The Role of Time-Dependent Deformation in Intergranular Crack Initiation of Alloy 600 Steam Generator Tubing Material

Manuscript Completed: March 1998
Date Published: March 1998

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Prepared for
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Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

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ABSTRACT

Intergranular stress corrosion cracking (IGSCC) of two commercial alloy 600 conditions (600LT, 600HT) and controlled-purity Ni-18Cr-9Fe alloys (CDMA, CDTT) were investigated using constant extension rate tensile (CERT) tests in primary water (0.01M LiOH + 0.01M H₃BO₃) with 1 bar hydrogen overpressure at 360°C and 320°C. Heat treatments produced two types of microstructures in both commercial and controlled-purity alloys: one dominated by grain boundary carbides (600HT and CDTT) and one dominated by intragranular carbides (600LT and CDMA). CERT tests were conducted over a range of strain rates and at two temperatures with interruptions at specific strains to determine the crack depth distributions. Results show that in all samples, IGSCC was the dominant failure mode. For both the commercial alloy and the controlled-purity alloys, the microstructure with grain boundary carbides showed delayed crack initiation and shallower crack depths than did the intragranular carbide microstructure under all experimental conditions. This data indicates that a grain

boundary carbide microstructure is more resistant to IGSCC than an intragranular carbide microstructure. Observations support both the film rupture/slip dissolution mechanism and enhanced localized plasticity. The advantage of these results over previous studies is that the different carbide distributions were obtained in the same commercial alloy using different heat treatments, and in the other case, in nearly identical controlled-purity alloys. Therefore, observations of the effects of carbide distribution on IGSCC can more confidently be attributed to the carbide distribution *alone* rather than other potentially significant differences in microstructure or composition. Crack growth rates increased with increasing strain rate according to a power law relation with a strain rate exponent between 0.4 and 0.64. However, crack growth rate measured in m/unit strain decreased with increasing strain rate indicating an effect of either the environment or creep. The temperature dependence of the crack growth rate was consistent with the literature.

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Acknowledgements

The authors wish to acknowledge the U.S. Nuclear Regulatory Commission for support of this work under grant #NRC-04-94-090. The authors also acknowledge Dr. Alan McIlree of the Electric Power Research Institute for supplying the commercial alloy, and the High Temperature Corrosion Laboratory and the Electron Microbeam Analysis Laboratory of the University of Michigan.

1 INTRODUCTION

Alloy 600 is used extensively for steam generator tubing and for reactor vessel head penetrations in pressurized water reactors (PWRs). Since the first recorded laboratory failure of alloy 600 by IGSCC (Ref. 1) there have been numerous failures in-service on both the primary and secondary sides. Considerable work has been done to understand the IGSCC behavior of alloy 600 in high purity water at elevated temperature (Refs. 2-5). In earlier studies, efforts focused on the effects of alloying elements (Refs. 6, 7), water impurity, pH levels (Refs. 8-10), grain size (Ref. 11), residual stress and temperature (Refs. 10-12). In 1977, the effect of heat treatment on alloy 600 IGSCC behavior was raised by Domian, *et al.* (Ref. 13).

Heat treatment changes the microstructure of alloy 600, which is one of the most important variables influencing the IGSCC behavior. Thermal treated alloy 600 has higher IGSCC resistance in deaerated, high purity water at elevated temperature than does the mill annealed condition (Ref. 13). Previous studies have shown that increasing IGSCC resistance is generally associated with grain boundary carbides, and more recent work (Ref. 14) has demonstrated that grain boundary precipitates are indeed beneficial in the prevention of IGSCC of alloy 600 in hydrogenated primary water at elevated temperature.

Although this beneficial trend has been established for many years, the mechanism by which intergranular carbides improve the IGSCC resistance of alloy 600 in deaerated, high purity water still remains unclear. Bruemmer (Ref. 15) suggested that grain boundary carbides function as dislocation sources resulting in relaxation of local stresses on the grain boundaries which may blunt the crack tip and decrease the crack propagation rate. But grain boundary carbides alone cannot explain the observations since in high temperature primary water, a slight anodic polarization above the open

circuit potential results in preferential matrix dissolution. (Ref. 16) Hence, the role of grain boundary carbides in IGSCC has remained unclear due to the difficulty in isolating this microstructural feature in commercial alloys. Unless all other microstructural variables are held constant, attributing IGSCC changes to carbide distribution is almost impossible.

Another problem with determining microstructure contributions to IGSCC is the characterization of intergranular cracking. Alloy 600 undergoes considerable plastic deformation prior to failure which obscures and distorts the fracture surface of round bar CERT samples. Hence, observations of the fracture surface are of limited value in relating microstructure to IGSCC susceptibility and are of no value in separating crack initiation from crack propagation. A more quantitative characterization of IG crack initiation and propagation in CERT samples can be obtained by measuring the crack depth distribution at different strain levels using interrupted CERT tests. In this way, one can obtain a better picture of when cracks initiate and how propagation occurs with increasing strain. This methodology forms the basis for the present study.

In this work, the effect of carbide distribution on IGSCC in hydrogenated primary water at elevated temperature is evaluated by comparing cracking propensity, as characterized by the crack depth distribution, in a microstructure consisting of predominantly grain boundary carbides against one containing predominantly transgranular carbides at different strain rates and different temperatures. This comparison is made for both commercial alloy 600 and controlled-purity alloys, making it possible to relate the IGSCC behavior of controlled-purity laboratory heats to those of commercial alloys, and in both cases, eliminating the effects of other potentially significant microstructure changes.

2 EXPERIMENT

2.1 Materials

Commercial alloy 600 in two conditions (600LT, 600HT), and controlled-purity alloys (CDMA, CDTT) were used in this study, the chemical compositions of which are listed in Table 1. The commercial alloy was supplied by the Electric Power Research Institute, while the controlled-purity alloys were fabricated at Ames Laboratory.

The 600LT condition was hot worked at 982°C until a reduction of 80% was achieved, yielding a microstructure containing a high density of transgranular carbides and a bimodal grain size distribution. The microstructure contained 70% (vol.) fine, equiaxed grains with an average grain size of 20 μm and 30% (vol.) coarse, elongated grains, with an average grain length of 90 μm . The 600HT condition was hot worked at 1093°C until a reduction of 80% was obtained, yielding a microstructure containing mostly grain boundary carbides with an average grain size of 27 μm . A dissolution method was used to determine the amount of carbon in solution in the 600LT and 600HT conditions. Samples were suspended in a platinum wire basket which was submerged in a solution of methanol containing 10% (vol.) HCl.

