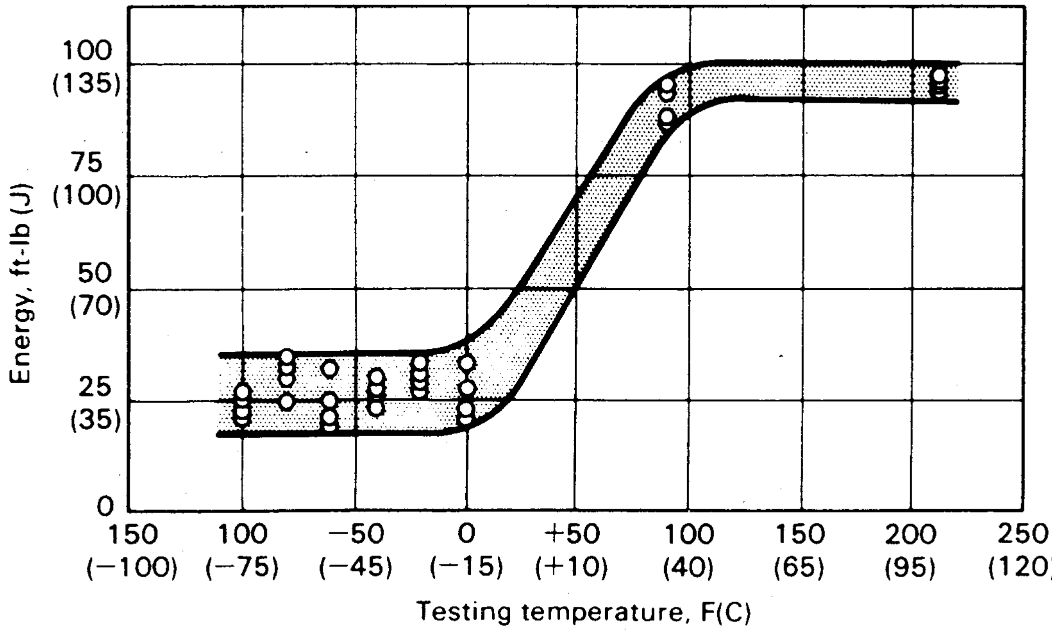


Figure 4-5
Izod Data For Unaged Type 410 After Quenching From 1800°F and Tempering at 1150°F (HB 228). [71]

5
ALLOYS X-750, 718, AND A-286

Precipitation hardenable Alloys X-750, 718, and A-286 are extensively used by the nuclear power industry due to their high strength and superior corrosion resistance. Applications include core internals bolting, springs, and guide pins [72]. Alloys X-750 and 718 are nickel-base alloys and A-286 is classified as stainless steel. The chemical compositions of these alloys are listed in Table 5-1[73].

5.1 Alloy X-750

Alloy X-750 is a precipitation-hardenable nickel-base austenitic alloy used for its corrosion and oxidation resistance and high temperature strength. The composition of Alloy X-750 is very similar to that of Alloy 600, except for a higher Ti and Al content and the addition of 1% Nb. Precipitation of intergranular carbides has a similar effect of increasing IGSCC resistance as in Alloy 600. The precipitation of gamma prime γ' [Ni_3 (Al, Ti)] intermetallic compound is responsible for the high strength at elevated temperature. As listed in Table 5-2 [74, 75, 76], a variety of precipitation heat treatments have been used in PWRs in the past. Their mechanical properties are listed in Table 5-3 [77].

Failures of Alloy X-750 helical holddown springs in the No. 1 spring temper condition were observed in B&W design PWRs in the early 1980's [78]. The springs were produced from forged billet which was hot rolled to 1.59 cm diameter rod. The rod was reduced to the final wire diameter by two or three cold drawing/annealing cycles. Prior to the last drawing operation the wire was solution annealed at 1149°C. The final drawing produced a reduction in area of 16%. After the last draw, the wire was cold coiled into the spring and was precipitation heat treated at 732°C for 16 hours. This sequence placed the Alloy X-750 in the No. 1 spring temper condition per AMS 5698 specification. These springs operate at temperatures ranging from ambient to 315°C with an estimated lifetime fluence of 10^{20} to 10^{21} n/cm^2, E>1.0 MeV. These springs failed through fatigue initiation and propagated to failure by either high cycle low amplitude fatigue or intergranular stress corrosion cracking (IGSCC). Fatigue initiation was facilitated by a coarse grain size rim and by surface damage in the initiation area due to wear or fretting. Failures of control rod drive guide tube support pins (also called split pins) due to IGSCC were reported in Westinghouse design PWRs [73, 79]. These pins were fabricated from Alloy X-750 in various heat treatment conditions. Alloy X-750 in the HTH and CIB conditions has better resistance to IGSCC than other conditions. Slow strain-rate tensile testing in laboratory indicates that Alloy X-750 is susceptible to hydrogen embrittlement at room temperature in hydrogenated water. The presence of hydrogen reduced both tensile elongation and reduction of area by 50%, but produced no discernible effect at 288°C [80].

There has been no indication of Alloy X-750 thermal aging embrittlement from operating experience or from past failure investigations in PWRs. The impact properties of Alloy X-750 is shown in Figure 5-1. Because of the austenitic matrix, Alloy X-750 has no distinctive ductile-brittle transition behavior typical of body centered cubic (bcc) materials. Hence, Alloy X-750 is not expected to become thermally embrittled due exposure at elevated temperatures in PWRs. A recent study of irradiation and thermal aging effects on reactor structural alloys included Alloy X-750 thermally aged at 371°C (700°F) for 71,800 hours. The results showed little effect on Alloy X-750 room temperature tensile properties. In addition, Izod impact tests at temperatures between –50 to 250°C (-58 to 482°F) showed increase in impact energy (see Figure 5-2) [54].

5.2 Alloy 718

Alloy 718 is an age-hardenable austenitic nickel alloy originally developed for the aerospace industry, but has seen much use in the nuclear industry as a structural alloy due to its high strength and corrosion resistance [73]. A significant increase in strength is achieved by two precipitation reactions from solid solution involving γ' (fcc - Ni_3Al, Ni_3 (Al, Ti)) and γ" (bct, Ni_3Nb) secondary phase [81]. The addition of niobium sets this alloy apart from other high-strength nickel alloys (i.e., X-750) and stainless steels (A-286) strengthened by γ' alone. Both γ' and γ" precipitates are extremely fine (5 to 10 nm) and can only be resolved with an TEM. Because of this, the microstructure of the solution annealed and age-hardened conditions are often indistinguishable with light microscopy.

Blocky MC intragranular carbides are also present in both solution annealed and age-hardened conditions, and are resolvable with a light microscope. MC carbides do not affect strength, corrosion behavior, or other material properties of significance. Other phases of significance can also be developed in this alloy. If lower solution anneal temperatures, and/or higher aging temperatures are applied, other phases can precipitate. Delta phase (orthorhombic Ni_3Nb) is a desirable intergranular phase from the standpoint of high temperature grain boundary strength and grain refinement for aerospace application. Precipitation of Ni_3Nb is dependant on solution annealing temperature and can precipitate either during low temperature solution annealing or during high temperature aging.

Hexagonal Laves phase is another secondary phase of importance and is considered undesirable for any application. Laves has an embrittling effect on room temperature mechanical properties. Laves is often seen as blocky or globular intergranular precipitates and can develop during initial melting, forging or heat treatment. Control of Laves is therefore an important consideration for the entire material process, from melting, through ingot reduction/forging and into final heat treatment. Table 5-2 lists the heat treatments that have been used in PWRs [73]. Failures of Alloy 718 in PWRs have been rare compared to Alloy X-750 and Alloy A-286. The known failures of Alloy 718 were of fuel-assembly and barrel-design hold down springs due to fatigue [73]. There has been no indication of Alloy 718 thermal aging embrittlement from operating experience or from failure investigations in PWRs. Like Alloy X-750, Ally 718 is not expected to become thermally embrittled due exposure at elevated temperatures in PWRs.

5.3 Alloy A-286

Alloy A-286 is an Fe based, age hardenable austenitic alloy that is often used in place of Type 300 series stainless steels (as noted below) when a higher yield strength is required. Unlike martensitic or semi-austenitic precipitation-hardening stainless steels, the matrix of Alloy A-286 retains the austenitic face centered cubic structure (fcc) at all temperatures. After a solution anneal at 900-980°C (1650-1800°F), Alloy A-286 is rapidly cooled (often by quenching) to prevent precipitation. After forming and machining, the precipitation hardening or aging heat treatment is performed at 718°C (1324°F) for 16 hours. The choice of solution anneal temperature affects the matrix grain size and final properties. Higher solution anneal temperatures (980°C or 1800°F) results in larger grain size and better creep strength at elevated temperature. Lower solution anneal temperature results in finer grain size and better room temperature properties. The precipitation phase responsible for hardening is a coherent Ni_3Ti phase.

Because of the compatibility of its coefficient of thermal expansion with 300 series austenitic stainless steels, high yield strength in the age-hardened condition, and anti-galling characteristics, Alloy A-286 was used for internals bolting applications in both PWRs and BWRs. Extensive cracking of Alloy A-286 (ASTM A453 Grade 660) core grid screws and cover beams due to IGSCC was discovered in BWRs (ASEA-ATOM) in 1982 [82]. Failures of Alloy A-286 reactor vessel internals bolts were also discovered in PWRs in 1980s [83]. It is now accepted that Alloy A-286 is susceptible to IGSCC especially when they are loaded at or close to their yield strength. There has been no indication of Alloy A-286 thermal aging embrittlement from operating experience or from failure investigations in PWRs. The impact properties of precipitation hardened Alloy A-286 is shown in Figure 5-3 [84]. Because of the austenitic matrix, Alloy A-286 has no distinctive ductile-brittle transition behavior. Figure 5-4 shows the effects of long term exposure at elevated temperature and low levels of neutron fluence on impact energy. Figure 5-4 shows that the impact energy is unaffected by exposure at 550°F for 5311 hours. Hence, Alloy A-286 is not expected to become thermally embrittled due exposure at elevated temperatures in PWRs.

5.4 Conclusions:

Alloys X-750, 718, and A-286 in various precipitation hardened conditions are commonly used in LWRs. Like unirradiated wrought austenitic stainless steels, these precipitation hardenable alloys (with an austenitic matrix) possess no distinctive ductile-brittle transition behavior. Limited data indicates that the impact properties of these three alloys are insensitive to exposure at LWR operating temperatures. Failures of these materials due to IGSCC or fatigue have been well documented and studied in the past. However, there have been no indications of thermal aging embrittlement from long term exposure at elevated temperatures either from failure investigation or operating experience. Therefore, it can be concluded the response of these alloys to thermal aging embrittlement at PWR temperatures is similar to wrought austenitic stainless steels, i.e., these alloys will not become thermally embrittled due long term exposure at PWR temperatures.

Table 5-1
Chemical Composition of A-286, and Alloy X-750 and 718 [73]
(wt%, maximum unless range or minimum is indicated)

	Ni	Cr	Fe	C	Cb+ Ta	Ti	Al	Mn	Si	S	Co	Mo	B	Cu	P	V
A-286	24.00-27.00	13.50-16.00	Bal.	0.08	--	1.90-2.35	0.35	2.00	1.00	0.030	--	1.00-1.50	0.0010-0.010	--	0.040	0.10-0.50
X-750	70.00 min.	14.00-17.00	5.00-9.00	0.08	0.70-1.20	2.25-2.75	0.40-1.00	1.00	0.50	0.01	1.00	--	--	0.50	--	--
718	50.00-55.00	17.00-21.00	Bal.	0.08	4.75-5.50	0.65-1.15	0.20-0.80	0.35	0.35	0.015	1.00	2.80-3.30	0.006	0.30	0.015	--

Table 5-2
Heat Treatment of Alloys X-750, 718, and A-286Used In PWRs [74, 75, 76]

Alloy X-750

AH (equalized and aged)	Hot worked; equalize 24 h at 885°C (1625°F), air cool; age 20 h at 704°C (1300°F), air cool
BH (low temperature anneal)	Hot worked; solution anneal 1 h at 982°C (1800°F), air cool; age 20 h at 704°C(1300°F), air cool
HTH (high temperature anneal)	Hot worked; solution anneal 1 h at 1093°C (2000°F), air cool; age 20 h at 704°C(1300°F), air cool
AMS-No. 1 Temper	solution anneal at 1149°C; 15% cold reduction in area; age 16 h at 732°C (1350°F), air cool
AMS- No. 2 Temper (spring)	solution anneal at 1149°C(2100°F); 30-65% cold reduction in area; age 4 h at 649°C (1200°F), air cool
CIB (core internal basic)	solution anneal 1-2 h at 1080°C (1976°F), water or oil quench; age 20 h at 715°C (1319°F), air cool

Alloy 718

ASTM A637, Gr. 718	Solution anneal ½ h min. at 927-1010°C (1700-1850°F); age 8h at 718°C (1324°F) + 10h at 621°C (1150°F)
AMS 5596 & 5597	Solution anneal at 1010-1066°C (1850-1950°F); age 10h at 760°C (1400°F) + age 20h at 649°C (1200°F)
O-ring Application	Solution anneal ½ h max. at 1066°C (1950°F); age 3 to 16 h at 732°C (1350°F)
Spring Applications	Anneal at 1038°C (1900°F); cold draw; anneal at 982°C (1800°F); cold draw and coil; age 8h at 718°C (1324°F) + 10h 621°C (1150°F)
Spring Applications	Anneal at 982-1038°C (1800-1900°F); cold draw and coil; age 8h at 718°C (1324°F) + 10h 621°C (1150°F)

