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for

FEASIBILITY OF A NOVEL APPROACH FOR FAST, ECONOMICAL
DETERMINATION OF RADIATION DAMAGE IN NUCLEAR REACTOR CORES

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Progress has been made in several areas in the first year of grant activity. This includes radiation induced segregation (modeling and experiment), deformation of the irradiated microstructure, stress corrosion cracking of irradiated microstructures and the development of an apparatus to determine the role of deformation on the radiation microstructure in-situ. The following sections treat each of these sub-programs.

1. Radiation Induced Segregation

Experiments: Experiments have focused on two issues, the segregation behavior in controlled-purity, high nickel alloys and the segregation behavior during irradiation at 200°C. The first program is aimed at investigating the role of nickel in the segregation behavior. It has been suggested that nickel enhances both the amount of Cr depletion and Ni segregation at grain boundaries in austenitic iron-base alloys. [1] If this is true, and the grain boundary chromium level is an important factor in the IASCC of these alloys, then the nickel content may be used to modify the IASCC behavior. However, there has been no systematic study of the effect of nickel on grain boundary segregation or IG cracking. Therefore, three new heats were fabricated containing 24 wt% Ni and either 15, 20 or 24 wt% Cr, table 1. The intermediate amount of chromium is similar to that in the UHP 304L alloy and represents the case where the Cr level is unchanged and iron is exchanged for nickel. The other two alloys are designed to investigate the effect of varying bulk chromium in a high nickel alloy.

Alloys were irradiated under the standard conditions of 3.2 MeV protons at a displacement rate of 7.6×10^{-6} dpa/s at 400°C to a dose of 1 dpa using the Tandetron accelerator in the Michigan Ion Beam Laboratory. Samples were then hydrogen charged and fractured in the analysis chamber of the Scanning Auger Microprobe (SAM) and grain boundary analysis was conducted according to procedures described elsewhere. [2] Between 17 and 23 grain boundaries were analyzed in these new alloys, table 2. The results of the analysis is shown in fig. 1 which gives the grain boundary concentration after the 400°C irradiation to 1 dpa for the three high nickel alloys and the reference UHP alloy. From both table 2 and figure 1 it is evident that the extent of Cr depletion is more severe than that in the UHP 304L alloy and the resulting grain boundary Cr concentrations are significantly lower even though the bulk levels were equivalent to or higher than the UHP alloy in two of the three cases. In fact, a higher bulk level of nickel is responsible for a greater amount of chromium depletion in Fe-Cr-Ni alloys. The resulting IASCC behavior of these alloys is discussed in section 3.

The second investigation was aimed at determining whether the grain boundary chemistry was controlling the IG cracking that has consistently been observed in the UHP alloy tested in 288°C water containing 2 ppm O₂ at 0.5 μS/cm conductivity. As such, a UHP alloy and a 24/24 alloy were irradiated at 200°C to suppress RIS and allow for the study of the effect of irradiation damage without the complicating influence of changing grain boundary composition. The grain boundary composition of the irradiated 24/24 alloy only has been obtained to date, but it shows only a very minor amount (<3 at%) of Cr depletion and Ni enrichment (<1 at%). This compares with 13 at% depletion of Cr and 15 at% enrichment of Ni following irradiation to the same dose at 400°C, table 2. In fact, the lower irradiation temperature was quite successful in suppressing RIS while permitting the development of the irradiation damage structure. The IASCC results of these alloys are discussed in section 3.

Modeling: The use of RIS models in helping to predict grain boundary segregation following specific irradiations is of great value in linking grain boundary chemistry to

microstructure and IASCC susceptibility. However, existing models are fraught with shortcomings that severely limit their usefulness. Both the Perks [3] and Lam [4] models consistently overpredict the amount of segregation observed at grain boundaries by either STEM-EDS or AES following neutron, ion or proton irradiation. The possible causes are numerous and the utility of these codes will continue to be restricted unless the problems are addressed. We have begun a program to assess the accuracy and correctness of these models. The first step in such a process is to ensure that the input parameters to the models are correct since the predicted composition profiles can be quite sensitive to the input parameters. Modeling a 304 SS alloy is beyond the present state of the field. The Lam and Perks codes can treat a three component alloy and Damcott has modified it to treat a 4 component system. We have written our own code which is essentially the same as the Perks or Lam codes but which includes several additional features. However, the number of input parameters quickly becomes unmanageable. Therefore, we have simplified the problem to a binary alloy system and narrowed the number of critical parameters to three; the ratio of pre-exponential factors in the diffusion equations, the difference in the vacancy migration energies and the thermodynamic factor for the binary alloy of interest.