The alloy matrix was dissolved by applying an anodic current density of 0.5 A/cm². Carbides fell to the bottom of the beaker and were collected using a vacuum filtration method, rinsed with methanol, dried at 150°C for two hours and then weighed to an accuracy of 0.1 mg. The collected carbides were then examined by X-ray diffraction, revealing that Cr₇C₃ is dominant carbide in batches A and D. The final results of carbide fraction and derived values of carbon in solution are presented in Table 2. The levels of carbon in solution for 600LT and 600HT were obtained by subtracting the amount of carbon presented in the carbides from the total carbon level. Prior to dissolution, the volume fractions of titanium carbide of both materials were first obtained by area fraction calculated from scanning electron micrographs of polished specimens. Titanium carbides, confirmed by energy dispersive X-ray analysis (EDXA), exist in the form of relatively large precipitates in both alloys, which can be easily distinguished from chromium carbides. The Dx condition was made from batch D and underwent an additional thermal treatment at 700°C for 82 hours in an attempt to obtain a concentration of carbon in solution that is comparable with batch A.

Table 1 Composition, grain size and grain boundary carbide fraction of controlled-purity and commercial alloy 600 (wt%)

Designation	Heat	Ni	Cr	Fe	C Total	C in solution	C in carbides	Grain Size (μm)	Grain Boundary carbide fraction
CDMA	AGK-54	Balance	16.8	9.0	0.0305	0.0140	0.0165	35	0.09
CDTT	AGC-7	Balance	16.8	9.0	0.0305	0.0140	0.0165	35	0.51
600LT*	NX8844	Balance	15.0	8.3	0.0590	0.0069	0.0521	20/90	0.13
600HT*	NX8844	Balance	15.0	8.3	0.0590	0.0171	0.0419	27	0.73

* Alloy also contains 0.22% Cu, 0.29% Ti, 0.27% Al, 0.26% Mn, 0.15% Mo, 0.24% Si and 0.009% P.

Table 2 Dissolution Experiment Results of Commercial Alloy (NX8844)

Batch (sample)	A(1)	A(2)	D(1)	D(2)	Dx
weight of sample (g)	11.83±0.0002	12.48±0.0002	12.19±0.0002	12.11±0.0002	9.67±0.0002
weight of carbides (g)	0.074±0.0003	0.076±0.0003	0.060±0.0003	0.063±0.0003	0.069±0.0003
area fraction of TiC	$(1.03±0.051)×10^{-3}$	$(1.03±0.051)×10^{-3}$	$(0.96±0.048)×10^{-3}$	$(0.96±0.05)×10^{-3}$	$1.004×10^{-3}$
weight of TiC (mg)	7.08±0.35	7.47±0.37	6.81±0.34	6.76±0.34	5.66
weight of carbon as TiC (mg)	1.42±0.07	1.50±0.07	1.36±0.07	1.35±0.07	1.13
conc. of carbon as TiC (wppm)	120.0±6	120.0±6	112.0±6	112.0±6	117.0
weight of Cr ₇ C ₃ (mg)	66.92±0.35	68.33±0.47	54.29±0.44	55.74±0.44	62.95
weight of carbon as Cr ₇ C ₃ (mg)	6.03±0.032	6.15±0.032	4.89±0.032	5.02±0.03	5.67
conc. of carbon in Cr ₇ C ₃ (wppm)	510±3	493±3	401±3	415±3	586
conc. of carbon in carbides (wppm)	629±7	613±7	513±7	526±7	703
total carbon in heat NX8844 (wppm)	690	690	690	690	690
carbon solubility (wppm)	650 (at 982°C)	650 (at 982°C)	1700 (at 1093°C)	1700 (at 1093°C)	22 (at 700°C)
conc. of carbon in solution (wppm)	61±7	77±7	177±7	164±7	~0

1. Density of Alloy 600 = 8.43 g/cm³

2. Density of TiC = 4.91 g/cm³

Both batches A and D have nominal carbon concentrations of 690 wppm. As the result of a higher hot working temperature, batch D has higher carbon in solution concentration than does A; 171 wppm versus 69 wppm. The amount of carbon in solution for D and A are lower than the equilibrium values for Ni-Cr-Fe-C at the corresponding hot working temperatures, which should be 1700 wppm and 650 wppm, respectively. One reason for the difference is the formation of the more stable titanium carbide which reduces the availability of carbon in the materials. Also, slow cooling during processing is likely to have precipitated additional carbon as chromium carbides. The dissolution method has a detectability limit around 15 wppm. This also explains the near zero result for specimen Dx. Apparently, 82 hours thermal treatment at 700°C reduced the carbon level to near the solubility limit of 22 wppm. This is close to the detectability limit of the dissolution technique, hence, the near zero result. We will repeat the thermal treatment for shorter time in an effort to achieve a carbon in solution value close to that for batch A.

The controlled-purity CDMA alloy was hot worked at a temperature of 880°C in four stages, yielding a 60% reduction in thickness after the final pass. The alloy was then heat treated for 30 minutes at 920°C, resulting in 35 μm grains with both transgranular and grain boundary carbides, reflecting a mill annealed-type (MA) microstructure. Because of the small volume of controlled-purity alloy available, dissolution was not an option for determining carbide volume fraction. Instead, the alloy was etched in a solution containing 25 ml H_2O , 25 ml ethanol, 25 ml HCl , and 5 g CuSO_4 for 30 s to reveal the grain size and carbide distribution. Image analysis via the NIH Image Program 1.59[®] was used to estimate the carbide volume fraction. Judging from this analysis, approximately 165 wppm carbon was in the form of Cr_7C_3 , with ~140 wppm carbon remaining in solution.

The controlled-purity CDTT alloy was thermomechanically processed to yield a thermally treated-type (TT) microstructure containing predominantly intergranular carbides. A solution anneal at 1100°C for 20 minutes was followed by room temperature compression of 45% in the thickness direction. The alloy was then recrystallized at 920°C for 5 minutes to produce 35 μm grains. In order to precipitate grain boundary carbides, the alloy was thermally treated at 700°C for 6.5 hours. The thermal treatment was prescribed using the DEplete code (Refs. 17-18) in order to retain 140 wppm carbon in solution. This was done in order to isolate the effect of carbide distribution by retaining a similar level of carbon in solution as the CDMA alloy. Table 1 shows the total carbon content for each alloy condition, the amount of carbon in carbides and the amount remaining in solution as determined by the techniques just discussed.

Microstructures of each of the alloy conditions, shown in Figures 1 (a) - (d), were produced by etching in a CuSO_4 solution for 30 seconds in order to reveal both the grain structure and carbide distribution. Grain boundary carbide coverage fraction was determined in scanning electron microscopy, by measuring the fraction of the length of the grain boundaries that were covered with carbides.