Alloy A-286

ASTM A453, Gr. 660, Class A (Condition A)	Hot rolled + 2h min. at 899°C (1650°F); age 16h at 718°C (1324°F)
ASTM A638, Gr. 660, Type 1	Solution anneal 2 h at 899°C (1650°F); age 16h at 704-760°C (1300-1400°F)
AMS 5737C; ASTM A453, Gr. 660, Class B	Hot rolled + 1h min. at 982°C (1800°F); age 16h at 718°C (1324°F)

Table 5-3
Mechanical Properties of Alloys X-750 [77]

Heat Treatment	Orientation	Temperature	Tensile Strength	Yield Strength	Elong. (2 in)	Red. of Area	Reference
		°C	ksi	ksi	%	%	Sheeks 83
Hot Rolled	L	25	184	124	38	54	Sheeks 83
	T	25	184	124	36	43	Sheeks 83
AH	L	25	190	129	30	43	Sheeks 83
	T	25	187	128	29	39	Sheeks 83
	L	300	181	120	32	41	Sheeks 83
BH	L	25	183	114	37	44	Sheeks 83
	T	25	179	112	38	40	Sheeks 83
	L	300	166	112	35	41	Sheeks 83
HTH	L	25	178	114	38	33	Sheeks 83
	T	25	176	113	40	34	Sheeks 83
	L	300	158	104	41	42	Sheeks 83
No. 1 Temper			200	150	16		McIlree 83 & Baty 83
No. 2 Temper (spring)			295	290	1		McIlree 83
CIB			160 min.	100 min.	20 min.	20 min.	EPRI-90-Rev.1

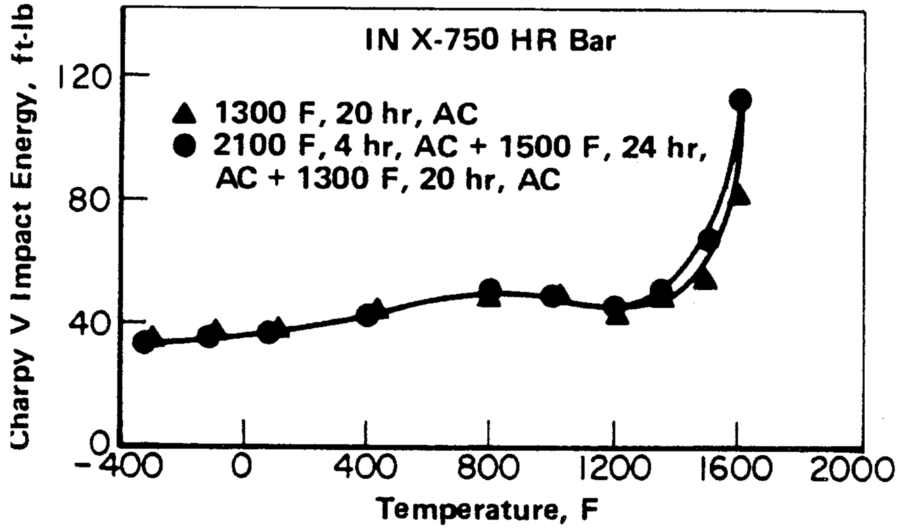


Figure 5-1
Charpy V-notch Impact Energy of Alloy X-750. [84]

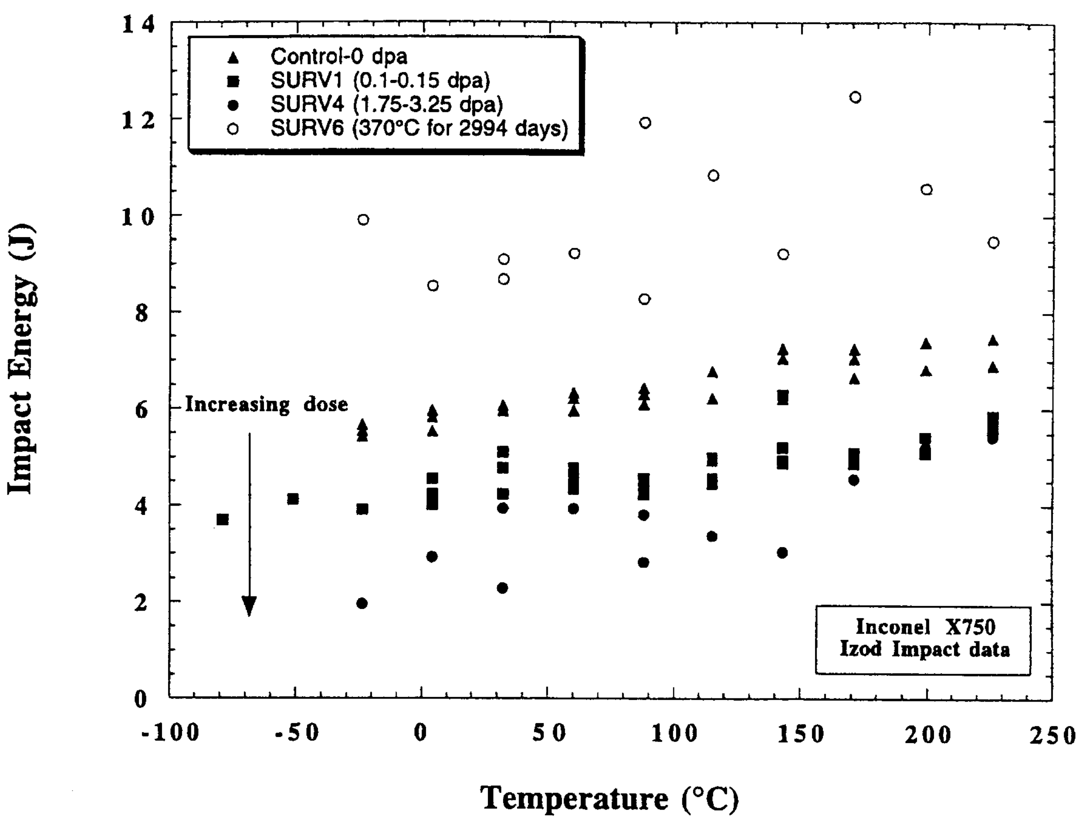


Figure 5-2
Izod impact energy of X750 thermally aged at 370°C (700°F) for 2994 days (71,800 hours) as a function of test temperature. [54]

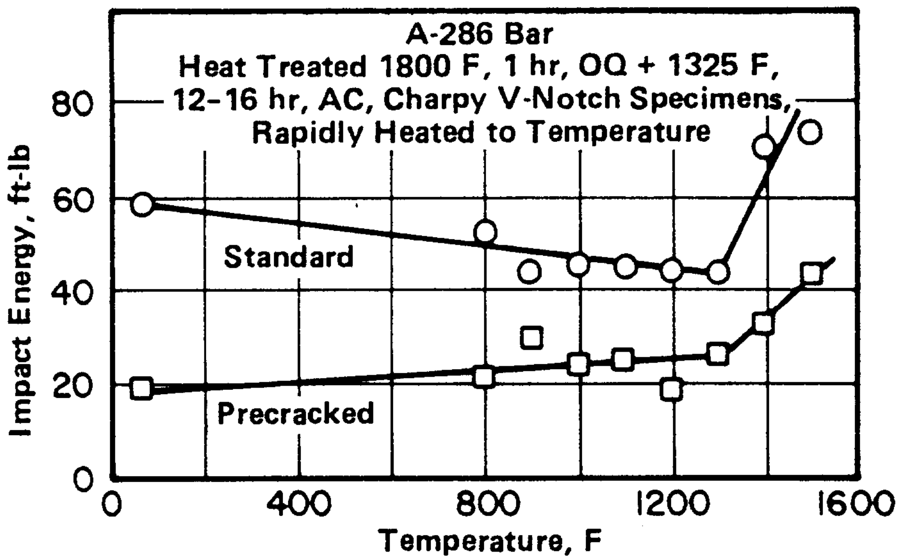


Figure 5-3
Charpy V-notch Impact Energy of Precipitation Hardened Alloy A-286 as a Function of Test Temperature. [84]

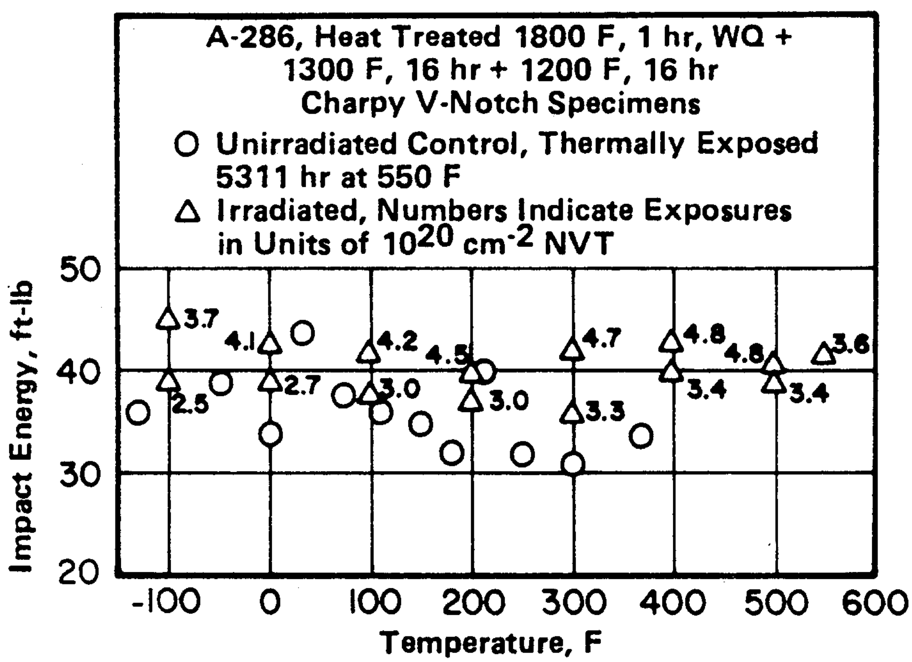


Figure 5-4
Effect of Exposure to Elevated Temperature and Neutron Fluence on Charpy V-notch Impact Energy of Precipitation Hardened Alloy A-286. [84]

6 AUSTENTIC STAINLESS STEELS AND WELDS

6.1 Introduction

Stainless steels have been used extensively in light water power reactors due to their superior corrosion resistance and fracture toughness. The PWR internals components were largely fabricated from wrought austenitic stainless steels, which possess excellent ductility and toughness and no distinct DBTT behavior. Besides irradiation embrittlement of materials next to the core, the thermal aging embrittlement concern in the PWR reactor internals had been associated only with cast austenitic stainless steel (CASS) and stainless steel weldments metals due to thermal aging. Thermal aging embrittlement of CASS and stainless steel welds at 482-662°F (250-350°C) has been well established and the embrittlement is manifested by increase in hardness and strength, loss of ductility and impact strength, and increase in DBTT [85].

Unlike wrought austenitic stainless steels, CASS and welds have a duplex microstructure consisting of austenite and ferrite phases. The presence of ferrite phase provides the welds with increased tensile strength and resistance to hot cracking tendencies, but is also the primary cause of thermal aging embrittlement due to the precipitation of α’ by spinodal decomposition in the ferrite phase. Additional embrittlement comes largely from precipitation of $M_{23}C_6$ carbides or growth of existing carbides at the ferrite/austenite interface. The G-phase precipitation and the accompanying Ni depletion from the ferrite matrix affect the α’ spinodal decomposition kinetics, but the effect on thermal aging embrittlement is complex. Therefore, susceptibility of CASS and welds to thermal aging embrittlement depend on the amount, size, and distribution of the ferrite phase and carbides on the ferrite-austenite interface.

6.2 Wrought Stainless Steels

Wrought stainless steels possess exceptional ductility. A review of fracture toughness data shows that and that J_{Ic} fracture toughness value for unirradiated Type 304 and 316 stainless steels can vary by a factor of ten, from 169 to 1660 MPa/m^2 [86]. The scatter is due to heat-to-heat variation and crack orientation effects. Mills performed a statistical analysis of fracture toughness data after the establishment of ASTM E 813 in 1981 and found that J_{Ic} and tearing modulus dJ/da follow a log-normal distribution as shown in Figure 6-1. The operative cracking mechanism for austenitic stainless steels is microvoid coalescence at both room and elevated temperatures. Heat-to-heat variability is attributed mainly to differences in the density and morphology of inclusions and secondarily to matrix strength. Typical inclusions are MC-type carbides, calcium aluminates, and manganese sulfides. A high density of large inclusions and a high matrix strength are both detrimental to fracture toughness. Heats with higher J_{Ic} values also tend to have higher dJ/da values irrespective of testing temperature. This indicates that the same underlying microstructural features control both crack initiation and stable propagation.

No statistical difference between fracture toughness was found between Type 304 and Type 316 and the test results are combined in Figure 6-2. The mean and lower bound fracture toughness values at room and elevated temperature are summarized in Table 6-1 [86]. The lower bounds bracket 90% of the total population at a 95% confidence level. At room temperature, the lower bound J_{Ic} for unirradiated Type 304 and Type 316 is 215 kJ/m^2 and lower bound dJ/da is 59 MPa. The fracture toughness of Type 304 and 316 decreases with increasing temperature as seen in Figure 6-1 [86]. The decrease is less pronounced for heats with low room temperature J_{Ic}. However, the dJ/da (hence the tearing modulus *T*) is essentially unchanged at elevated temperature with moderate lower median value and higher lower bound value. At elevated temperature, the lower bound J_{Ic} for unirradiated Type 304 and Type 316 is 96 kJ/m^2 and lower bound dJ/da is 79 MPa, which is equivalent to a lower bound tearing modulus *T* of 130. This shows that even the low toughness heats of unirradiated Type 304 and 316 possess high fracture toughness at room or elevated temperatures up to 550°C (1022°F).

