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ASSESSMENT OF STRESS-CORROSION CRACKING IN A WATER-COOLED ITER

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OBJECTIVE

The objective of this evaluation was to assess the effects of material chemistry and processing and water temperature and chemistry on the stress-corrosion cracking (SCC) of austenitic stainless steels in high-purity water. The emphasis of this evaluation is non-irradiation effects on SCC. Recommendations regarding material chemistry and processing temperatures and water chemistry limits are also objectives of this study.

SUMMARY

Water-cooled, near-term reactors will operate under conditions at which SCC is possible; however, control of material purity and processing and coolant chemistry can either eliminate or greatly reduce the probability of this type of structural failure. This evaluation has focused on an assessment of water impurity effects on SCC of austenitic stainless steel at temperatures below 100°C and on the conditions controlling sensitization in the fusion heat of Type 316 SS and the fusion materials heat of modified Type 316 SS designated as PCA. This assessment identifies the dominant effect of small concentrations of impurities in high-purity water on SCC such that crack growth rates at 25-75°C in water with as little as 5-15 ppm Cl⁻ are equal to the crack growth rates at 200-300°C in high-purity water. These effects are primarily for sensitized Type 304 SS, so analysis of sensitization behavior of fusion austenitic alloys was also undertaken. An SSDOS model developed at PNL was used to make these assessments, and correlation to experimental results for Type 316 SS was very good. Both the fusion heat of Type 316 SS and PCA can be severely sensitized but with proper thermal treatment it should be possible to avoid sensitization.

PROGRESS AND STATUS

Water Purity Effects on Stress-Corrosion Cracking

Stress-corrosion cracking (SCC) of austenitic stainless steel has been studied extensively at temperatures exceeding 100°C and especially at 288°C, because of impetus from the light-water reactor industry. At temperatures lower than 100°C there have been relatively few studies. However, conclusions from these studies indicate that 1) neither transgranular nor intergranular stress-corrosion cracking has been reported in deionized (DI) high-purity water; 2) impurities such as Cl⁻, F⁻, S₂O₃⁼, can cause intergranular SCC at temperatures as low as 25°C with crack growth rates equal to or exceeding those observed at 288°C; 3) there has been a report that impurities can cause transgranular SCC at 98°C, but not below; and 4) crack initiation is a very slow process at low temperatures even though the crack growth rate may be equal to or greater than those observed at 288°C.

Stress-corrosion cracking occurs with selected combinations of material microchemistry and microstructure, environment, and mechanical stress. In austenitic stainless steels, the most severe material condition coincides with the precipitation of chromium-rich carbides at the grain boundaries, producing a condition known as sensitization; however, transgranular stress-corrosion cracking (TGSCC) which is unrelated to this grain boundary condition, has also been observed. Important environmental variables include oxygen, chloride, fluoride and sulfur ions, temperature, and pH. Mechanical stress from external loads, or residual stresses from welding or cold working, can cause SCC. A threshold stress or stress intensity below which SCC does not occur has been measured for most materials which exhibit SCC. Available data on SCC of austenitic stainless steel at temperatures lower than 100°C indicate that the controlling parameters are the same at low and elevated temperatures, so experience at elevated temperatures can be extrapolated to low-temperature water.

An assessment of intergranular stress-corrosion cracking (IGSCC) in a spent fuel pool component, which was in contact with water at temperatures ranging from 7°C to 33°C, was reported by Jones et al. (1,2). Cracks propagated through the 0.6-cm-thick wall of the piping in this fuel pool in less than 5 yrs of service. It was concluded that crack growth was by IGSCC of a high-carbon (0.07 wt%) 304 SS, which was sensitized by welding. Cracks propagated in the heat-affected zone (HAZ) with the probable assistance of either Cl⁻ or sulfur compounds in the water. Surface defects produced by grinding during weld preparation may also have contributed to the relatively fast SCC observed in this component.