2.2 Testing Method and Environment

Constant extension rate tensile (CERT) tests were used to determine the IGSCC susceptibility for different microstructures. The samples had nominal dimensions of 15.0 mm gauge length, 3.0 mm width and 1.0 mm thickness (Fig. 2). All surfaces were ground through 2400 grit paper, followed by polishing with 5 μm , 1 μm and 0.5 μm alumina powders. Two fine scratches were made on the gauge area of each sample in order to calculate the actual plastic deformation and locate the reference area for crack growth monitoring.

(a)

(b)

(c)

(d)

Figure 1 Micrographs of alloys: (a) 600LT, (b) 600 HT, (c) CDMA, and (d) CDTT. Samples were etched in CuSO_4 solution for 15 seconds to reveal grain size and carbide distribution.

Figure 2 Schematic diagram of the constant extension rate tensile (CERT) test sample. All dimensions are in mm.

Before the test samples were examined by scanning electron microscopy (SEM) and the dimensions of the gauge area and the original distance between the reference marks were recorded.

The reference environment for all CERT tests was primary water (0.001 M LiOH + 0.01 M H_3BO_3) containing 1 bar hydrogen overpressure at 360°C. Prior to application of load, the autoclave was deaerated with high purity Ar for at least 30 hours to bring the dissolved oxygen level below 10 ppb. The variance in the test temperature control was $\pm 2^\circ\text{C}$. The nominal strain rate was $3 \times 10^{-7} \text{s}^{-1}$, and strain rate effects on cracking were determined by conducting tests at $1 \times 10^{-6} \text{s}^{-1}$ and $8 \times 10^{-8} \text{s}^{-1}$. One test at 320°C with a initial strain rate of $3 \times 10^{-7} \text{s}^{-1}$ was performed in order to verify the temperature effect on IGSCC behavior of different carbide distributions. All CERT tests were interrupted at 10%, 16%, 19% and 28% strain levels so that information could be obtained on crack growth.

2.3 Crack Characterization

At each interruption, crack length density and crack depth distribution were determined from sample side surfaces using a replica technique. In this technique, samples were coated with acetone, and acetate strips were then carefully placed on the side surface and allowed to dry. The strips were peeled off after 10 minutes and a double sticky tape was used to hold these replicas on a flat metal plate. The replicas then were coated with carbon and subsequently shadowed with gold at a 45° angle. Images of replicas and of the side surfaces directly, were captured using a Philips XL30 SEM. Crack length and crack depth measurements were made using the NIH Image 1.59 Program®. For each sample, a reference point was identified so that after each strain interval, crack morphology as a function of plastic strain could be traced.

In order to quantitatively evaluate the IGSCC behavior, a set of damage parameters, determined from crack length and

crack depth distributions were introduced, as defined in Figure 3. Their definitions are as follows:

- D_{CL} —crack length density ($\mu\text{m}/\mu\text{m}^2$) = total crack length / measured area. A higher D_{CL} value indicates that more cracks have been initiated on the sample surface.
- CD_{max} —maximum crack depth (μm) = depth of the deepest crack measured.

The crack length density is used to study crack initiation phenomena and the maximum crack depth is utilized to analyze crack growth. Crack growth rates were determined from crack depth measurements taken after known strains and exposure times.

Figure 3 Schematic illustration of the parameters characterizing IGSCC cracks

3. RESULTS

3.1 Stress-Strain Behavior

Stress-strain curves of commercial alloy conditions 600LT and 600HT, and controlled-purity CDMA, CDTT alloys tested in primary water containing 1 bar hydrogen overpressure at three strain rates and two temperatures are shown in Figures 4 (a)-(d). The 600LT and 600HT tests reported in Figures 4(a) and (b) were taken to failure at 360°C with the initial strain rates of $1 \times 10^{-6} \text{ s}^{-1}$ and $3 \times 10^{-7} \text{ s}^{-1}$, respectively, and the maximum stresses and failure strains are given in Table 3. Commercial alloy conditions 600LT and 600HT had significantly higher flow stresses than did those of the controlled-purity alloys. At both strain rates, the 600HT condition had a total elongation of more than 38%, while the 600LT condition failed around 28% strain. The failure strains of CDMA and CDTT were comparable in both tests and close to 40%. As the strain rate increased from $3 \times 10^{-7} \text{ s}^{-1}$ to

$1 \times 10^{-6} \text{ s}^{-1}$, the maximum stresses for 600LT and CDMA, with predominantly transgranular carbides, increased from 641 MPa to 740 MPa and from 571 MPa to 613 MPa, respectively. In contrast, the maximum stresses for 600HT and CDTT, with predominantly intergranular carbides remained around 730 MPa and 542 MPa at both strain rates.

The test at a strain rate of $8 \times 10^{-8} \text{ s}^{-1}$, shown in Figure 4(c), was stopped before failure occurred, due to fracture in the sample threads in two of the samples. Nevertheless, up to this point, the relative behaviors of the commercial and controlled-purity alloys were similar to that for the test at $3 \times 10^{-7} \text{ s}^{-1}$, in which the commercial alloys showed a higher strength than the controlled-purity alloys and little difference between alloy conditions. The test at 320°C in Figure 4(d) showed a greater separation in strain hardening behavior than at 360°C. But as in the other tests, the commercial alloys had the higher strength.

Table 3 Maximum load and failure strain for CERT tests in primary water and lab air

test condition	parameter	600LT	600HT	CDMA	CDTT
360°C PW $\dot{\epsilon} = 3 \times 10^{-7} \text{ s}^{-1}$	max. load (MPa)	641	732	571	541
	failure strain (%)	28	38	38	38
360°C PW $\dot{\epsilon} = 1 \times 10^{-6} \text{ s}^{-1}$	max. load (MPa)	740	727	613	544
	failure strain (%)	29	39	40	42
360°C air $\dot{\epsilon} = 3 \times 10^{-7} \text{ s}^{-1}$	max. load (MPa)	748	722	ND	ND
	failure strain (%)	34	40	ND	ND

ND = not determined

(a)

(b)

(c)

(d)

Figure 4 Stress-strain curves of commercial alloy conditions 600LT and 600HT, and controlled-purity alloys CDMA and CDTT, in primary water containing 1 bar hydrogen overpressure at the following temperatures and initial strain rates: (a) 360°C; $1 \times 10^{-6} \text{ s}^{-1}$, (b) 360°C; $3 \times 10^{-7} \text{ s}^{-1}$, (c) 360°C; $8 \times 10^{-8} \text{ s}^{-1}$, and (d) 320°C; $3 \times 10^{-7} \text{ s}^{-1}$

Micrographs of the fracture surfaces and side surfaces of the commercial alloy condition 600HT are illustrated in Figures 5(a) and (b). Figure 5(a) shows that less than 3% of the fracture surface can be attributed to intergranular cracks, while the balance is due to ductile fracture. Figure 5(b) is an SEM micrograph of the side surface of the same sample showing significant intergranular cracking with almost all cracks oriented perpendicular to the tensile direction. These observations illustrate the problem with using %IG fracture on alloys which undergo considerable plastic deformation. The following sections focus on the characterization of cracks determined from SEM examination and replica analysis of the sample surface.