Wrought stainless steels possess a certain amount of anisotropy in mechanical properties and microstructure, which gives rise to different fracture toughness values with respect to crack orientation. Inclusions provide the nucleation sites for microvoids ahead of the crack front. Coalescence of these microvoids reduces the plastic deformation required to advance the crack. Hence, fracture toughness is severely degraded when the crack propagation direction is aligned with the inclusion stringers, which are normally aligned with the principal working direction. The effect of crack orientation on J_{Ic} for unirradiated Type 304 and Type 316 and their welds is shown in Figure 6-3 [86]. For rectangular sections or cylindrical pipes and bars, the crack orientation is defined by two letters with the first letter representing the direction normal to the crack plane and the second letter the crack propagation direction.

Figure 6-3 shows that J_{Ic} for rolled plate corresponds to the crack plane (the first letter) with the highest in L-S and L-T orientations, the intermediate in the T-S and T-L orientations, and the lowest in the S-T and S-L orientations. Cross-rolling usually produces plates with about the same toughness values for both L-T and T-L orientations, but causes additional toughness loss in the S-L orientation. However, the low S-L orientation is typically not a concern due to minimal through-thickness loading in most situations. For cylindrical pipes, due to stringer alignment in the longitudinal direction, toughness in the C-L orientation could be 30% to 70% lower than the L-C orientation.

Cold work causes significant increases in the strength and decreases in the ductility and fracture toughness of wrought austenitic stainless steels. Testing of one heat of Type 316 shows that the initial J_{Ic} value of 254 kJ/m^2 is reduced to 121 kJ/m^2 after 5% cold work and to 70 kJ/m^2 after 30% cold work [86]. Results from two heats of Type 316 solution annealed and cold worked with approximately the same final yield and tensile strengths showed that cold work reduced the J_{Ic} from 798 to 538 kJ/m^2 for one heat and from 233 to 39 kJ/m^2 for the other heat [87]. The final fracture toughness could not be predicted by the final strength levels or the amount of cold work due to a variability in the inclusion morphology. The decrease in toughness is partly attributed to the cold work effect on secondary particle alignment and toughness degradation is more significant for heats with a high density of stringers and low initial toughness.

Below 450°C (842°F), long-term thermal aging has minimal effect on the J_{Ic} of unirradiated wrought austenitic stainless steels [86, 88, 89]. Aging at ~550°C (1022°F) for 50,000 hours reduces J_{Ic} by 35% due to precipitation of grain boundary carbides. These carbides cause isolated intergranular cracking during fracture toughness testing.

Hence, at PWR temperatures, the effect of long term thermal aging on fracture toughness of unirradiated wrought austenitic stainless steels is expected to be negligible. This is due to the fact that the ferrite content of most wrought austenitic stainless steels is very low, less than 1 percent. For austenitic stainless steels, precipitations of embrittling phases, sigma, laves, and chi intermetallic will not form at temperatures below 1100°F (~600°C).

6.3 Stainless Steel Castings and Welds

Thermal aging embrittlement of austenitic stainless steel welds and castings at PWR operating temperatures has been well established [85, 90, 91, 92]. The thermal aging embrittlement increases the hardness and tensile strength, and decreases ductility, impact strength, and fracture toughness. Austenitic welds and castings have a duplex microstructure consisting of austenite and δ–ferrite phases. Although the ferrite content is beneficial in preventing hot cracking and stress corrosion cracking, it is also the source of thermal aging embrittlement for austenitic welds and castings at PWR temperatures. The miscibility gap below 500°C (932°F) causes the δ–ferrite to segregate (spinodal decomposition) into the Fe-rich α phase and the Cr-rich α' phase [85]. The low temperature embrittlement is caused primarily by the precipitation of a fine, coherent body centered α' phase, which is also responsible for the 475°C (885°F) embrittlement of ferritic stainless steels. An additional contribution to embrittlement comes from the precipitation of a G phase (a nickel and titanium rich silicide) in the δ–ferrite and precipitation and growth of carbides at ferrite/austenite interface. The effect of thermal aging embrittlement of austenitic stainless steel welds and castings is manifested in cleavage fracture in the ferrite phase or separation of the ferrite/austenite phase boundary. Materials with high ferrite content and/or large phase boundary carbides are more prone to thermal aging embrittlement. Significant reduction in fracture toughness is likely when ferrite volume fraction exceeds 10% and above [88].

Among the many investigations related to duplex casting stainless steels, the most comprehensive and systematic studies were performed by Chopra et. al., who investigated the microstructures of different grades of CASS after their long term exposure to PWR relevant temperatures [93, 94, 95, 96, 97]. Chopra and Chung also performed tensile tests, hardness tests, Charpy tests, and fracture toughness tests on many heats of experimental and commercial of CF-3, CF-8, and CF-8M castings, which had been thermally aged between 554 to 842 °F (290 to 450°C) for up to 10,000 hours. The high carbon and Ni retained in the ferrite matrix was found to accelerate spinodal decomposition and α' formation. The effect of thermal aging embrittlement can be mitigated by annealing at 1022°F (550°C) for 1 hour, which restores the room temperature toughness before the aging embrittlement. The annealing dissolves α' from spinodal decomposition in the ferrite phase. The low carbon CASS such as CF-3 is the least susceptible to thermal aging embrittlement while high carbon Mo-bearing CF-8M is the most susceptible to thermal aging embrittlement. The reduction in Charpy impact energy was found to correlate similar reduction in J_{Ic} fracture toughness and tearing modulus as shown in Figure 6-4. Aging of a CF-8 steel with 24% ferrite at 752°F (400°C) for 10,000 hours reduces the room temperature Charpy impact energy from 220 to 50 J and J_{Ic} value from 2170 to 250 kJ/m^2. Based on the test results, Chopra et al. have developed correlations for estimating fracture toughness, tensile, and Charpy impact properties of CASS based on chemical composition, aging temperatures and times.

Austenitic stainless welds have similar chemical composition and duplex structures to those of CASS. austenitic stainless welds such as Type 308 generally contain 5 to 15% ferrite. Fracture toughness of austenitic stainless welds is found to be dependent on weld process, but insensitive to filler metal [85]. Figure 6-3 shows the room temperature J_{Ic} of several commonly used stainless steel welds by five different weld processes including gas tungsten arc (GTA), shielded metal arc (SMA), submerged arc (SA), gas metal arc (GMA), and flux cored arc (FCA) [86]. Welds produced by the GTA process obtain the highest toughness values while welds produced by the SA process consistently have the lowest toughness values. This is mainly due to the fact that GTA welds have the lowest inclusion density due to the inert gas protecting the molten pool from oxygen and the absence of a flux. No statistical differences are found between J-R curves for SA and SMA welds. The J_{Ic} fracture toughness data for GMA and SMA weld processes are intermediate.

Welds produced by the SMA process can have significant variation in toughness due to the manual nature of the welding process. Lower bound fracture toughness for SMA welds are conservatively assumed to be comparable to the toughness of SA process welds. The log-normal distribution J_{Ic} and dJ/da of stainless steel weld test data produced by the GTA and SA processes are plotted in Figure 6-5 [86]. The mean and lower bound fracture toughness values in reference 17 are listed in Table 6-1. The lower bound values, bracketing 90% of the total population at a 95% confidence level, are 192 kJ/m^2 (J_{Ic}) and 139 MPa (dJ/da) for GTA welds and 67 kJ/m^2 (J_{Ic}) and 72 MPa (dJ/da) for SA welds. Figure 6-7 shows the effect of temperature on fracture toughness of different weld processes [86]. The lower bound values, bracketing 90% of the total population at a 95% confidence level, are listed for GTA welds in Table 6-1. The 180 kJ/m^2 (J_{Ic}) and 107 MPa (dJ/da) lower bound indicate a slight decrease in toughness at elevated temperature of 400-550°C (752-1022°F). The minimum observed values are 55 kJ/m^2 for J_{Ic} and 62 MPa for dJ/da, which are 15% less than the lower bound for SA welds near room temperature. Although the J_{Ic} is relatively low for SA and SMA welds compared to that of GTA welds, their tearing modulus remains high. Thus, unstable fracture is unlikely without significant plastic deformation. Similar to wrought stainless steels, welds with higher J_{Ic} values also tend to have higher dJ/da values irrespective of testing temperature.

Figure 6-3 shows that the fracture toughness of welds is essentially independent of crack orientation. This is attributed to the fact that inclusion particles are not preferentially aligned with any particular direction. The crack plane of fracture toughness test specimens typically lie in the center of the weld where the grains are equiaxed from solidification or due to the tempering treatment effect from subsequent weld beads. However, the fracture toughness is expected to be affected by crack orientation in the weld metal near the fusion line due the anisotropy of solidification microstructures in this area. For castings, the low carbon CF-3 castings are the most resistant to thermal aging embrittlement and the high carbon CF-8M (containing Mo) castings are the least resistant. For a given ferrite content, austenitic stainless steel welds have higher tensile strength and lower fracture toughness than austenitic stainless steel castings. However, austenitic stainless steel welds (e.g. from SA or SMA) and castings with relatively lower fracture toughness values are also relatively insensitive to a thermal aging effect

[85]. Figure 6-8 shows that for long-term thermal aging at 400-450°C (752-842°F), the reduction in J_{Ic} is most significant for welds with high initial fracture toughness values, but moderate for welds with low initial fracture toughness values.

Fracture data from many sources, including J-R curve data from work conducted for the U.S. Nuclear Regulatory Commission (NRC) and compiled in the Pipe Fracture database (PIFRAC) have been analyzed. It was found that the lower bound J-R curve, based on power law fitting, for SA and SAW welds at 288-427°C (550-801°F) can be represented by the following expression. The lower bound is defined as the mean minus one standard deviation J-R curve.

$$J\ (\mathrm{kJ/m^2}) = 73.4 + 83.5\Delta a^{0.643} \qquad \text{where } \Delta a \text{ is in units of mm.}$$

where 73.4 kJ/m² is the J_{Ic} fracture toughness. However the lower bound J-R curve for fully thermally embrittled SA and SAW welds (aging was sufficient to achieve saturation toughness) at 288°C (550°F) is slightly lower than Eq. 6 and is conservatively expressed as

$$J\ (\mathrm{kJ/m^2}) = 40 + 83.5\Delta a^{0.643} \qquad \text{where } \Delta \mathrm{a} \text{ is in units of mm.}$$

where 40 kJ/m² is the J_{Ic} fracture toughness. Hence, the minimum J_{Ic} fracture toughness of thermally embrittled stainless steel welds is conservatively estimated to be 40 kJ/m². For both unaged and thermally aged conditions, the fracture toughness of stainless steel welds is higher at room temperature than at elevated temperatures [85]. A similar lower bound line given by reference 20 for aged Type 316 welds by manual metal arc (SMA) and tungsten inert gas shielded (GTA) processes has the following form:

$$J\ (\mathrm{kJ/m^2}) = 118\Delta a^{0.599} \qquad \text{where } \Delta a \text{ is in units of mm.}$$

The welds by the GTA process have much higher toughness values compared to welds by the SMA process. The flux-coated electrodes used in the SMA process are rich in Mn and Si deoxidants whose oxides are trapped in the molten pool during weld solidification. In contrast, the shielding gas and uncoated consumable used in the GTA welding result in particle volume fraction an order of magnitude lower in the GTA weld compared with the MMA weld. Fracture toughness of thermally aged GTA welds are higher than unaged SMA or SA welds [89].

6.4 Heat Affected Zones

Data on the thermal embrittlement of the heat affected zone is very limited. The chemical composition in the HAZ is the same as the base metal and ferrite content in HAZ is insignificant. Therefore, there is no embrittlement from precipitation of α' by spinodal decomposition in the ferrite phase. Hence, the thermal aging embrittlement potential in the HAZ is much less than the welds. Result shows that J_{Ic} of the HAZ of Types 304 and 316 remains close to the base metals and much higher than the weld materials regardless of welding process and heat inputs. Testing of Type 316L welds by GTA shows that fracture toughness near the fusion line in the HAZ or weld metal after aging is intermediate between those of the base metal and the weld (see Figure 6-9) [89]. Thus, the thermal aging embrittlement in the HAZ is not a concern and the loss of fracture toughness will be bounded by that of the welds.

6.5 Conclusions

For wrought austenitic stainless steels, the ferrite content is very low, less than 1 percent. Hence, there is virtually no potential for thermal aging embrittlement due to precipitation of α' by spinodal decomposition in the ferrite phase. For austenitic stainless steels, precipitations of embrittling phases, sigma, laves, and chi intermetallic will not form at temperatures below 1100°F (~600°C). Aging at ~550°C (1022°F) for 50,000 hours reduces J_{Ic} by 35% due to precipitation of grain boundary carbides. These carbides cause isolated intergranular cracking during fracture toughness testing. Hence, at PWR temperatures, the effect of long term thermal aging on fracture toughness of unirradiated wrought austenitic stainless steels is expected to be negligible.