We have proposed a series of experiments which are designed to determine the correct values of these three parameters (or combinations of parameters) and have decided to focus on the Ni-Cr system. The objective will be to first benchmark the Ni-15Cr binary alloy system and then to increase the complexity of the system by the addition of 9 at% Fe or P and then Fe+P to arrive at a ternary alloy with P as an impurity. The ternary alloy is essentially a high purity version of alloy 600, an alloy commonly used in core components in both BWRs and PWRs. The selection of a nickel-base alloy instead of an iron-base alloy was necessitated in order to permit the study of a 2-component system without a change in crystal structure. The immediate objective will be to achieve a full benchmarking of the physical model described by the code. The plan is discussed in more detail in the Continuation Proposal.

2. Deformation of Irradiated Microstructures

Tensile bars of the UHP alloy were irradiated to 1 dpa at 400°C using the standard proton irradiation conditions of 3.2 MeV protons and a displacement rate of 7.6×10^{-6} dpa/s. Samples were then pulled in uniaxial tension at a strain rate of $3 \times 10^{-7} \text{ s}^{-1}$ in an argon environment to strains of 3% and 9%. Surfaces of the samples were analyzed in the SEM and TEM disks were cut from the tensile samples and analyzed in a JEOL-2000FX transmission electron microscope.

SEM Observations: Unirradiated samples show no traces of slip activity on the surfaces when examined in the SEM. The surfaces are featureless except for small cracks scattered across the surface. These cracks are across the widths of the spinel particles that are visible on the surface, and end at the edges of these particles. All cracks are perpendicular to the load axis. The only visible difference between the 3% and 9% strained samples is the density of these surface cracks.

The irradiated sample deformed to 3% also exhibits these cracked particles on the surface. More obvious and important, however, are the slip steps that are observed. These steps are relatively well-defined and are similar to those observed in the SCC samples tested in water environment, except with more well-defined edges and smaller in magnitude. The edges are sharper because of the lack of corrosive environment in which

the deformation samples were tested, which also explains why they are visible at such low strains.

The irradiated sample deformed to 9% does not exhibit the cracked particles on the surface that are found in the other samples. There are, however, pits and dimples on the surface which were not observed in the other samples. These pits and dimples are most likely the holes left behind after the spinel particles completely disintegrated under the applied stress and fell completely out of the surface. SEM examination of small bits of particle left behind in some of these holes corroborates this theory. Slip steps are very prominent after deformation to 9% strain. Steps are clearly visible even optically, and stand out as ledges in the SEM. Each grain has one or two directions in which slip has occurred, and at the intersections when two slip systems are active, cross slip is readily apparent. Cross slip is not visible in the 3% sample, though in some grains a second slip system is visible. Slip steps are more closely spaced in the 9% sample than the 3% sample as well, indicating that saturation of the density of these slip bands occurs after 3% strain.

TEM Observations: The unirradiated sample pulled to 3% strain exhibits inhomogeneous deformation. This is known through TEM examination of the microstructure after deformation, in which the dislocation density increases markedly in some grains, while other grains remain at their pre-deformation density. The formation of a cellular substructure in the interactions of the dislocation is not present at this relatively low deformation. After deformation to 9%, the dislocation density becomes much higher than at 3%, and is homogeneous throughout the examined region. The onset of a cellular dislocation substructure has begun through interaction and tangling of mobile dislocations.

After irradiation and deformation to 3%, the irradiated microstructure is still the dominant feature. Dislocation channels are present in all of the grains and are fairly widely spaced. These channels are confined to the $\langle 111 \rangle$ slip planes. Parallel to these channels are bands of martensite, which likely were previously dislocation channels that transformed to martensite, either due to stress or exposure to low temperature during TEM sample preparation. The dislocation channels consist of multiple parallel planes in which one dislocation after another travels across the breadth of the grain to the opposite grain boundary. Dislocation pile-up is observed at the boundaries. No cross-boundary slip of dislocations into the next grain has been observed.

TEM examination of a sample deformed to 9% after irradiation reveals a more closely spaced and higher channel density than that found in the 3% sample. Every grain shows evidence of at least two different slip systems, though there are no more than two systems that have clearly defined channels. The other systems consist of scattered dislocations proceeding through the grains, but without being confined to a specific visible channel. The channels in the 9% sample, again parallel to the primary active channels, most probably resulted from transformation of these channels. Whether this transformation was due to stress or low temperatures has yet to be determined.

3. Stress Corrosion Cracking Experiments

Three tests were conducted, using samples irradiated at both 200°C and 400°C. The data is presented in table 3, and stress-strain curves for these tests are shown in figure 2. As the irradiated thickness of the samples was only 2.5% of the total sample thickness,

the bulk mechanical properties of the samples did not reflect the mechanical properties of the irradiated region. Consequently, intergranular cracks were found at multiple sites in the irradiated surface of each sample, generally halting when they had penetrated the depth of the irradiated region, i.e. the proton range. Transgranular cracks were observed to propagate from the tip of the intergranular crack, leading to complete sample failure at elongations significantly lower than those found for unirradiated samples. As a result, both the number of cracks in the irradiated region and the total elongation could be used to assess the cracking susceptibility of the samples. The number of cracks decreased as the total elongation increased from one sample group to another.