3.2 Crack Initiation

Crack length densities (D_{CL}) were used to obtain information on the crack initiation phase. The relationship between crack length density and plastic strain at different strain rates and temperatures is shown in Figures 6(a)-(d). Commercial alloy 600LT and 600HT had higher crack length densities than did the controlled-purity analogues at a given amount of strain in all test conditions, suggesting that the commercial alloy is more susceptible to IGSCC initiation. The crack length density for commercial alloy 600LT and 600HT conditions at 360°C and the nominal strain rate of $3 \times 10^{-7} \text{ s}^{-1}$ increased with strain up to a value of 15% strain, after which it plateaued and then decreased with further plastic strain, Figure 6(b). This maximum crack length density represents a condition of crack saturation where, based on SEM observation, almost all grain boundaries lying perpendicularly to the tensile direction have been opened. At greater strain, existing cracks opened wider with no increase in crack length. This increased crack opening (width) reduced the mea-

sured crack length value per unit area because cracks near the edge of the examination area moved out of the field of view. Hence, the saturation of crack length density is real, while the subsequent decrease is an artifact of the measurement technique.

For commercial alloy 600, the value of D_{CL} at saturation was higher for 600LT than for 600HT in all test conditions. When the strain rate increased from $3 \times 10^{-7} \text{ s}^{-1}$ to $1 \times 10^{-6} \text{ s}^{-1}$, the saturation point for 600HT was postponed because of the lower crack initiation rate caused by the higher strain rate (Fig. 6(b)). A drop in temperature had a much greater effect on crack initiation rate than did changes in strain rate. After lowering the test temperature to 320°C, D_{CL} values for 600LT and 600HT at 15% strain were only one third of the D_{CL} values at 360°C for the same strain rate (Fig. 6(c)).

Unlike the commercial alloy 600, D_{CL} values of controlled-purity alloys CDMA and CDTT never reached saturation points before the failure in any test condition, due to the extremely low crack initiation rate.

SEM (Figs. 7(a)-(c) and 8(a)-(c)) clearly show the processes of crack initiation, crack growth and crack saturation for 600LT and 600HT with increasing plastic deformation. After 16% strain, no new cracks appeared in the micrographs for either condition. It is also clear that 600LT had a higher D_{CL} at 10% strain and larger crack widths at 16% and 19% strains than did 600HT. The larger crack width in the 600LT condition implies a larger crack depth, which correlates with a greater IGSCC susceptibility for a microstructure with mainly transgranular carbides in hydrogenated, high purity water. Similar observations (not shown) were also obtained for controlled-purity alloys.

(a)

(b)

Figure 5 Micrographs showing (a) the fracture surface, and (b) the side surface of alloy condition 600LT following failure in a CERT test in 360°C primary water containing 1 bar hydrogen overpressure, and an initial strain rate of $3 \times 10^{-7} \text{s}^{-1}$

(a)

(b)

(c)

(d)

Figure 6 Crack length density vs. strain of commercial alloy conditions 600LT and 600HT, and controlled-purity alloys CDMA & CDTT during interrupted CERT tests in primary water containing 1 bar hydrogen overpressure at the following temperatures and initial strain rates: (a) 360°C; $1 \times 10^{-6} \text{ s}^{-1}$, (b) 360°C; $3 \times 10^{-7} \text{ s}^{-1}$, (c) 360°C; $8 \times 10^{-8} \text{ s}^{-1}$, and (d) 320°C; $3 \times 10^{-7} \text{ s}^{-1}$

Figure 7

Micrograph showing a marked area of the 600LT alloy condition during an interrupted CERT test using an initial strain rate of $3 \times 10^{-7} \text{ s}^{-1}$ in 360°C primary water containing 1 bar hydrogen overpressure: (a) 10% strain, (b) 16% strain, and (c) 19% strain

Figure 8

Micrograph showing a marked area of the 600HT alloy condition during an interrupted CERT test using an initial strain rate of $3 \times 10^{-7} \text{ s}^{-1}$ in 360°C primary water containing 1 bar hydrogen overpressure: (a) 10% strain, (b) 16% strain, and (c) 19% strain

3.3 Crack Depth

Maximum crack depth as a function of plastic strain for 600LT, 600HT, CDMA and CDTT are presented in Figures 9 (a)-(d). The lines through the data points were determined using a linear regression analysis. Conditions 600HT and CDTT, with intergranular carbides, had lower maximum crack depths at a given amount of plastic strain than did conditions 600LT and CDMA, respectively for all strain rates and both temperatures. However, there was not a clear difference between the commercial purity alloy and the controlled-purity alloys in terms of crack depth at a given value of strain.

The effect of strain rate on IG crack propagation is evident from the slopes of the curves. The slopes become steeper with decreasing strain rate, indicating that crack growth rate per unit of strain increases with decreasing strain rate. This is not necessarily true, however, for the crack growth rate per unit of time. This behavior will be discussed further in the discussion section.

3.4 Crack Depth Distribution

Additional information can be gained from crack depth distributions plotted as a function of increasing strain. Figures 10(a)-10(c) show the crack depth distribution in the commercial alloy conditions 600LT and 600HT as a function of strain from CERT tests at 360°C with strain rates of $1 \times 10^{-6} \text{ s}^{-1}$ and $3 \times 10^{-7} \text{ s}^{-1}$, and at 320°C with a strain rate of $3 \times 10^{-7} \text{ s}^{-1}$. For all test conditions and all strain levels, the crack depth distribution for the 600LT condition extended to greater crack depths than for

the 600HT condition. At 10% strain, 600LT had more cracks than did 600HT in all three test conditions, indicating that crack nucleation was easier in the 600LT condition. Samples tested at 360°C with a strain rate of $3 \times 10^{-7} \text{ s}^{-1}$ had much higher crack densities at each crack depth interval compared with those tested at 320°C with the same strain rate. Comparing the crack depth distributions from different strain rates at 360°C, the higher strain rate test produced crack depth distributions that extended to slightly greater depths, but had considerably lower crack densities at short depths. This indicates that the lower strain rate promoted greater crack nucleation.