For CASS and welds, thermal aging can lead to severe embrittlement. The thermal aging embrittlement of CASS has been extensively studied and as a result well established. Thermal aging embrittlement increases the hardness and tensile strength, and decreases ductility, impact strength, and fracture toughness. Austenitic welds and castings have a duplex microstructure consisting of austenite and δ–ferrite phases. The miscibility gap below 500°C (932°F) causes the δ–ferrite to segregate (spinodal decomposition) into the Fe-rich α phase and the Cr-rich α' phase. The low temperature embrittlement is caused primarily by the precipitation of a fine, coherent body centered α' phase, which is also responsible for the 475°C (885°F) embrittlement of ferritic stainless steels. An additional contribution to embrittlement comes from the precipitation of a G phase (a nickel and titanium rich silicide) in the δ–ferrite and precipitation and growth of carbides at the ferrite/austenite interface. Thermal aging embrittlement of austenitic stainless steel welds and castings is manifested by cleavage fracture in the ferrite phase or separation of the ferrite/austenite phase boundary. Materials with high ferrite content and/or large phase boundary carbides are more prone to thermal aging embrittlement. Significant reduction in fracture toughness is likely when ferrite volume fraction exceeds 10% and above.

Data on the thermal embrittlement of the heat affected zone is very limited. The chemical composition in the HAZ is the same as the base metal and ferrite content in HAZ is insignificant. Therefore, there is no embrittlement from precipitation of α' by spinodal decomposition in the ferrite phase. Hence, the thermal aging embrittlement potential in the HAZ is much less than the welds. Result shows that J_{Ic} of the HAZ of Types 304 and 316 remains close to the base metals and much higher than the weld materials regardless of welding process and heat inputs. Thus, the thermal aging embrittlement in the HAZ is not a concern and the loss of fracture toughness will be bounded by that of the welds.

Because thermal aging embrittlement of austenitic stainless welds and castings in PWRs has been well documented and is being managed by existing programs, no additional thermal aging embrittlement study program is recommended.

Table 6-1
Fracture Toughness of Unirradiated Stainless Steels [86]

Materials	Test Temperature	Mean J_{Ic}	Lower Bound[1] J_{Ic}	Mean dJ/da	Lower Bound[1] dJ/da	Mean T
		KJ/m²	KJ/m²	MPa	MPa	----
304, 316 Base metal	20 - 125°C (68 - 257°F)	672	215	292	59	350
	400 - 550°C (752 - 1022°F)	421	96	263	79	450
304, 308, 316, 16-8-2 GTA weld	20 - 125°C (68 - 257°F)	492	192	390	139	340
	400 - 550°C (752 - 1022°F)	293	180	307	107	350
304, 308, 316, 16-8-2 SA weld	20 - 125°C (68 - 257°F)	147	67	150	72	130

1. The lower bound corresponds to 90% bracketing of the total population at a 95% confidence level.

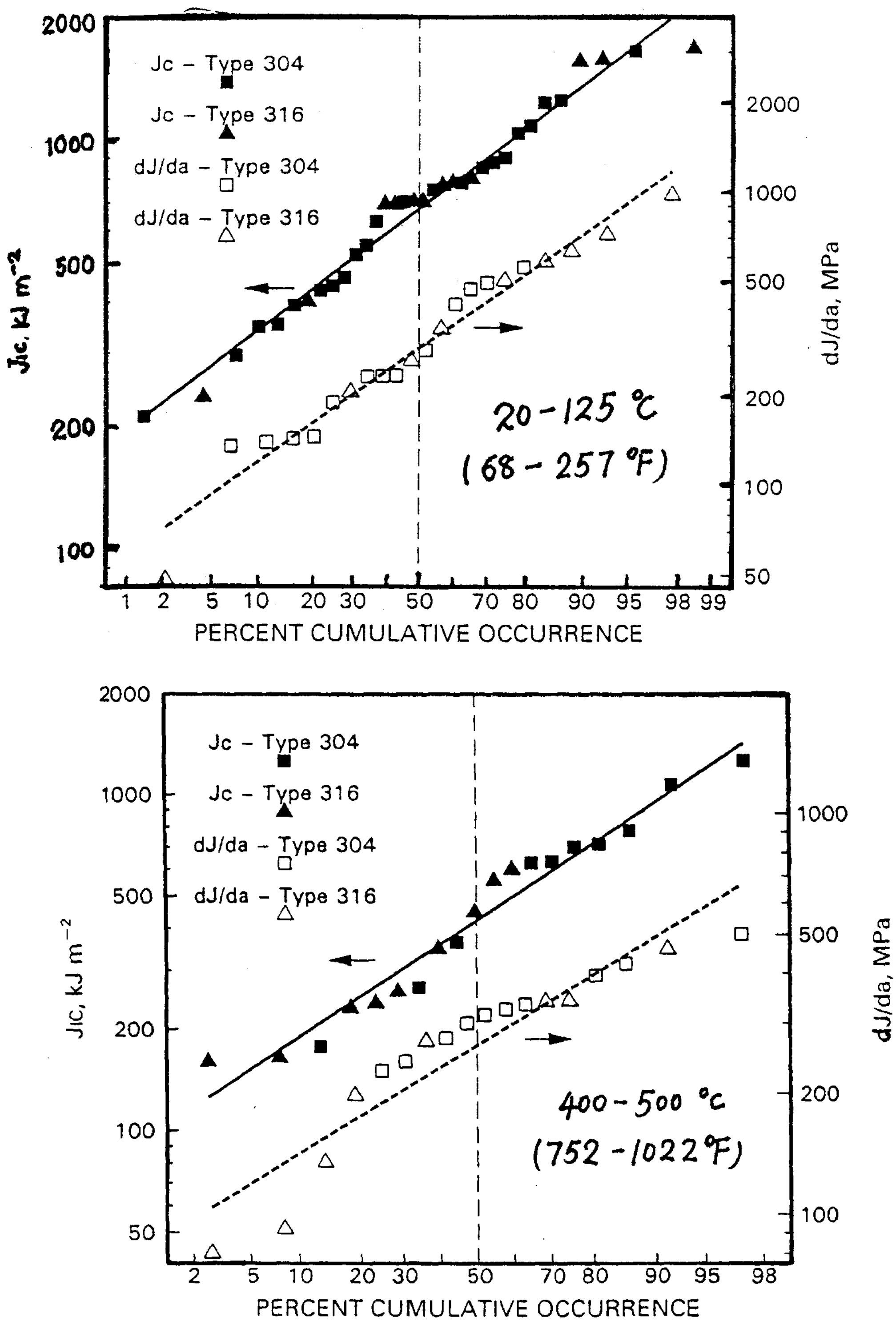


Figure 6-1
Cumulative frequency of J_{Ic} and dJ/da of unirradiated Types 304 and 316 at room and elevated temperatures. [86]

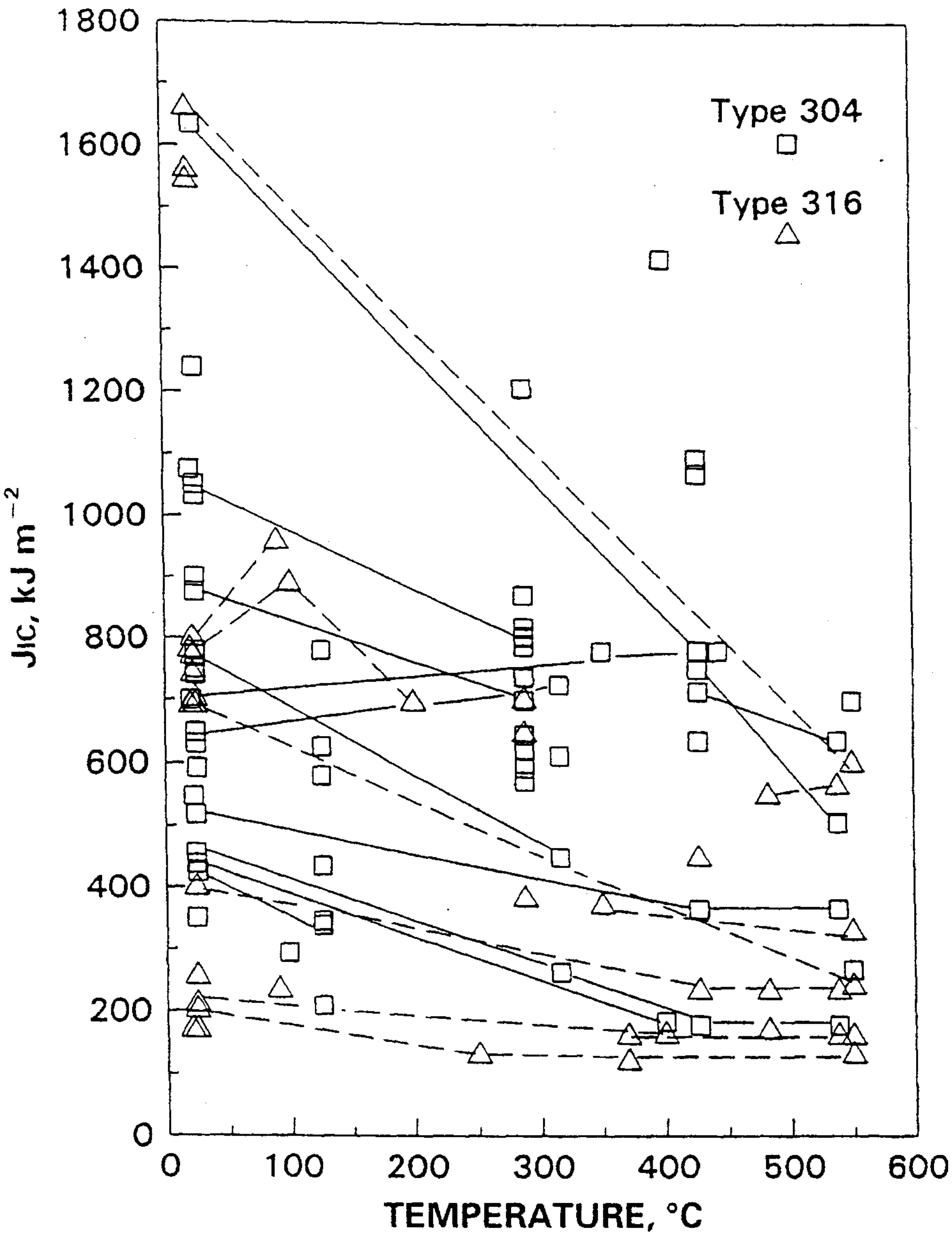


Figure 6-2
Effect of test temperature on J_{Ic} for unirradiated Types 304 and 316. J_{Ic} values for the same heat are connected by line. [86]

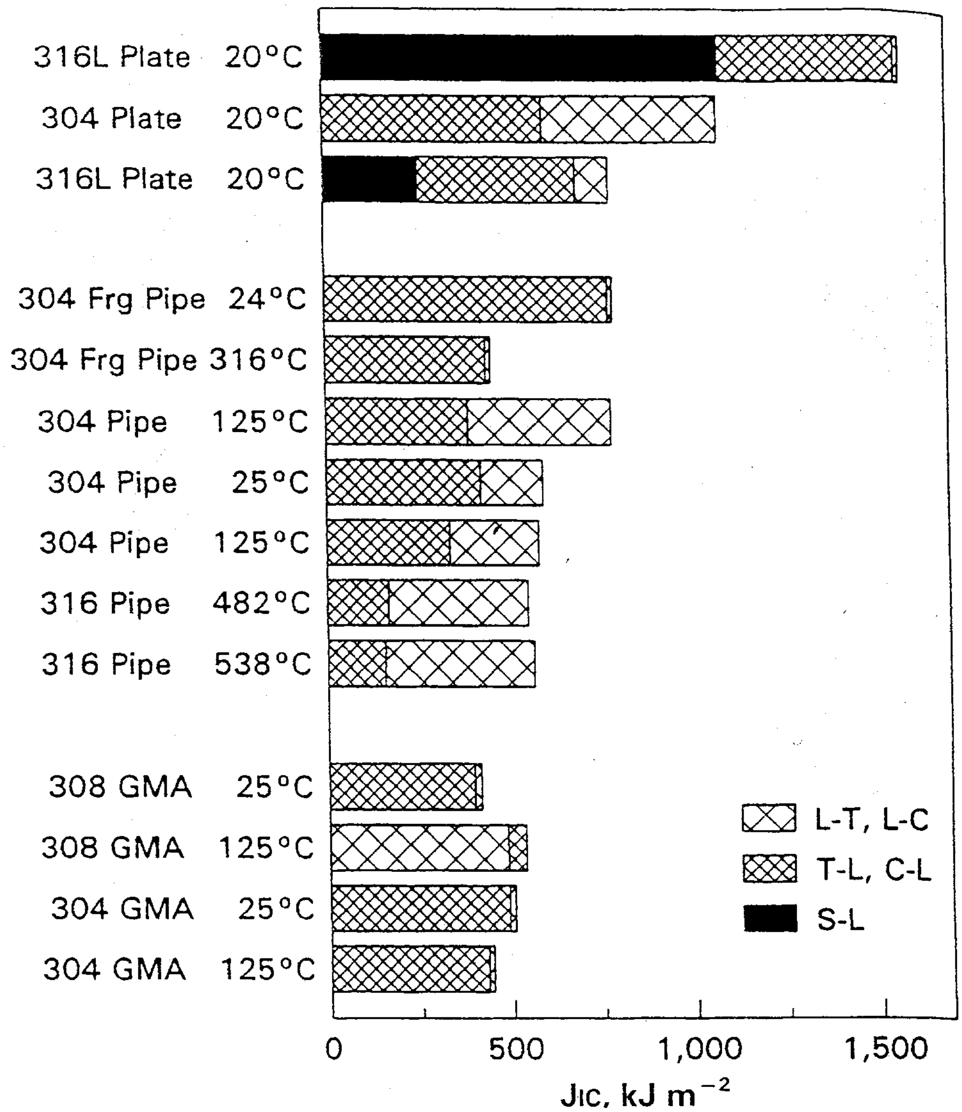


Figure 6-3
Effect of crack orientation on JIc of unirradiated stainless steels and welds. [86]