Laboratory SCC tests conducted by Bruemmer et al. (3) and by Bruemmer and Johnson, Jr. (4) corroborated most of the conclusions reached by Jones and Johnson, Jr. regarding the role of C concentration of the steel and Cl⁻ or S₂O₃⁼ effects in the water on SCC at 30°C. These tests were conducted using constant load samples, which were loaded to 1.8 to 2.4 of their yield strengths for 640 hrs. Using compact tension samples, Jones

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et al. (5) observed crack growth rates approaching 10^{-4} mm/s at 90°C , and using constant load samples loaded to 1.2 of their yield strength, a crack growth rate of 3×10^{-5} mm/s at 25°C in DI water with 15 ppm $\text{S}_2\text{O}_3^{=}$ (6). Ford and Povich (7) observed IGSCC in sensitized Type 304 SS at 100°C in DI water using a constant extension rate test (CERT); Ford (8) also reported IGSCC results at 98°C in 0.01 M Na_2SO_4 . Other reports on the effect of specific impurities on IGSCC include those by Shoji et al. (9) on IGSCC during cyclic loading in water with 15 ppm O_2 at 83°C , and Ward et al. (10), Sharfstein and Brindley (11), and Sieradzki et al. (12) on the effects of F^- , Cl^- and $\text{S}_2\text{O}_3^{=}$ ions, respectively. Using U-bend samples, Sharfstein and Brindley (11) observed TGSCC in both Type 304 and 347 SS at temperatures of 75°C and 98°C and 200 and 25 ppm Cl^- , respectively.

Crack growth rate data for austenitic stainless steels are shown as a function of temperature in Figure 1. The results of Ford and Povich (7) and Ford (8) for SCC of sensitized Type 304 SS in DI water (solid circles and squares), indicates that the crack growth rate decreases substantially at temperatures below 100°C . The conductivity of the DI water used by Ford and Povich was $0.4 \mu\text{mho/cm}$, while the addition of 0.01 M Na_2SO_4 increased the conductivity to $2400 \mu\text{mho/cm}$ and the crack growth rate by a factor of 100 at 100°C . At temperatures above 200°C , a decrease in the O_2 concentration from 8 to 0.2 ppm produced TGSCC in a sensitized Type 304 SS with 0.07 wt% C. Transgranular SCC was also observed in a Type 347 SS tested at 98°C in water with 25 ppm Cl^- . The TGSCC velocity is about a factor of 10 slower than the IGSCC velocity at 288°C , but at temperatures below 100°C , the crack velocities are primarily a function of the Cl^- concentration, Figure 2. Stress corrosion data on other austenitic stainless steels such as 316 SS are not as plentiful as for Type 304 SS; however, in general the 300 series stainless steels behave similarly, given equal grain boundary Cr microchemistries. The SCC behavior of a low-C Type 304 SS and Type 316 SS are similar; the Type 316 SS exhibits more resistance to TGSCC. Thus, so the data presented in Figures 2 and 3 are expected to apply to Type 316 SS, even though there are no data on low-temperature SCC of Type 316 SS.

Figure 1. Stress-Corrosion Crack Growth Rate Versus Water Temperature for Austenitic Stainless Steel Showing the Effect of Impurities in the Water.

Figure 2. Stress-Corrosion Crack Growth Rate Versus Chloride Ion Concentration in Water for Austenitic Stainless Steel.

A key parameter that correlates the grain boundary microchemistries of austenitic stainless steels with their resistance to IGSCC is degree of sensitization (DOS). This electrochemically derived parameter has been shown to correlate with IGSCC resistance. A high DOS corresponds to low IGSCC resistance or high susceptibility to IGSCC. Bruemmer et al. (13) have evaluated the DOS of Types 304L, 304, 316L, 316 and 316LN SS with C concentration ranging from 0.013 to 0.072. Their results indicate that Type 316L SS with 0.014 wt% C could not be sensitized much above 1 or 2 C/cm², while a Type 316L with 0.02 wt% C was sensitized to 10 at 600°C and 25 C/cm² at 700°C. A DOS value of 10 C/cm² is sufficient to produce IGSCC. Also, a Type 316 SS with 0.035 wt% C was sensitized to 20 and 50 C/cm² at 600°C and 700°C. The specification for C concentration in Type 316L SS is 0.035 wt%. Clearly, C concentrations within the specification for Type 316L SS are sufficient to produce a sensitized material that can undergo IGSCC.