3.5 Creep Experiments

Specimens A1 and D1 were tested in constant load tensile (CLT) tests at a stress level of 544 MPa for 750 hours (following CLT tests at stress levels of 512 MPa for specimen A1 and 544 MPa for specimen D4 for 145 hours). The testing environment was primary water containing 1 bar hydrogen overpressure at 360°C. Figure 11 presents the strain-time curves from last 750 hours CLT tests. For specimen A1, the transient creep lasted the entire testing period and the average creep rate was calculated by using data after the initial 200 hours, which was $3.8 \times 10^{-9} \text{ s}^{-1}$. However, specimen D1 showed a steady state creep behavior after 400 hours, with a corresponding creep rate of $6.8 \times 10^{-10} \text{ s}^{-1}$. It is clear that these creep rates will underestimate the total creep strain for the corresponding specimens. Figures 12 (a) and (b) show the side surface cracking of specimens A1 and D1 after total 895 hours CLT test, respectively. Specimen A1 had more IG cracking than specimen D1, which is consistent with CERT test results.

(a)

(b)

(c)

(d)

Figure 9 Maximum crack depth vs. strain for commercial alloy conditions 600LT and 600HT, and controlled-purity alloys CDMA and CDTT during interrupted CERT tests in primary water containing 1 bar hydrogen overpressure at the following temperatures and initial strain rates: (a) 360°C; $1 \times 10^{-6} \text{ s}^{-1}$, (b) 360°C; $3 \times 10^{-7} \text{ s}^{-1}$, (c) 360°C; $8 \times 10^{-8} \text{ s}^{-1}$, and (d) 320°C; $3 \times 10^{-7} \text{ s}^{-1}$

(a)

(b)

(c)

Figure 10 Crack depth distribution as a function of strain for commercial alloy conditions 600LT and 600HT during interrupted CERT tests in primary water containing 1 bar hydrogen overpressure at the following temperatures and initial strain rates: (a) 360°C; $1 \times 10^{-6} \text{ s}^{-1}$, (b) 360°C; $3 \times 10^{-7} \text{ s}^{-1}$, and (c) 320°C; $3 \times 10^{-7} \text{ s}^{-1}$

Figure 11 Creep curves of commercial alloy NX8844 (samples A1 and D1) in primary water containing 1 bar hydrogen overpressure at 360°C

Figure 12 SEM micrographs showing side surfaces of samples A1(a) and D1(b) after 895 hours in a CLT test in primary water containing 1 bar hydrogen overpressure at 360°C at 544 MPa

4. DISCUSSION

The discussion will focus on the processes of crack initiation (as measured by crack length density) and crack propagation (as measure by crack depth and crack growth rate) and their dependence on carbide distribution, strain rate and temperature in CERT tests. The behavior of the commercial alloys in CLT tests will also be discussed. Comparisons will be made between the commercial alloy 600 conditions and controlled-purity alloys, and with the literature.

4.1 Effect of Carbide Distribution

The effects of carbide distribution on IGSCC initiation and propagation behavior of commercial alloy 600 are presented Figures 13 and 14, which show crack length density and maximum crack depth as a function of grain boundary carbide coverage, respectively. The controlled-purity alloys (not shown) behave in a similar manner. Figure 13 shows the relationship between crack length density at 10% plastic strain and grain boundary carbide coverage for the commercial alloy for different test conditions. Crack initiation is most sensitive to strain at lower strain levels (see Figure 6) and saturation of the surface crack density begins to occur at strains above 15%. For both commercial alloy 600 and the controlled-purity alloys, a higher grain boundary carbide coverage results in lower crack length density, irrespective of strain rate and temperature. Taking crack length density as a measure of the propensity for crack initiation, these results indicate that intergranular carbides do indeed have a beneficial effect on IGSCC initiation of Ni-16Cr-9Fe alloys in hydrogenated, high purity water at elevated temperature.

Information on crack propagation is given in Figure 14, in which the maximum crack depth at 28% plastic strain is plotted vs. the grain boundary carbide coverage. Here

again, irrespective of strain rate or temperature, the crack depth decreases monotonically with grain boundary carbide coverage. Using relative crack depth as a measure of propensity for crack propagation, results indicate that microstructures with a higher amount of grain boundary carbides correlate with reduced crack propagation. While not plotted, the same is true for the controlled-purity alloys.

These results are consistent with observations of the dependence of IGSCC on carbide distribution. Bulisheck et al. (Ref. 19) reported some of the first observations of increased IGSCC resistance of samples with greater amounts of grain boundary carbides. The issue was addressed more extensively by Norring et al. (Refs. 20- 21) who tested over 100 reverse U-bend (RUB) specimens taken from 25 different tubes, from 5 different PWRs and showed that IGSCC initiation time in 365°C water increased with grain boundary carbide coverage. A semi-continuous grain boundary carbide network offered the maximum improvement in cracking resistance (Refs. 21-22). Majo (Ref. 23) reported that alloy tubing containing mostly M_7C_3 IG carbides was more crack resistant than that with mostly intragranular carbides in a primary water environment. Most recently, Rios (Ref. 24) found that crack depths of alloy 600 containing grain boundary carbides were one-fifth of those in alloy 600 containing matrix carbides in 360°C primary water containing 4 bar hydrogen overpressure. The advantage our results over previous studies is that the different carbide distributions were obtained in the same commercial alloy using different heat treatments, and in the other case, in nearly identical, controlled-purity alloys. As such, observations of the effects of carbide distribution on IGSCC can more confidently be attributed to the carbide distribution alone rather than other potentially significant differences in microstructure or composition.