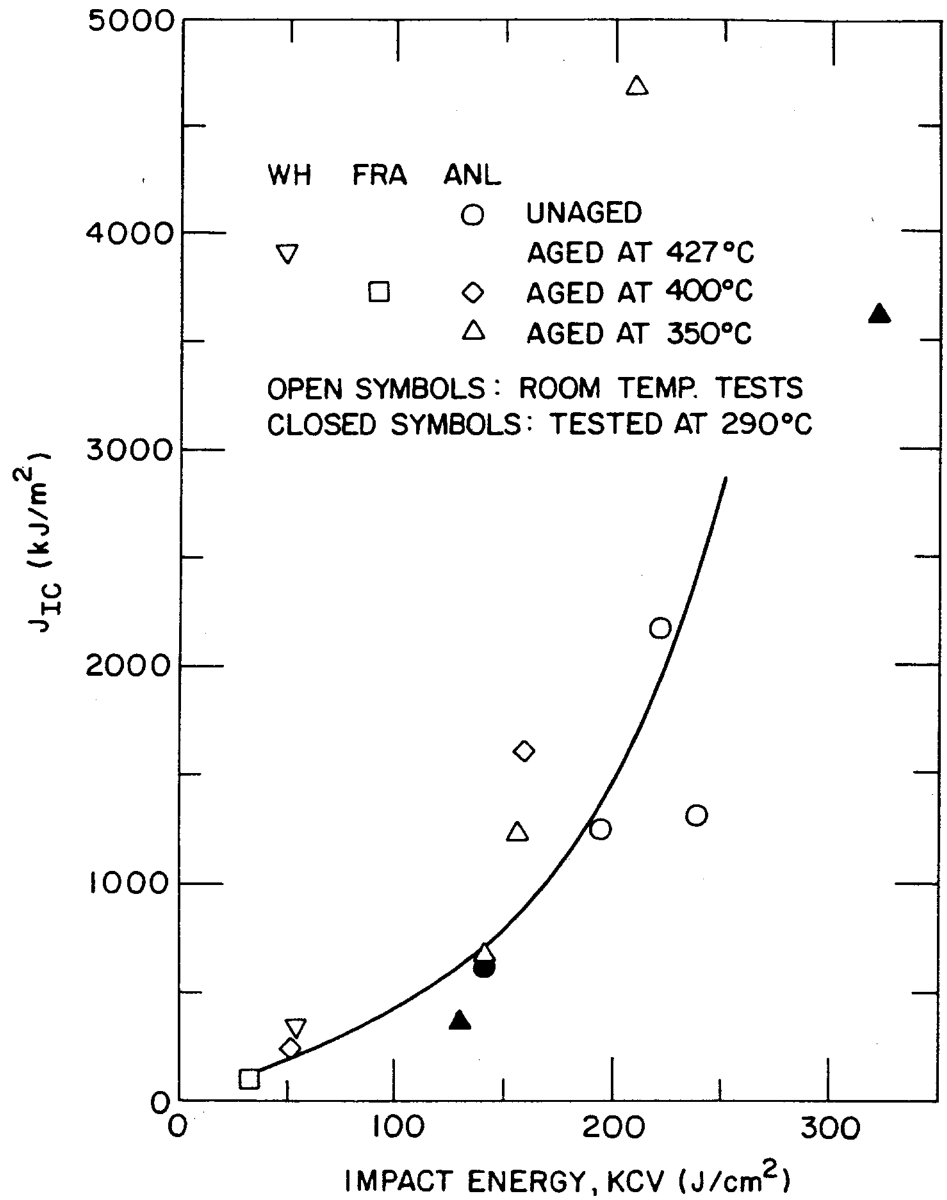


Figure 6-4
Correlation Between of J_{Ic} and Impact Energy for Thermally Embrittled CASS. [95]

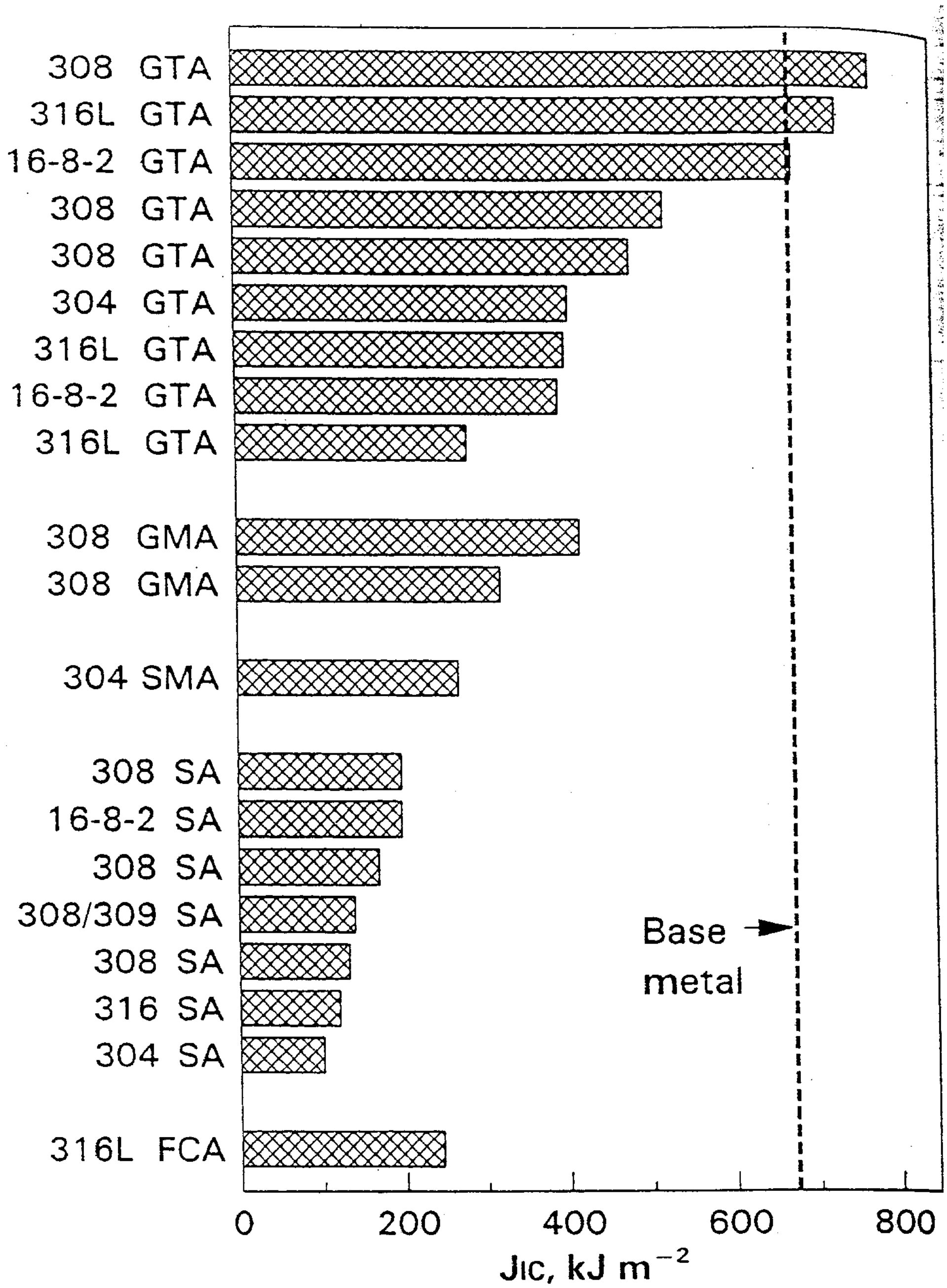


Figure 6-5
Comparison of J_{Ic} of unirradiated stainless steel weld by different processes. [2]

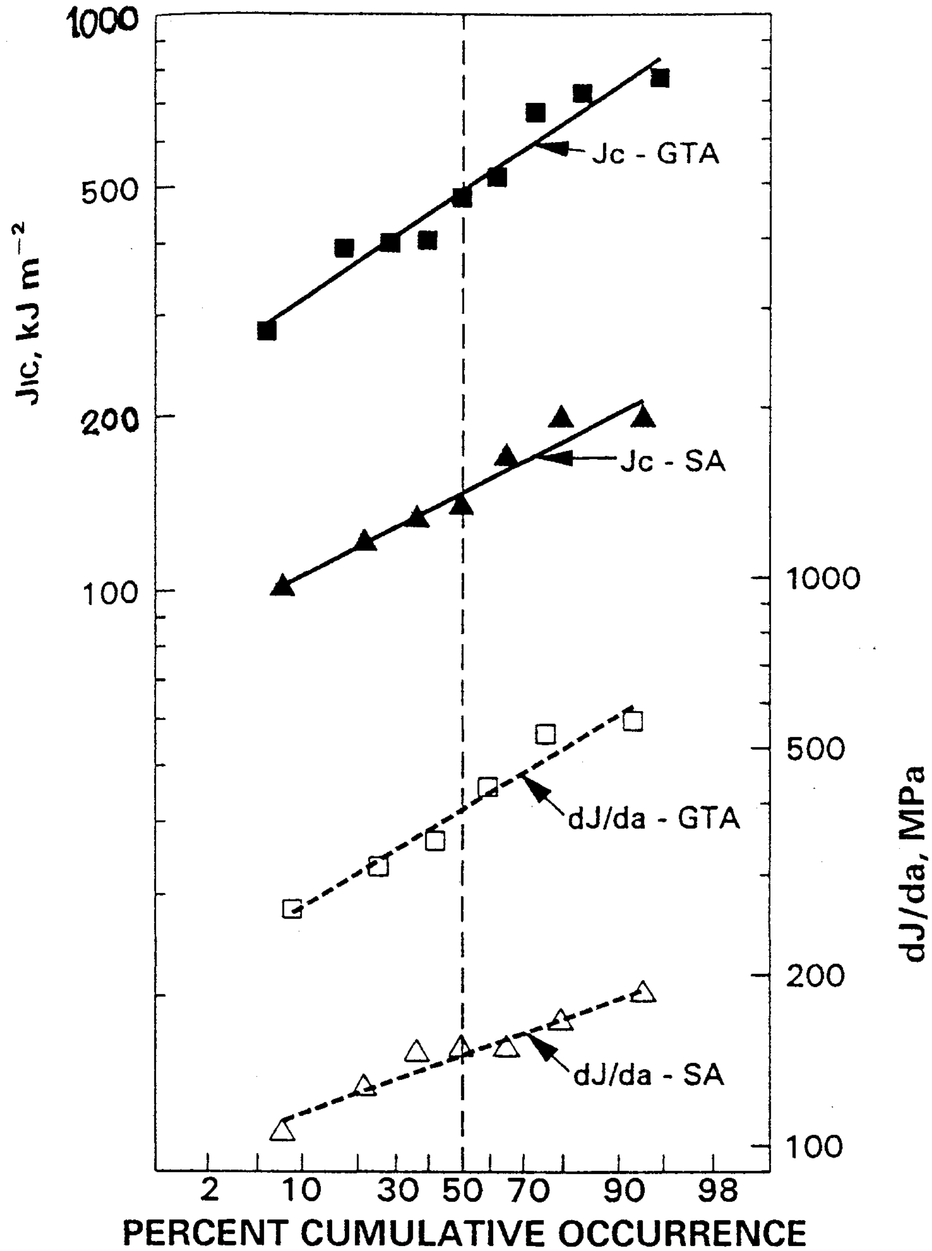


Figure 6-6
Cumulative frequency of J_{Ic} and dJ/da for unirradiated stainless steel welds by GTA and SA process (tested between 20-125°C) [86].