The detrimental effect of impurities in water is clearly shown by the data in Figures 1 and 2. In Figure 1 the effect of concentrations, as low as 15 ppm of Cl⁻ and S₂O₃⁼ on the crack growth rate, is apparent from the reversal of the temperature dependence shown for DI water. Impurities such as Cl⁻ and S₂O₃⁼ clearly modify the rate-limiting step for crack growth in DI water so that velocities equal to or exceeding those at 288°C result. The smooth increase in the crack velocity with increasing Cl⁻ concentration shown in Figure 2 also illustrates the detrimental effect of water impurities. Their effect is sufficient also to override the dominance of Cr depletion on crack growth rate so that both TGSCC and IGSCC data fit the same curve. Fluoride ions are clearly more detrimental than Cl⁻ ions, and may be even more detrimental than S₂O₃ ions. Fluoride ion concentrations as low as 0.5 ppm produced IGSCC at stresses above 350 MPa. Residual stresses usually do not substantially exceed the yield strength of a material (200-250 MPa for Type 304 SS), so stresses equal to or exceeding 350 MPa generally require an external load.

Stress thresholds for SCC are generally equal to or exceed the yield strength of the material. Again, for low-temperature SCC there is a scarcity of data to evaluate the stress dependence of SCC, but the data given in Figure 3 give some indication of their magnitude. These results suggest that the stress must be equal to or exceed the yield strength of the material for IGSCC in low-temperature water. The MgCl₂ data from results of Jones and Wang (14) are shown only for comparison purposes, as this test is conducted at 155°C in a concentrated Cl⁻ environment, and are not considered typical for aqueous SCC. The crack morphology is transgranular and the threshold is considerably less than the yield strength. Crack advance is probably due to a hydrogen-induced process, unlike aqueous environments, which is primarily an anodic dissolution process. Stress intensity thresholds are another method for describing the limiting mechanical loading condition for SCC. The stress intensity is a function of both the stress and the square root of the crack length. In DI water at 97°C Ford (8) measured a stress intensity threshold of about 12 MPa-m^{1/2} for sensitized Type 304 SS, while in DI water with 15 ppm S₂O₃⁼, Jones et al. (5) measured a threshold of about 25 MPa-m^{1/2}. These are relatively low values, as the fracture toughness of Type 304 SS exceeds 100 MPa-m^{1/2}.

Figure 3. Stress-Corrosion Crack Growth Rate Versus Applied Stress for Austenitic Stainless Steel in Various Environments.

Sensitization Development in Fusion Reactor Materials

Quantitative sensitization development in two austenitic SS heats from the fusion materials stockpile was predicted using the model SSDOS (15,16). Compositions for the heats, X-15893 (316 SS) and K-280 (PCA), are listed below. SSDOS enables prediction of chromium depletion and degree of sensitization (DOS) as measured by the electrochemical potentiokinetic reactivation (EPR) test from material composition and initial condition. The model has been shown to accurately predict sensitization development in a large number of 304 and 316 SS heats (16,17).

Table 1. Compositions of Fusion Heats of Austenitic Stainless Steels

Heat	C	Cr	Ni	Mo	Mn	Si	Ti	N
316	0.056	16.7	12.0	2.4	1.7	0.7	-	-
PCA	0.046	14.0	15.9	1.9	1.7	0.5	0.3	0.01

Isothermal sensitization behavior for both heats was assessed for heat treatment temperatures between 500 and 1000°C. Predictions for the 316 heat showed rapid sensitization at temperatures from 700 to 850°C. Sensitization is thermodynamically limited at higher temperatures and kinetically limited at lower temperatures. Time-temperature-sensitization (TTS) behavior is illustrated in Figure 4 using a critical EPR-DOS value of 5 C/cm² to indicate the onset of sensitization.

A direct comparison can be made between measured and predicted EPR-DOS for this heat, as shown in Figure 5. Limited sensitization measurements were performed previously (17) after solution annealing at 1100°C. The quantitative nature of the predictive capability is documented by comparing data at 600, 700, and 800°C. Although predictions are not exact, EPR-DOS is reasonably estimated at most temperatures and times.

Figure 4. Time-Temperature-Sensitization Curve for 316 Heat X-15893.