Figure 13 Crack length density vs. grain boundary carbide coverage for commercial alloy 600 after 10% strain in primary water containing 1 bar hydrogen overpressure as a function of strain rate and temperature

Figure 14 Maximum crack depth vs. grain boundary carbide coverage for commercial alloy 600 after 28% strain in primary water containing 1 bar hydrogen overpressure as a function of strain rate and temperature

The two most likely mechanisms to explain these observations are film rupture/slip dissolution or enhanced localized plasticity. It is possible that differences in the surface film at the grain boundary account for differences in IG cracking propensities, following a film rupture/slip dissolution based model. A Cr-rich surface film is thermodynamically stable in 360°C primary water (pH~8). At this pH, the Ni-Ni(OH)₂ stability line falls between the 0 and 1 bar hydrogen lines, favoring a thermodynamically unstable Ni-rich surface film at 1 bar hydrogen (Ref. 14). A less stable film would result in increased cracking according to a film rupture/slip dissolution based model. Chromium carbide dissolution at the grain boundary might result in the formation of a more stable, Cr-rich film at the crack tip in CDTT and 600HT, compared to a relatively Ni-rich film at the crack tip in CDMA and 600LT. As a result of these local differences, less frequent film rupture and quicker film repair would result in both low corrosion and hydrogen evolution rates in the grain boundary carbide microstructure under 1 bar hydrogen conditions. Support for this idea is provided by Shei et al. Ref. 25 who found that Cr-rich oxides formed preferentially at the crack tips of several nickel-base alloys in high temperature caustic environments. They proposed that the formation of Cr-rich oxides near the crack tip was responsible for the high SCC resistance of thermally treated alloy 600.

A second possible mechanism is one in which grain boundary carbides enhance localized plasticity to reduce crack initiation and propagation. Recall from Figure 5 that IGSCC initiated preferentially at grain boundaries oriented perpendicular to the tensile direction, with very little cracking observable at grain boundaries parallel to the tensile direction. Dissolution processes alone can not explain the IGSCC initiation behavior, and stress must play an important role in initiation. Enhanced localized plasticity may occur due to either vacancy injection or hydrogen absorption

caused by localized dissolution. According to this mechanism, the key process is slip localization at the grain boundaries and blunting of the crack tip by the grain boundary carbide. Blunting may occur by dislocation emission and consequent reduction of local stresses as proposed by Bruemmer (Ref. 15). This reduction of stress will result in delayed IGSCC initiation and also a lower crack growth rate as observed in this study. Alternatively, the more tortuous, carbide-laden path for intergranular cracks in the 600HT and CDTT treatments may contribute to reduced initiation and propagation by mechanically "interfering" with crack propagation. In either case, the role of grain boundary carbides is to alter the deformation characteristics at the grain boundary.

4.2 Effect of Strain Rate

The effect of carbide distribution on crack initiation and propagation as a function of strain rate is shown in Figures 15-17. For both commercial alloy 600 and controlled-purity alloys, the strain rate change from $8 \times 10^{-8} \text{ s}^{-1}$ to $1 \times 10^{-6} \text{ s}^{-1}$ has no significant effect on crack initiation behavior, except that the controlled-purity alloys appear to be less susceptible to crack initiation than is the commercial alloy (Fig. 15). However, crack propagation is more sensitive to strain rate (Table 4). Crack propagation, represented as crack growth rate is shown in Figure 16 (in units of m/s) where the crack growth rate increases with strain rate. This is not surprising if crack propagation is strongly driven by stress. However, when the crack growth rate is plotted as crack depth per unit of strain (Fig. 17), there is a strong inverse dependence on strain rate. Per unit of deformation in the sample, the crack advance is greater at lower strain rates, indicating that the environmental effect is greatest at lower strain rates, as expected. Also, regardless of which measure of crack growth rate is used, the conditions with high grain boundary carbide coverage (600HT and CDTT) show consistently lower crack growth rates than do those with lower carbide coverage.

Figure 15 Crack length density vs. strain rate for commercial alloy conditions 600LT and 600HT, and controlled-purity alloys CDMA and CDTT after 10% strain in 360°C primary water containing 1 bar hydrogen overpressure

Figure 16. Crack growth rate in m/s vs. strain rate for commercial alloy conditions 600LT and 600HT, and controlled-purity alloys CDMA and CDTT in 360°C primary water containing 1 bar hydrogen overpressure

Figure 17. Crack growth rate in m/unit strain vs. strain rate for commercial alloy conditions 600LT and 600HT, and controlled-purity alloys CDMA and CDTT in 360°C primary water containing 1 bar hydrogen overpressure

In his analysis of CERT tests, Santarini (Ref. 26) showed that the crack propagation rate is related to strain rate by a power law in which the strain rate exponent should be close to a value of 0.5. Noel et al. (Ref. 27) and Boursier et al. (Ref. 28) investigated the effect of strain rate on IGSCC of alloy 600 in hydrogenated primary water at 360°C and found such a behavior in that increasing strain rate resulted in increased crack growth rates over the strain rate range 6×10^{-9} to $3 \times 10^{-7} \text{ s}^{-1}$. The slope of a log-log plot of crack growth rate vs. strain rate yielded a value of 0.58 for the strain rate exponent. This value agrees well with data from Combrade (Ref. 29) who measured a value of 0.66 under similar conditions. Analyzed in the same way, the slope of a log-log plot for the four alloy conditions used in this study vary from 0.4 to 0.64 (Table 4) in close agreement with the literature data. The fact that the slope is less than 1.0 means that the crack growth rate measured in units of (m/unit strain) will increase with a decreasing strain rate. This

is significant in that it shows that for a given amount of strain, a slower strain rate will produce deeper cracks, as observed. It also implicates the role of creep in the cracking process, as slower strain rates allow more time for creep processes to occur. (Refs. 30-31)

4.3 Effect of Temperature

The effect of temperature is shown in Figures 18 and 19 where crack length density and crack growth rate, respectively, are plotted vs. temperature. Both are higher at 360°C than at 320°C, as expected of a thermally activated process. However, crack initiation in the commercial alloy was much more dependent on temperature than in the controlled-purity alloys (Fig. 18). The temperature dependence of crack depth was quite consistent across all alloy conditions. The activation energy for crack growth determined from this data ranges between 7 and 18 kcal/mol (Table 5).

Table 4 Maximum crack growth rates for different samples from different CERT tests

	360°C, $8 \times 10^{-8} \text{ s}^{-1}$	360°C, $3 \times 10^{-7} \text{ s}^{-1}$	360°C, $1 \times 10^{-6} \text{ s}^{-1}$	320°C, $3 \times 10^{-7} \text{ s}^{-1}$
600LT	$2.14 \times 10^{-11} \text{ m/s}$	$3.80 \times 10^{-11} \text{ m/s}$	$1.11 \times 10^{-10} \text{ m/s}$	$2.58 \times 10^{-11} \text{ m/s}$
600HT	$2.11 \times 10^{-11} \text{ m/s}$	$2.51 \times 10^{-11} \text{ m/s}$	$7.15 \times 10^{-11} \text{ m/s}$	$1.27 \times 10^{-11} \text{ m/s}$
CDMA	$3.83 \times 10^{-11} \text{ m/s}$	$9.12 \times 10^{-11} \text{ m/s}$	$1.72 \times 10^{-10} \text{ m/s}$	$3.87 \times 10^{-11} \text{ m/s}$
CDTT	$2.85 \times 10^{-11} \text{ m/s}$	$8.56 \times 10^{-11} \text{ m/s}$	$7.63 \times 10^{-12} \text{ m/s}$	$3.17 \times 10^{-11} \text{ m/s}$