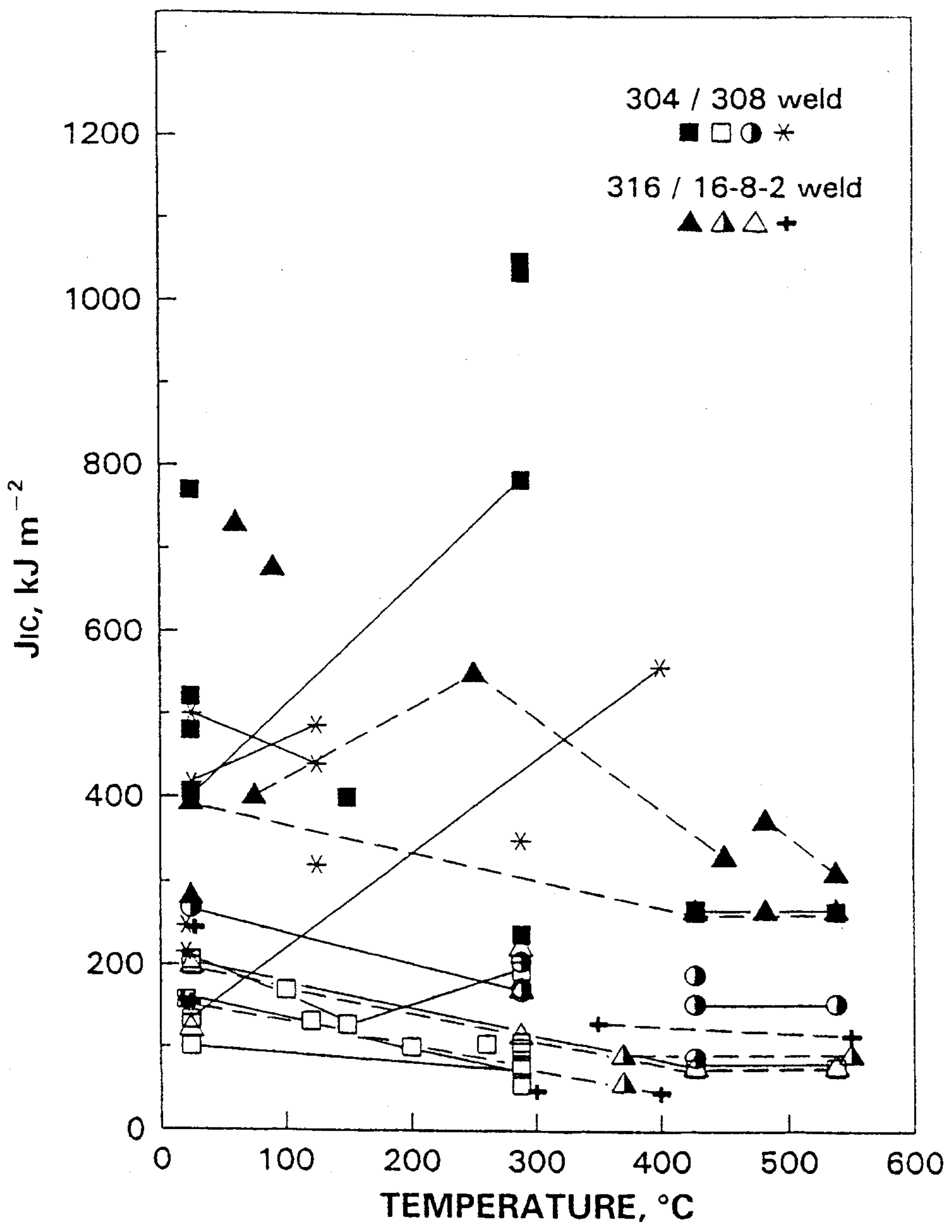


Figure 6-7
Effect of test temperature on J_{Ic} for unirradiated Types 304 and 316. J_{Ic} values for the same weld are connected by line; GTA, SMA, and SA welds are represented by closed, partly closed, and open symbols, respectively; a plus symbol or asterisk represents either another welding process or unidentified process [86].

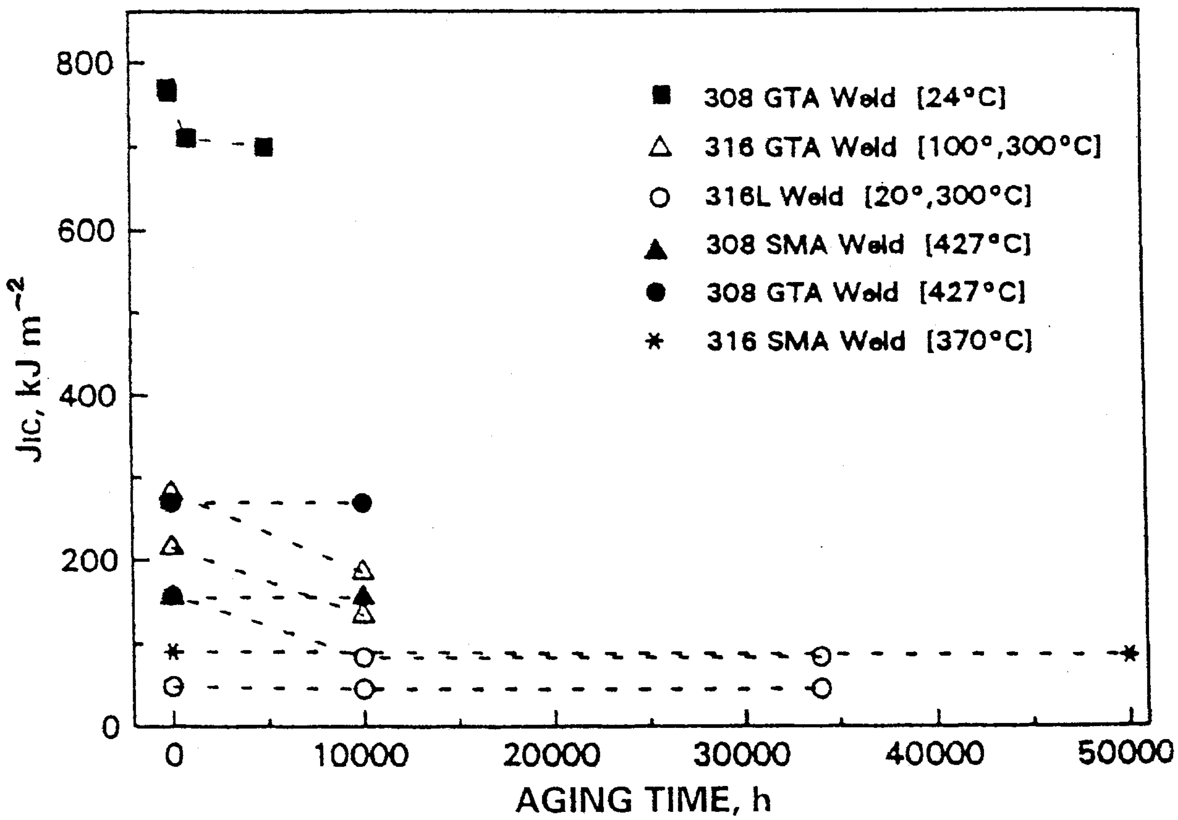


Figure 6-8
Effect of aging at 400-450°C (752-842 °F) on JIc of unirradiated austenitic welds. Test temperatures are shown inside brackets [86].

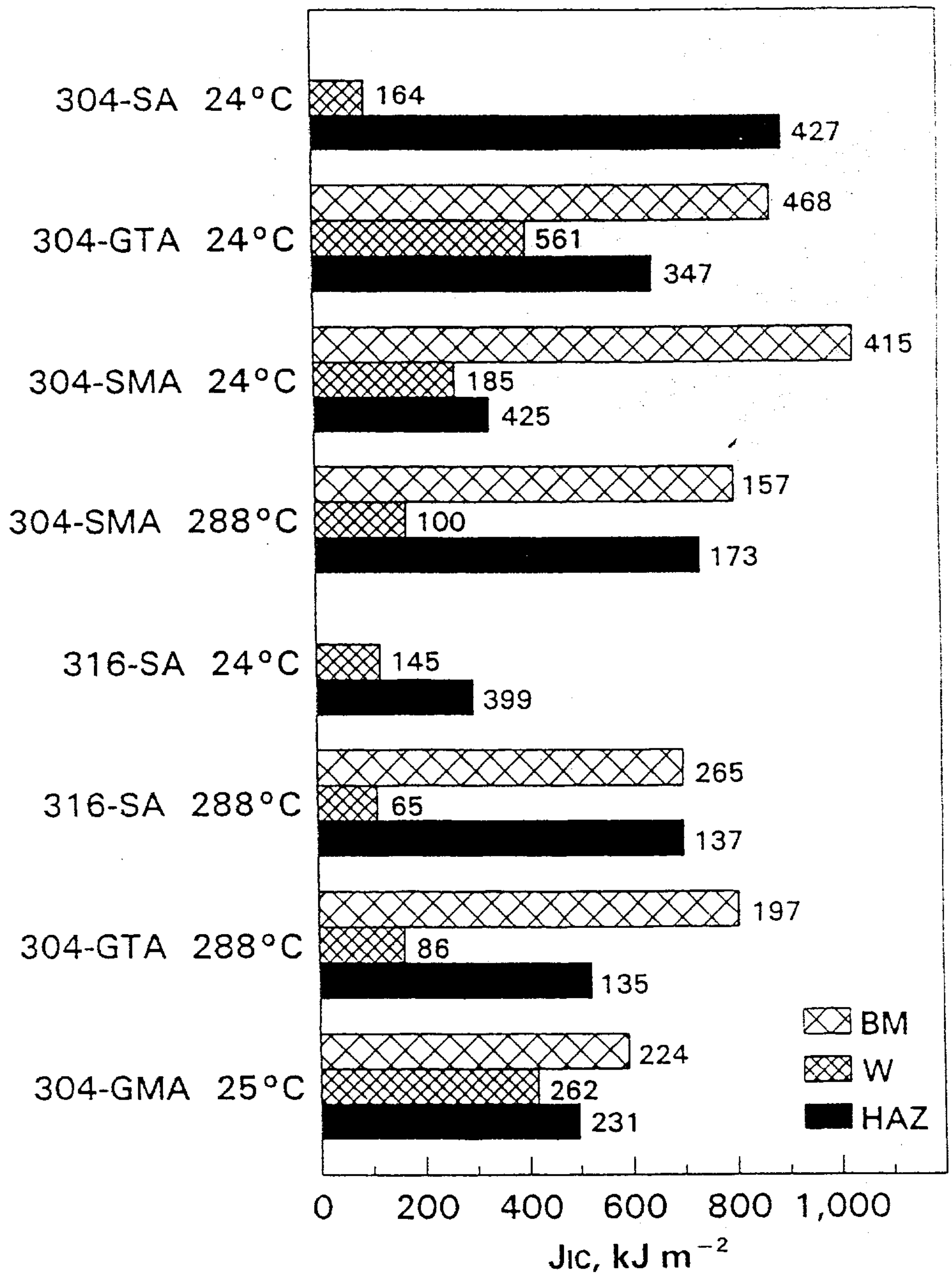


Figure 6-9
Comparison of J_{Ic} for unirradiated HAZ, Weld (W), and base metal (BM). Values of dJ/da in MPa are shown next each bar. [89]

7 ALLOYS 600, 690 AND WELD METALS

Alloy 600 and its weld metal Alloys 82 and 182 was extensively used in fabricating of PWRs during the 1960s and 1970s. Primary water stress corrosion cracking (PWSCC) of Alloy 600 components and its welds has been a major challenge to plant operation and maintenance over the last two decades. Since the 1980s, Alloy 690 and its equivalent weld metals Alloys 52 and 152 have been used for repair and replacement of degraded Alloy 600 components including steam generator tubings, CRDM nozzles, and penetrations in pressurizers and RCS pipings. The nominal chemical composition of Alloys 600 and 690 and their weld metals, Alloys 82/182, 52/152 is listed in Table 7-1 [98, 99, 100]. Vast amount of studies and investigative effort have been performed on the PWSCC of Alloys 600 and 690 in the past three decades, but none of them have been on the thermal aging embrittlement of these materials. It is due to the fact that these austenitic alloys are exceptionally ductile and not expected to suffer from thermal aging embrittlement. Indeed, there have never been any observations or failures linked to thermal aging embrittlement from numerous PWSCC investigations and decades of operating experiences involving Alloys 600, 690, and their welds.

7.1 Alloys 600 and 690

Despite numerous PWSCC failures of Alloy 600 and its welds in PWRs, there has been no report or observation indicative of thermal aging embrittlement. Due to its austenitic matrix, Alloy 600 and 690 do not have distinctive ductile-brittle transition behavior as shown in Figure 7-1 for Alloy 600 [84]. Alloy 690 contains higher content of Cr and correspondingly lower Ni content, but its microstructure is similar to Alloy 600, i.e., an austenitic matrix with secondary phases of predominantly chromium carbides precipitating intergranularly and intragranulary. The other secondary phases in Alloys 600 and 690 are titanium nitrides, titanium carbides, and carbonitrides. The austenitic matrix phase is stable up the melting temperature. Both alloys are non-heat treatable through phase changes and can not be hardened through secondary phase precipitation. The extent of intragranular and intergranular carbides precipitation depends on the thermal mechanical history and the carbon content. Most research efforts on Alloys 600 and 690 have been focused on the grain boundary, especially the grain boundary carbide precipitation due to the intergranular nature of the Alloy 600 failures. The grain boundary carbide precipitates are found to be both M_7C_3 and $M_{23}C_6$ types in Alloy 600 and mostly globular $M_{23}C_6$ type in Alloy 690 [101, 102]. Precipitation of carbides along the grain boundaries has been found to be beneficial for PWSCC resistance in primary water. Any effect of carbide precipitation from the initial heat treatment on the fracture toughness is not a concern for Alloys 600 and 690 due to the exceptionally high fracture toughness of austenitic alloys in the annealed or hot rolled conditions (see Figure 7-1). The impact toughness increases with increasing test temperature for the Alloy 600 in the cold worked condition. The PWR operating temperature is too low for additional carbides precipitation or coarsening of existing carbides. Review of Alloys 600 and 690 studies has not identified the presence or precipitation of embrittling intermetallic phases such as sigma (σ), chi (χ), or alpha prime (α') phases in different thermomechanical conditions used in the light water reactors. Hence, it can be concluded that thermal aging embrittlement is not a concern for Alloys 600 and 690 or the HAZ due to welding at elevated temperatures in PWRs.

7.2 Weld Metals 82/182, 52/152

Alloys 182 and 82 were extensively used in the construction of PWRs for dissimilar metal welds joining Alloy 600 with low alloy steels or stainless steels. Following the discoveries of Alloy 600 PWSCC, the degraded components are being replaced by Alloy 690 and Alloy 52/152 weld metals. The chemical compositions of the unwelded Alloys 82/182, and 52/152 are listed in Table 7-1. The actual chemical compositions in the butter or the actual weld tend to be non-uniform due to dilution from the base metal and segregation from weld solidification. In the weld metals, the grain boundaries separate colonies of similarly oriented dendrites. Studies of these weld metals have identified MC, M_7C_3, and $M_{23}C_6$ carbides precipitating along the grain boundaries and in the dendritic regions, and gamma prime (γ') intermetallic compounds precipitating in the matrix [103, 104]. The gamma prime intermetallic compounds, which are also responsible for precipitation-hardening in Alloy X-750, are due to the addition of Al and Ti in the weld metals to produce welds stronger than their base metals. Chapter 6 has concluded that the thermal aging embrittlement is not a concern for Alloy X-750. No other embrittling phases such as sigma (σ), chi (χ), or alpha prime (α') phases which is the primary cause of austenitic stainless steel welds and castings, have ever been identified in Alloys 82/182, 52/152 weld metals.