Figure 5. Comparison of Measured and Predicted Sensitization Development in 316 SS Heat X-15893.

considerably less than the yield strength. Crack advance is probably due to a realistic DOS predictions. A relationship for carbon solubility in titanium-modified SS was developed based on literature data(4,5). This relationship is shown in Figure 6 along with measured solubilities as a function of temperature. It is important to note that this information is for an 18-8 alloy which may be different than that for the PCA composition. As expected, carbon solubility drops with decreasing temperature, reaching values below 0.01 wt% at temperatures of 950°C. The PCA bulk level of 0.046 wt% carbon corresponds to a temperature of about 1130°C. Since mill-annealing temperatures were reported to be 1050°C, the available carbon should be about 0.021 wt%.

The TTS curves for the PCA heat are presented in Figure 7. Three initial conditions are evaluated: (1) all carbon in solution (0.046%), (2) after annealing at 1050°C (-0.021% in solution), and (3) 0.01% in solution. Sensitization is predicted to occur after very short treatments (<0.1 h) at temperatures between 700 and 900°C. Times to sensitize are less than 30 s at 800 to 850°C. This rapid sensitization over a rather large range of temperatures is due to the extremely low chromium content in the PCA material. Intergranular attack and SCC of 304 and 316 SS have been shown to occur when grain boundary chromium levels drop below 13 to 13.5 wt% (20,21). The initial chromium concentration in PCA is only slightly above this critical amount and 2 to 4 wt% below typical SS. As a result, any chromium carbide precipitation tends to promote sufficient localized chromium depletion to cause susceptibility. Titanium additions will reduce this susceptibility by

Figure 6. Carbon Solubility for a Ti-Modified 18-8 Stainless Steel.

Figure 7. Time-Temperature-Sensitization Curves for PCA Heat K-280.

limiting the carbon available for precipitation. However, dropping the soluble carbon to 0.021% still produces a predicted sensitization response comparable to the high-carbon 316 heat (Figure 4). A further reduction to 0.01% carbon in solution (950°C heat treatment) significantly reduces the tendency for sensitization.

These results suggest that effectively tying up carbon may be critical to ensure SCC resistance in service. The worst case would be a high-temperature treatment followed by a low-temperature exposure where chromium carbide precipitation is favored over titanium carbide precipitation. If service construction requires welding, high-temperature exposures which could put significant carbon back into solution are possible. Sensitization that might develop during cooling will depend on the specific thermomechanical history in the weld HAZ. In order to indicate potential welding-induced sensitization, SSDOS was used to predict continuous-cooling sensitization. Cooling rate effects on sensitization development for the 316 and PCA heats are shown in Figure 8. Critical cooling rates to cause sensitization are on the order of 0.1 C/s for the 316 heat, 0.3 C/s for PCA with all carbon in solution, and 0.03 C/s for PCA with 0.021% C in solution. Once again the high sensitivity of the PCA heat is predicted, along with the importance of carbon in solution.

Figure 8. Continuous-Cooling Sensitization of 316 and PCA Heats.

microstructure. Both of these conditions can be eliminated in an ITER machine. Water treatment capabilities can maintain high-purity water conditions while proper material treatment during processing and fabrication can minimize the DOS. Use of a low-carbon Type 316 SS is recommended, while a thermal treatment is desirable for PCA that precipitates the maximum volume fraction of TiC and therefore minimizes the amount of dissolved carbon. However, welding can re-dissolve the TiC and thereby cause sensitization. Specific fabrication and joining information relative to the ITER will be needed before a detailed sensitization analysis can be completed for ITER applications.

FUTURE DIRECTIONS

The calculated DOS for PCA will be compared to experimental values for material given variable solution and intermediate annealing treatments. These data and the data for the Type 316 SS will be used to give guidelines for fabrication of the ITER vessel using these materials. Also, sensitization analyses of FeCrMn low-activation alloys will be conducted using both the SSDOS and experimental EPR measurements. Stress-corrosion cracking measurements of Type 316 SS and PCA in the solution-annealed and sensitized conditions will be conducted in a gamma irradiation facility to measure the effects of radiolysis on SCC of these materials.

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