Table 5 Strain rate exponents and crack growth rate activation energies for the alloy conditions

	strain rate exponent	activation energy (kcal/mole)
600LT	0.64	7.2
600HT	0.48	12.7
CDMA	0.60	16.0
CDTT	0.40	18.4

Figure 18
Crack length density vs. temperature for commercial alloy conditions 600LT and 600HT, and controlled-purity alloys CDMA and CDTT after 10% strain in primary water containing 1 bar hydrogen overpressure

Figure 19
Crack growth rate in m/s vs. temperature for commercial alloy conditions 600LT and 600HT, and controlled-purity alloys CDMA and CDTT in primary water containing 1 bar hydrogen overpressure

Figure 20 Comparison of crack growth rate dependence on temperature for several authors

The crack growth rates at 320°C and 360°C are plotted in Figure 20 against existing data compiled by Cassagne et al. (Ref. 32) from the literature. As reported by Staehle (Ref. 4), there appear to be basically two different activation energies reported by different authors. Our data falls into the category of the lower activation energy also observed by Totsuka et al. and Shen et al. in Figure 20. Nevertheless, as shown by the comparison in Figure 20, the crack growth rates for both the controlled-purity alloys and the commercial alloy are consistent with laboratory tests on alloy 600 in primary water in the same temperature range. They are also in agreement with crack growth rates measured on-site in reactor pressure vessel head penetrations. Pichon et al. (Ref. 33) reported in 1994 that the mean value of the maximum crack growth rate for 20 alloy 600 vessel head penetrations was 4.2×10^{-11} m/s. This value compares favorably with the crack growth rate range $1.3 - 3.9 \times 10^{-11}$ m/s measured for the alloy conditions in this study in 320°C primary water, the condition most comparable to the on-site measurements. Thus, the crack growth rates measured here for both commercial and controlled-purity alloy conditions are well within the range of those measured on commercial alloys both in the laboratory and on-site.

4.4 Creep

One of the major objectives of this study, the role of creep in the intergranular cracking process, was investigated by using the constrained crack opening model proposed by Rice (Ref. 34). The average grain boundary separation rate and thus, the average crack opening can be calculated from this model and compared to the experimental data from the CLT test in order to assess the role of creep in intergranular stress corrosion cracking (IGSCC). The basic assumptions of this model are: (a) all grain boundaries perpendicular to the tensile stress direction are evenly separated, and (b) the crack opening rate is limited by the neighboring grains that deform accord-

ing to the creep law. As proposed by Rice, the average opening rate of a grain facet is given by

$$\dot{\delta} = \alpha[(\sigma_{\infty} - \sigma) / \sigma_{\infty}] \dot{\epsilon}_{\infty} d \quad (1)$$

Where σ_{∞} is the remotely applied uniaxial tensile stress, σ is the tensile stress on the cavitating surfaces, $\dot{\delta}$ is the creep rate, d is the average grain diameter, and α is a dimensionless factor. For power-law controlled creep in the absence of grain boundary sliding, it was estimated by Rice that $\alpha=0.64$ for $n=1$ and $\alpha=0.90$ for $n=5$, where n is the creep exponent in the relationship. Rice also noted that the presence of freely sliding grain boundaries would increase α over previous values, and a doubling of the previous α values should be appropriate, which would give 1.28 for $n=1$ and 1.80 for $n=5$. According to Leclercq et al. (Ref. 35), a stress exponent of $n=2.76$ is the best fit value for the experimental data of commercial alloy 600. Boursier (Ref. 36) used the same n value and got good fitting for alloy 600. Santarini (Ref. 37) also used $n=2.76$ in his model to calculate the defect initiation rate. However, values as high as 5 or 6 have been reported for controlled-purity Ni-Cr-Fe alloy (Ref. 30). Assuming a value of 2.8 for n , values for α , determined by interpolation, are 0.75 for the absence of grain boundary sliding and 1.5 for freely sliding grain boundaries. Since we have measured crack opening rather than opening rates, equation (1) is integrated over time to yield the average crack opening at the end of the test:

$$\delta_{cal} = \alpha[(\sigma_{\infty} - \sigma) / \sigma_{\infty}] \times \epsilon_{ave} \times d \quad (2)$$

Where δ_{cal} is the calculated average crack opening, ϵ_{ave} is the average creep strain. The average crack opening (δ_{cal}) values calculated from Equation (2) are compared with

the experimental data for specimens A1 and D1 which underwent CLT tests at two different stress.

From the observation that cracks are continuous along the grain boundaries with the very shallow crack depth, the value of σ in Equation (2) is taken as zero. The grain diameters are 38 μm for A1 and 27 μm for D1. The average creep rates used for first 145 hour CLT test are $1.13 \times 10^{-9} \text{s}^{-1}$ for specimen A1 and $1.32 \times 10^{-9} \text{s}^{-1}$ for specimen D1, and creep rates for the next 750 hours are $3.8 \times 10^{-9} \text{s}^{-1}$ for specimen A1 and $6.8 \times 10^{-10} \text{s}^{-1}$ for specimen D1. Multiplying the creep rates with corresponding test time, the values of average creep strains are 0.059% and 0.069% for A1 & D1 for first 145 hour CLT test, and 1.03% and 0.18% for A1 & D1 for the next 750 hours, respectively. Using these average creep strains, corresponding average grain size values for A1 & D1, and 0.75 & 1.5 as α values, calculated average crack opening values for different test periods can be obtained according to Equation (2). The results are listed in Table 6. Summing the average crack openings over the two CERT tests gives a total calculated average crack opening of 0.309 μm for specimen A1 and 0.0512 μm for specimen D1 for the case of grain boundaries without sliding. For freely sliding grain boundaries, = 0.619 μm , for specimen A1 and 0.102 μm , for specimen D1.

It is clear from Figs. 12 (a) and (b) that some of the grain boundaries perpendicular

to the tensile direction have not been opened for both specimens A1 and D1 after the 895 hour CLT test. For comparison to Rice's model prediction, the normalized crack opening δ_N is obtained by using the value of measured mean crack opening (CW_{mean} , 0.354 μm for A1 and 0.391 μm for D1) multiplied by the value of opened grain boundary fraction (R_{open} , 0.915 for A1 and 0.195 for D1). R_{open} is determined by dividing the measured crack length density by one-half of the grain boundary length density (D_{gl}). The D_{gl} values for batches A and D are $6.1 \times 10^{-2} (\mu\text{m}/\mu\text{m}^2)$ and $8.5 \times 10^{-2} (\mu\text{m}/\mu\text{m}^2)$, giving δ_N values of 0.32 μm for batch A and 0.076 μm for batch D.