The only embrittlement mechanism identified for these weld materials is called “low temperature crack propagation” or LTCP. One study tested the fracture toughness of Alloy 690, Alloy 600, Alloy 82 and Alloy 52 in 129°F and 640°F alkali-treated deionized water with a hydrogen concentration ranging from 125 to 200 cc H_2/kg H_2O. The test results showed that all these materials exhibited excellent fracture toughness at 640°F. However, Alloy 690, Alloy 82 and Alloy 52 experienced significant decreases in fracture toughness when tested 129°F water. This loss of fracture toughness at low temperature was attributed to hydrogen embrittlement due to hydrogen buildup in the crack tip. The hydrogen level used in the experiment was significant higher than that in the PWRs. Because LTCP is neither operative at PWR operating temperatures nor an aging mechanism, it has no impact on the thermal aging embrittlement. From the above discussion, it can be concluded that thermal aging embrittlement is not a concern for Alloys 82/182, 52/152 weld metals at elevated temperatures in PWRs.

7.3 Conclusion

Alloys 600, 690, and their weld metals 82/182, 52/152 possess very high ductility. No embrittling intermetallic phases such as sigma (σ), chi (χ), or alpha prime (α') phase precipitations responsible for thermal aging embrittlement of austenitic stainless steel welds and castings have been identified from extensive investigations related to stress corrosion cracking. It can be concluded that thermal aging embrittlement is not a concern for Alloys 600, 690, the weld metals 82/182, 52/152 or the HAZ at elevated temperatures in PWRs. Therefore, it can be concluded that these materials will not become thermally embrittled due long term exposure at PWR temperatures.

Table 7-1
Chemical Composition of Alloy 600, 690, Weld Metals Alloys 82/182, 52/152 [5-7]
(wt%, maximum unless range or minimum is indicated)

	Ni	Cr	Fe	C	Mn	Si	S	Ti	Nb + Ta	Cu	P	Al
Alloy 600	72.0 min	14.0-17.0	6.0-10.0	0.15	1.00	0.50	0.015	--	--	0.50	--	--
Alloy 690	58.0 min	27.0-31.0	7.0-11.0	0.05	0.50	0.50	0.015	--	--	0.50	--	--
Unwelded Alloy 82 (ERNiCr-3)	67.0 min	18.0-22.0	3.0	0.10	2.5-3.5	0.50	0.015	0.75	2.0-3.0	0.50	0.03	--
Unwelded Alloy 182 (ENiCrFe-3)	59.0 min	13.0-17.0	10.0	0.10	5.0-9.5	1.0	0.015	1.0	1.0-2.5	0.50	0.03	--
Unwelded Alloy 52 (ERNiCr-7)	Bal.	28.0-31.5	7.0-11.0	0.04	1.0		0.015	1.0	0.10	0.30	0.02	1.10
Unwelded Alloy 152 (ENiCrFe-7)	Bal.	28.0-31.5	7.0-12.0	0.05	5.0	0.75	0.015	0.50	1.0-2.5	0.50	0.03	0.50

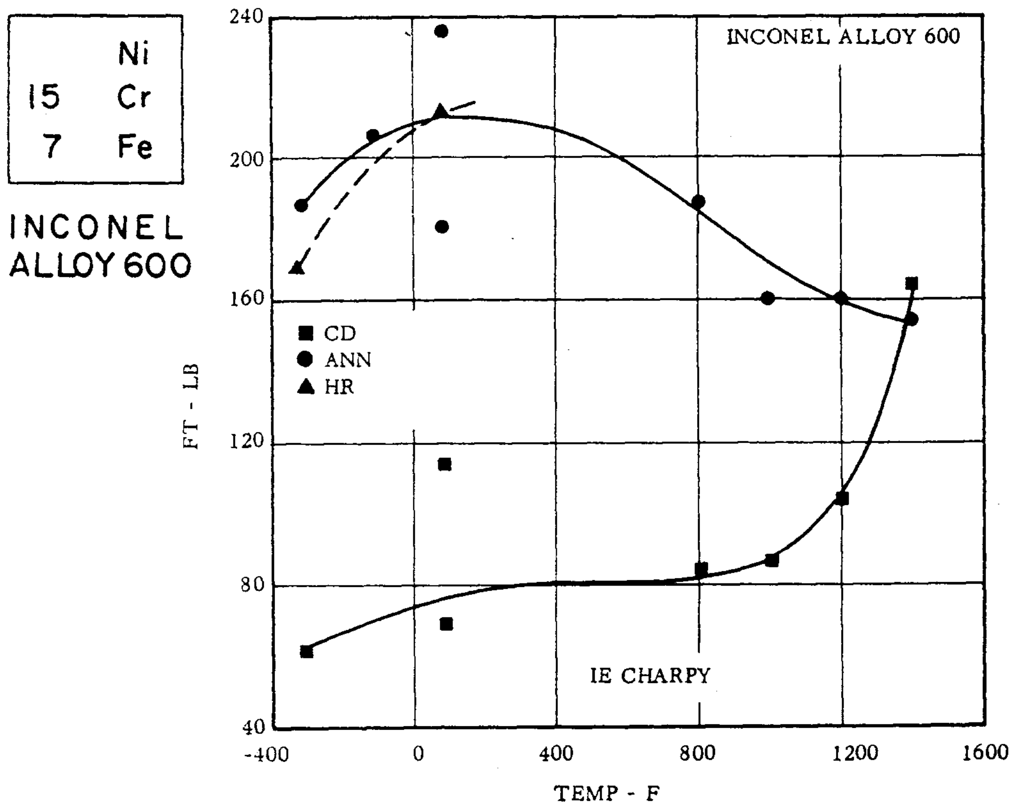


Figure 7-1
Charpy V-notch Impact Energy of Alloy 600, CD-cold draw, ANN-annealed, HR-hot rolled. [84]

8 TECHNICAL SUMMARY

This report has reviewed the thermal aging embrittlement for materials used in PWRs. The primary objective is to identify the materials and components that are potentially susceptible to thermal aging embrittlement during the PWR lifetime. The findings of this report are summarized below in two categories, materials and components that are potentially susceptible to thermal aging embrittlement and materials that are not expected to be a concern for thermal aging embrittlement. Materials and components identified to be potentially susceptible to thermal aging embrittlement are also listed in the summary table at the end of this section.

Materials and Components Potentially Susceptible to Thermal Aging Embrittlement

1. Carbon and Low Alloy Steels and Welds in the Pressurizer

Research studies of thermal aging embrittlement (also called temper embrittlement) of carbon and low alloys steels have been limited to reactor vessel steels, welds, and HAZ. Extensive experimental results have shown that the long term thermal aging embrittlement of reactor vessel steels and welds at PWR temperatures of 572°F (300°C) is very modest, with an increase in ductile to brittle transition temperature (DBTT) on the order of 50°C (80°F) or less. However, for domestic commercial PWRs, the highest operating temperature in the RCS is around 650°F (343°C) in the pressurizer. Hence, the location most susceptible to thermal aging embrittlement is expected to be the low alloy steel pressurizer shell material, especially the weld heat affected zone (HAZ). There is little long term aging data at 650°F (343°C) for low alloy steels, weld and HAZ. Although the lower end of temper embrittlement temperature range for low alloy steels has been traditionally estimated to be 707 to 752°F (375 to 400°C), models based on thermally activated equilibrium segregation of phosphorus indicated long term thermal aging embrittlement can be significantly higher at ~650°F (343°C) than at 572°F (300°C) by the end of the 40-year design life. It appears that an increase in DBTT exceeding 75-100°C is possible for the pressurizer shell materials operating at temperatures around 650°F for materials with impurities near the higher end of the allowable range, especially in the coarse grained HAZ region.

Recommendation

The effect of thermal aging embrittlement on the shell materials of PWR pressurizers can be evaluated in the same fashion as reactor vessel embrittlement due to neutron irradiation. The effect of embrittlement due to neutron irradiation is well studied and currently evaluated in accordance with Reg. Guide 1.99, Rev. 2. Since the ASME Code fracture toughness is indexed by the material parameter RTNDT, Reg. Guide 1.99, Rev. 2 provides a formula to include this irradiation embrittlement effect in the following form:

Adjusted RT_{NDT} = Initial (unirradiated) RT_{NDT} + ΔRT_{NDT} + Margin

The term ΔRT_{NDT} is the additional shift term due to irradiation induced embrittlement, which can be as high as approximately 140°F for the end of extended life of 60 years for the beltline of reactor pressure vessel materials, based on the following:

Adjusted RT_{NDT} = 270°F (PTS screening criteria)

Initial (unirradiated) RT_{NDT} = 60°F (approximately the worst heat being observed)

Margin = 65°F

For the long-term thermal aging of pressurizer shell materials with no appreciable embrittlement due to neutron irradiation, the shift (ΔRT_{NDT}) due to thermal aging can be accommodated is therefore approximately 140°F. Hence, the following tests are recommended on a section of pressurizer shell that have seen the highest temperature i.e. ~650°F from a decommissioned pressurizer.

Direct measurement of long-term aging embrittlement can be made by comparing transition range fracture toughness of an aged material to that of un-aged material. This can simply be accomplished by comparing T_0 values from the Master Curve method in accordance with ASTM E1921-02 standard. Actual theoretical background and applications are documented in PWRMRP-26 (December 2000).

The testing requires about 10 Charpy sized specimens with EDM notches with fatigue pre-cracking per product form (base metal, HAZ, and weld). Three point bending tests will be performed using these specimens with the resulting K_{Jc} values used for determining T_0 value of the material. Another set of 10 Charpy sized specimens are needed to establish a T_0 value for a un-aged material. This will depend on finding archived materials from the same shell that has not been exposed to long-term thermal aging. If this is not feasible, a T_0 from a similar material can be used from the literature. The T_0 shift between aged and un-aged material is very good indicator for thermal aging embrittlement, better than a Charpy shift value because T_0 shift is a direct measurement of fracture toughness in the ductile-to-brittle transition range. If the shift (ΔRT_{NDT}) is less than 140°F, then thermal aging embrittlement is not likely a concern for PWR pressurizers and similar low alloy steels in the PWRs. It is also desirable to perform multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact testing to verify thermal aging embrittlement or the lack of it.

2. High-Strength Low Alloy Bolting Materials, Reactor Vessel Closure Studs, Pressurizer and Steam Generator Manway Studs

High-strength low alloy (HSLA) bolting materials AISI 4140 and 4340 (SA-193 Gr. B7, SA-320 Gr. L43, and SA-540 Gr. B23 & B24) have been used extensively in PWRs, such as reactor vessel closure studs and steam generator manway studs. Compared to the carbon and low alloy steel forgings and plates used in PWRs, these bolting materials contain higher contents of carbon, nickel, and chromium to increase their hardenability, strength, and wear resistance. The most common form of embrittlement afflicting such HSLA steels is called tempered martensitic embrittlement (TME), also called the one-step temper embrittlement. It differs from the temper embrittlement of low alloy steel plate and forging. In the temper embrittlement (also called two-step embrittlement) of low alloys forging and plates, the steel is usually tempered at relatively higher temperature 1200°F (650°C) producing lower strength and hardness, and embrittlement occurs upon slow cooling or prolonged exposure in the temperature range of 707-1112°F (375-600°C).

For HSLA bolting materials, TME is caused by the as-quenched materials being tempered at relatively low temperature of ~662°F (350°C, hence also known as 350°C embrittlement) causing a sharp drop in room temperature impact fracture energy. Hence, the TME is due to improper heat treatment during manufacturing, rather than due to thermal aging at the designed operating temperature. Because of the minimum tempering temperature required to prevent TME, it should not be a concern for the low alloy bolting materials. On the other hand, should thermal aging embrittlement develop during service at ~500°F, it would not be considered the "one-step temper embrittlement" usually associated with TME. Regardless of the nomenclature, the long term aging effect of low alloy bolting materials at their relevant exposure temperatures in PWRs has not received much attention and embrittlement failures are usually attributed to TME without much probing. As a result there is dearth of aging degradation data of HSLA bolting materials in PWRs. However, the studies of two cracked reactor head closure studs at a BWR in 1989 indicates that the potential for aging embrittlement during service exists. The aging embrittlement is believed to be due to two mechanisms, the precipitation and coarsening of cementite and the transformation of some retained austenite into untempered martensite during prolonged exposure at 500°F. Research indicates that the lowering of carbon content from precipitation of interlath carbides at 500°F promotes the transformation of retained austenite into untempered martensite.

Recommendation

It is recommended that multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact tests to be performed on HSLA bolting materials removed from PWRs or BWRs. The selected components should have operating temperatures among the highest for this class of materials and should have accumulated substantial operating time, e.g., more than 100,000 hours. One possible specimen source is stuck reactor vessel head closure studs from units whose closure head operating temperatures is near 600°F. The test results will either show lack of thermal aging embrittlement or establish the extent of the thermal aging embrittlement from long-term exposure to the operating temperature. It is important that, in case of results indicating thermal aging embrittlement, the possibility of embrittlement due to the initial improper heat treatment can be ruled out. Hence, specimens should be removed from HSLA bolting materials with known initial mechanical and impact properties. If the DBTT transition temperature exceeds the room temperature and/or the loss of room temperature impact energy exceeds 50%, the material could be considered susceptible to thermal aging embrittlement.