The experimental result for A1 is close to the theoretical value assuming no grain boundary sliding. The result for D1 falls midway between the extremes. It is suggested by these results that specimen D1 with mainly intergranular carbides has more accommodating grain boundaries compared with matrix deformation. In contrast, specimen A1, with a majority of intragranular carbides has relatively rigid grain boundaries compared to matrix deformation. Since the creep rate is directly proportional to the mobility of dislocations in the material, if matrix dislocation motion cannot be accommodated at the grain boundaries, increased grain boundary damage will occur (Ref. 38). The accommodating grain boundaries in batch D, which probably comes from the intergranular carbides, may be the explanation of less grain boundary separation and lower cracking propagation.

Table 6 Measured and calculated parameters of samples A1 and D1 after CLT tests in primary water containing 1 bar hydrogen overpressure at 360°C

Sample	Test duration (hour)	Average creep strain (δ_{ave})	Applied stress (MPa)	Average grain size (μm)	Crack length density (D_{CL}) ($\mu\text{m}/\mu\text{m}^2$)	Grain boundary length density (D_{gl}) ($\mu\text{m}/\mu\text{m}^2$)	Opened grain boundary fraction (R_{open})	Mean crack opening (CW_{mean}) (μm)	Normalized crack opening (δ_N) (μm)	Calculated average crack opening without freely sliding grain boundaries $\alpha=.75$ (δ_{cal}) (μm)	Calculated average crack opening with freely sliding grain boundaries $\alpha=1.5$ (δ_{cal}) (μm)
A1	145	0.059%	512	38	ND	ND	ND	ND	ND	0.0168	0.0336
D1	145	0.069%	544	27	ND	ND	ND	ND	ND	0.0140	0.0279
A1	750	1.03%	544	38	ND	ND	ND	ND	ND	0.292	0.585
D1	750	0.18%	544	27	ND	ND	ND	ND	ND	0.0372	0.0744
A1*	895	1.089%	ND	38	2.8×10^{-2}	6.1×10^{-2}	0.915	0.354	0.32	0.309	0.619
D1*	895	0.249%	ND	27	8.3×10^{-3}	8.5×10^{-2}	0.195	0.391	0.076	0.0512	0.102

ND--not determined

A1* and D1* are the total results of 145 hour and 750 hour CERT tests for A1 and D1, respectively.

5 CONCLUSIONS

For all alloy conditions, IGSCC was the dominant failure mode. For both the commercial alloy and the controlled-purity alloys, the microstructure with grain boundary carbides showed delayed crack initiation and shallower crack depths than did the intragranular carbide microstructure under all experimental conditions. This data indicates that a grain boundary carbide microstructure is more resistant to IGSCC than an intergranular microstructure. Observations are consistent with both the film rupture/slip dissolution mechanism and enhanced

localized plasticity. Crack growth rates increased with increasing strain rate according to a power law relation with a strain rate exponent between 0.4 and 0.64. The fact that the exponent was less than 1.0 means that crack depth and crack growth rate measured in m/unit strain increases, as observed, with decreasing strain rate. This behavior is consistent with an effect of either the environment or creep. The temperature dependence and magnitude of the crack growth rate was consistent with the literature.

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BIBLIOGRAPHIC DATA SHEET

(See instructions on the reverse)

1. REPORT NUMBER
(Assigned by NRC, Add Vol., Supp., Rev.,
and Addendum Numbers, if any.)

NUREG/GR-0016

2. TITLE AND SUBTITLE

The Role of Time-Dependent Deformation in Intergranular Crack Initiation of Alloy 600
Steam Generator Tubing Material

3. DATE REPORT PUBLISHED

MONTH

YEAR

March

1998

4. FIN OR GRANT NUMBER

5. AUTHOR(S)

G. S. Was, K. Lian

6. TYPE OF REPORT

Technical

7. PERIOD COVERED (Inclusive Dates)

11/1/95-6/30/97

8. PERFORMING ORGANIZATION - NAME AND ADDRESS (If NRC, provide Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address; if contractor, provide name and mailing address.)

Dept. of Nuclear Engineering and Radiological Sciences
The University of Michigan
Ann Arbor, MI 48109-2104

9. SPONSORING ORGANIZATION - NAME AND ADDRESS (If NRC, type "Same as above"; if contractor, provide NRC Division, Office or Region, U.S. Nuclear Regulatory Commission, and mailing address.)

Division of Engineering Technology
Office of Nuclear Regulatory Research
U.S. Nuclear Regulatory Commission
Washington, DC 20555-0001

10. SUPPLEMENTARY NOTES

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11. ABSTRACT (200 words or less)

Intergranular stress corrosion cracking (IGSCC) of two commercial alloy 600 conditions and controlled-purity Ni-18Cr-9Fe alloys were investigated using constant extension rate tensile (CERT) tests in primary water with 1 bar hydrogen overpressure at 360°C and 320°C. Heat treatments produced two types of microstructures in both commercial and controlled-purity alloys: one dominated by grain boundary carbides and one dominated by intragranular carbides. CERT tests conducted over a range of strain rates and at two temperatures showed that in all samples, IGSCC was the dominant failure mode. For both the commercial alloy and the controlled-purity alloys, the microstructure with grain boundary carbides showed delayed crack initiation and shallower crack depths than did the intragranular carbide microstructure under all experimental conditions, indicating that a grain boundary carbide microstructure is more resistant to IGSCC than an intragranular carbide microstructure. Observations support both the film rupture/slip dissolution mechanism and enhanced localized plasticity. Crack growth rates increased with increasing strain rate according to a power law relation with a strain rate exponent between 0.40 and 0.64. However, crack growth rate measured in m/unit strain decreased with increasing strain rate indicating an effect of either the environment or creep. The temperature dependence of the crack growth rate was consistent with the literature.

12. KEY WORDS/DESCRIPTORS (List words or phrases that will assist researchers in locating the report.)

alloy 600
stress corrosion cracking
chromium carbide
crack growth rate
Ni-18Cr-9Fe

13. AVAILABILITY STATEMENT

unlimited

14. SECURITY CLASSIFICATION

(This Page)

unclassified

(This Report)

unclassified

15. NUMBER OF PAGES

16. PRICE