However, unlike the reactor vessel materials, there is no criteria or guidelines regarding how much embrittlement in terms of transition temperature shift or loss of fracture toughness can be tolerated for HSLA bolting materials without undermining safety. Hence, in case the material is susceptible to thermal aging embrittlement, a thermal aging program will be needed to establish the screening criteria based on operating temperature and time and to develop guidelines for safety assessment. One approach is to perform fracture toughness tests (K_{Ic} or J_{Ic}) and evaluate the critical flaw size for these components based on fracture mechanics. Because HSLA bolting components are typical outside the pressure boundary, it is possible that replacement would be preferable to safety analysis based on fracture mechanics.

3. Precipitation Hardenable Stainless Steels, Type 17-4 PH and 17-7 PH CRDM Components

For applications requiring high strength, precipitation hardenable (PH) stainless steels offer an alternative to cold worked austenitic and martensitic stainless steels. Intricate components can be fabricated easily in the annealed condition and hardened by heat treatments afterwards. Compared to martensitic stainless steels, a higher chromium content provides PH stainless steels with higher corrosion resistance. In PWRs, the failed Type 410 martensitic stainless steel pump shafts and valve stems were often replaced with components fabricated from Type 17-4 PH stainless steels. The martensitic 17-4PH (H-1100) and semi-austenitic Type 17-7 PH (TH1050) stainless steels are most commonly used in domestic PWRs. Past failure investigations revealed that long term exposure to elevated temperature can lead to severe embrittlement. Compared to martensitic stainless steels such as Type 403 and 410, Type 17-4 PH and 17-7 PH are more susceptible to thermal aging embrittlement due to the higher contents of chromium, nickel, and other alloying elements. Thermal aging embrittlement of Type 17-4 PH is accompanied by an increase in hardness. Exposure of Type 17-4 PH (H-1100) to 500-600°F can cause the DBTT to shift to well above room temperature and a severe decrease in USE. Although the embrittlement kinetics are sensitive to heat-to-heat differences in composition, significant thermal hardening and embrittlement would be reached for Type 17-4 PH (H-1100) near 600°F during the PWR lifetime. Very limited information is available on the long-term thermal aging embrittlement of Type 17-7 PH (TH1050). Based on the limited data, the thermal aging embrittlement kinetics of Type 17-7 PH (TH1050) could be similar to that of Type 17-4 PH (H-1100). Because of the very low impact toughness of the unaged Type 17-7 PH (TH1050) compared to Type 17-4 PH (H-1100), any embrittlement effect due to long term exposure to elevated temperatures could be more of a concern for Type 17-7 PH (TH1050).

Recommendation

A thermal aging management program is recommended for PH stainless steels. The program will identify the PH stainless steels used in PWRs at elevated temperatures. However, unlike the reactor vessel materials, there are no criteria or guidelines regarding how much embrittlement in terms of transition temperature shift or loss of fracture toughness can be tolerated. To establish the embrittlement kinetics, which can be used for establishing a thermal aging screening criteria, multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact testing should be performed. Therefore, the program also needs to establish criteria for safety assessment. One approach is to perform fracture toughness tests (K_{Ic} or J_{Ic}) for thermally embrittled materials and evaluate the critical flaw size for these components based on fracture mechanics. A possible source of test specimens is the Type 17-4 PH CRDM leadscrew couplings used in the CRDMs of B&W PWRs. The program should also investigate suitable replacement materials if they are needed or more economical than performing fracture toughness tests and analysis. One possible source of testing materials for Type 17-4 PH is the thermal aging specimens (hardness, tensile, and impact) of EBR-II reactor materials surveillance program. These Type 17-4 PH specimens have been thermally aged at 371°C (700°F) in a helium atmosphere for approximated 156,000 hours.

4. Martensitic Stainless Steels Type 403 and 410

The low carbon grade martensitic stainless steel Type 403, 410, and 416 have been used in PWRs, mainly for internal components of CRDM and motor tubes in the RCS, and for valve stems and pump shafts for both primary and the secondary side applications. Type 410 has also been used as holddown springs. Martensitic stainless steels are most commonly used in the quenched and tempered (950-1250°F) condition. Available embrittlement data are mostly related to Type 410. Thermal aging embrittlement of Type 403 is expected be similar to or bounded by Type 410. Significant thermal aging embrittlement of Type 410 due to long term aging at 500-600°F is probable, but becomes less pronounced with decreasing temperature below this range. The embrittlement is manifested in the DBTT from Charpy impact curves shifting to higher temperature. The transition temperature of unaged Type 410 is around room temperatures and long term aging at 500-600°F can cause the DBTT Type 410 to shift above room temperature. The upper-shelf and lower-shelf energy are not greatly affected by thermal aging. Thermal aging embrittlement of Type 410 is typically not accompanied by an increase in hardness. Therefore, testing and empirical relations correlating hardness increase with increase in transition temperature for austenitic stainless steel welds or martensitic PH stainless steels are not suitable for Type 410. Thermal aging embrittlement can also increases the material's susceptibility to SCC.

Recommendation

It is recommended that multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact tests on martensitic stainless steels removed from PWRs or BWRs. The selected components should have operating temperature among the highest for this class of materials and should have accumulated substantial operating time, e.g., more than 100,000 hours. The test result will either confirm the lack of thermal embrittlement or establish the extent of the thermal aging embrittlement from long-term exposure to the operating temperature. It is important that, in case of results indicating thermal aging embrittlement, the possibility of embrittlement due to the initial improper heat treatment can be ruled out. Hence, test specimens should be removed from materials with known initial mechanical, impact properties, and heat treatment records during fabrication. If the DBTT transition temperature exceeds the room temperature and/or the loss of room temperature impact energy exceeds 50%, the material could be considered susceptible to significant thermal aging embrittlement.

However, unlike the reactor vessel materials, there are no criteria or guidelines regarding how much embrittlement in terms of transition temperature shift or loss of fracture toughness can be tolerated. If the materials are determined to be susceptible to thermal aging embrittlement, an aging management program is needed to establish the aging kinetics for screening based on operating temperature and time and to develop guidelines for safety assessment. One approach is to perform fracture toughness tests (K_{Ic} or J_{Ic}) for the thermally embrittled materials and evaluate the critical flaw size for these components based on fracture mechanics. However, the program should also investigate suitable replacement materials if it is needed or more economical than performing fracture toughness tests and analysis.

5. Thermal aging embrittlement of Austenitic Stainless Steel Welds and Castings

For CASS and welds, thermal aging embrittlement has been extensively studied, and as a result well established. Thermal aging embrittlement increases the hardness and tensile strength, and decreases ductility, impact strength, and fracture toughness. Austenitic welds and castings have a duplex microstructure consisting of austenite and δ–ferrite phases. The miscibility gap below 500°C (932°F) causes the δ–ferrite to segregate (spinodal decomposition) into the Fe-rich α phase and the Cr-rich α' phase. The low temperature embrittlement is caused primarily by the precipitation of a fine, coherent body centered α' phase, which is also responsible for the 475°C (885°F) embrittlement of ferritic stainless steels. An additional contribution to embrittlement comes from the precipitation of a G phase (a nickel and titanium rich silicide) in the δ–ferrite and precipitation and growth of carbides at ferrite/austenite interface. The effect of thermal aging embrittlement of austenitic stainless steel welds and castings is manifested in cleavage fracture in the ferrite phase or separation of the ferrite/austenite phase boundary. Materials with high ferrite content and/or large phase boundary carbides are more prone to thermal aging embrittlement. Significant reduction in fracture toughness is likely when ferrite volume fraction exceeds 10% and above.

Recommendation

Because thermal aging embrittlement of austenitic stainless welds and castings in PWRs has been well documented and is being managed by existing programs, no additional thermal aging embrittlement study program is needed.

Materials Not Susceptible to Thermal Aging Embrittlement

1. Low Alloy Steels (SA533 Gr. B plate, and SA508 Class 2 forging) and Welds for the RPV

Research studies of thermal aging embrittlement of carbon and low alloys steels have been performed on reactor vessel steels, welds, and HAZ. Extensive experimental results show that the long term thermal aging embrittlement of reactor vessel steels and welds at PWR temperatures of 300°C (572°F) is very modest, with increase in DBTT on the order of 50°C or less.

2. Austenitic Precipitation Hardenable Alloys X-750, 718, and A-286

Precipitation hardenable Alloys X-750, 718, and A-286 are extensively used by the nuclear power industry due to their high strength and superior corrosion resistance. Applications include core internals bolting, springs, and guide pins. Alloys X-750 and 718 are nickel-base austenitic alloys and A-286 is classified as stainless steel. Alloys X-750, 718, and A-286 in various precipitation hardened conditions are commonly used in LWRs. These materials possess no distinctive ductile-brittle transition behavior, which is exhibited by martensitic precipitation hardened stainless steels. Limited data indicates that the impact properties of these three alloys are insensitive to exposure at LWR operating temperatures. Failures of these materials due to IGSCC or fatigue have been well documented and studied in the past. However, there have been no indications of thermal aging embrittlement from long term exposure at elevated temperatures either from reported failure investigations or operating experience. Therefore, it can be concluded that these materials will not become thermally embrittled due long term exposure at PWR temperatures.

3. Wrought Austenitic Stainless Steels

The PWR internals components were mostly fabricated from austenitic stainless steels, which possess excellent ductility and toughness and no distinct DBTT behavior. Besides irradiation embrittlement of stainless steel components next to the core, the thermal aging embrittlement concern in the PWR reactor internals had been associated only with cast austenitic stainless steel (CASS) and stainless steel weldments metals due to thermal aging. In general, unirradiated and moderately irradiated austenitic stainless steel base metals possess high degree of fracture toughness and fracture is preceded with extensive plastic deformation. Hence, thermal aging embrittlement of austenitic stainless steel base metal is not a concern.

The chemical composition in the HAZ next to the welds is the same as the base metal and ferrite content in HAZ is insignificant. Therefore, there is no embrittlement from precipitation of α' by spinodal decomposition in the ferrite phase. Hence, the thermal aging embrittlement potential in the HAZ is much less than the welds. Result shows that J_{Ic} of the HAZ of Types 304 and 316 remains close to the base metals and much higher than the weld materials regardless of welding process and heat inputs. Thus, the thermal aging embrittlement in the HAZ is not a concern and its loss of fracture toughness will be bounded by that of the welds.

4. Alloys 600 and 690, Weld Metal Alloys 82/182, 52/152

Alloy 600 and its weld metal Alloys 82 and 182 were extensively used for fabricating the PWRs during the 1960s and 1970s. The primary water stress corrosion cracking (PWSCC) of Alloy 600 components and its welds has been a major challenge to plant operation and maintenance over the last two decades. Since 1980s, Alloy 690 and its equivalent weld metals Alloys 52 and 152 have been used for repair and replacement of degraded Alloy 600 components including steam generator tubings, CRDM nozzles, and penetrations in pressurizers and RCS pipings. A vast amount of studies and investigative efforts have been performed on PWSCC of Alloys 600 and 690 in the past three decades, but none of them have been on the thermal aging embrittlement of these materials. Alloys 600, 690, and their weld metals 82/182, 52/152 possess very high ductility. No embrittling intermetallic phases such as sigma (σ), chi (χ), or alpha prime (α') phase precipitations responsible for thermal aging embrittlement of austenitic stainless steel welds and castings have been identified. It can be concluded that thermal aging embrittlement is not a concern for Alloys 600, 690, the weld metals or the HAZ at elevated temperatures in PWRs.

Summary of Materials Potentially Susceptible to Thermal Aging Embrittlement in PWRs

Materials	Potential Sources of Test Materials	Recommended Tests	Test Criteria
Carbon and Low Alloy Steels plate, forging, Welds, HAZ	Decommissioned Pressurizer operated at ~650°F for >100,000 hours	Perform fracture toughness test per ASTM E1921-02, and determine ΔRT_{NDT}. It is also desirable to perform multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact testing.	If shift (ΔRT_{NDT}) is less than 140°F, thermal aging embrittlement is not a concern.
High-Strength Low Alloy Bolting Materials AISI 4340 and 4140	Stuck RV Closure Studs operated at ~600°F for >100,000 hours	Perform multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact test. If thermal aging is confirmed, an aging program is needed to establish safety evaluation method and the required fracture tests and/or replacement materials.	If the DBTT exceeds room temperature and/or the loss of room temperature impact energy exceeds 50%, the material is considered susceptible to thermal aging embrittlement and further actions are needed.
Precipitation Hardenable Stainless Steels, Type 17-4 PH	EBR-II thermal aging surveillance capsule; CRDM male couplings	Perform safety evaluation through fracture mechanics method (obtaining the required fracture toughness by performing ASTM E 1820-99a) and/or finding suitable replacement materials.	The toughness values will be used for evaluation which is based on the component geometry and loading conditions.
Martensitic Stainless Steels Type 403, 410, Type 416	Valve Stems operated at ~600°F for >100,000 hours	Perform multi-temperature (from –50°F up to the highest operating temperature) Charpy V-notch impact test. If thermal aging is confirmed, perform safety evaluation through fracture mechanics method (obtaining the required fracture toughness by performing ASTM E 1820-99a) and/or finding suitable replacement materials.	If the DBTT exceeds room temperature and/or the loss of room temperature impact energy exceeds 50%, the material is considered susceptible to thermal aging embrittlement, and further action are needed.

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