The UHP samples irradiated at both temperatures failed at elongations between 10 and 13%, consistent with previously reported results [5]. The cracking behavior of the UHP samples was also consistent with the previously reported results, with a great deal of cracking in the irradiated region of both samples. In the previous study, the number of cracks in the irradiated region ranged from 14 to 24. The samples irradiated at 400°C had 13 (0.5 $\mu\text{S}/\text{cm}$ water) and 23 (1.0 $\mu\text{S}/\text{cm}$ water) intergranular cracks respectively on the irradiated surface, while the sample irradiated at 200°C had 8 (0.5 $\mu\text{S}/\text{cm}$ water). The opening of these cracks on the UHP sample tested in 1 $\mu\text{S}/\text{cm}$ water accounted for 0.85 mm of the 1.3 mm of elongation which occurred in the irradiated region, or 8 % of the 12% total elongation, such that the elongation due to deformation, rather than cracking, was an average of 4% in the irradiated region. Based on the results of previous experiments, where the number of cracks ranged from 14 to 24 in identical environments, the difference between 13 and 22 cracks (the range for samples irradiated at 400°C) is regarded as somewhat less significant than the difference between 13 and 8 cracks, i.e. the number of cracks found in the sample irradiated at 400°C vs. the number of cracks in the sample irradiated at 200°C. However, it is clear that the variation in the number of cracks is not large between either the different environmental or microstructural conditions.

The 16/24, 20/24 and 24/24 samples irradiated at 400°C and the 16/24 and 20/24 samples irradiated at 200°C all failed at high elongations, and only the 16/24 sample tested in 3.2 $\mu\text{S}/\text{cm}$ water showed any intergranular cracking in the irradiated region. These samples were irradiated and strained in a CERT test in parallel with the UHP samples (which cracked profusely), so irradiation and environmental conditions between these elevated nickel samples and the UHP samples were minimal. The elevation of conductivity from 0.5 $\mu\text{S}/\text{cm}$ to 3.2 $\mu\text{S}/\text{cm}$ did not induce any cracking in the 24/24 sample and only one crack in the 16/24 sample, indicating that cracking was only slightly sensitive to water purity over the range of conductivities tested. The grain boundary composition of the alloys irradiated at 200°C and 400°C is shown in fig. 3 as a function of the bulk composition and the elongation and cracking behavior is shown in relation to all other existing data from this program in fig. 4. Note that the high nickel alloys are among the most resistant. However, the UHP alloy irradiated at 200°C where minimal segregation is expected still falls into the severe cracking regime.

The irradiated surfaces of the 16/24, 20/24 and 24/24 samples contained surface slip steps similar to those reported previously. The difference in the irradiation temperature apparently had little effect on the nature of the slip steps. Bloom et al. [6] have shown that while the defects generated at different temperatures were distinct, the impact of these differences on the bulk mechanical properties was relatively small. If this is the case in these experiments, then it may be expected that the microstructures generated at 400°C and 200°C result in a similar increase in the yield strength.

In previous work, it was concluded that hydrogen did not contribute to the cracking of samples irradiated at 400°C then CERT tested at 288°C in water, mainly due to the

absence of cracking in samples strained in inert environments [5]. Similarly, the absence of cracking in the 20/24 or 15/24 samples irradiated at 200°C indicates that any hydrogen remaining from proton irradiation was unlikely to contribute to intergranular cracking in the UHP sample irradiated at 200°C, as these alloys have comparable cracking responses to hydrogen at temperatures greater than 25°C [7]. Thus, hydrogen was not considered to be a factor in the observed cracking.

These results have some interesting implications as to the origin of the increased susceptibility following irradiation. On the one hand, the severe reduction or elimination of cracking in the high nickel alloys as compared with the UHP alloy suggests that the grain boundary chemistry is a critical issue. However, it also suggests that it is not the chromium level which is controlling since the high nickel alloys all have lower grain boundary chromium concentrations than the UHP alloy. Further evidence implicating the grain boundary chemistry as the critical feature is our earlier results [5] (and those of Fukuya [8]) which show that independent of the irradiating specie, the presence of P and Si at the grain boundary correlate strongly with a reduction in IG cracking in high temperature water.

On the other hand, the observation of minimal grain boundary segregation in the low temperature irradiation of the 24/24 alloy implies that the same should be true for the UHP alloy irradiated at the same temperature and then the increased IG cracking susceptibility would be better correlated with radiation hardening. At this point, we are not in a position to answer this apparent contradiction. The continuation proposal describes experiments designed to separate the effects of radiation hardening from grain boundary composition.

4. In-situ Deformation Experiments

The role of the radiation damage microstructure is deemed to be a critical element in the understanding of the mechanism of IASCC. However, post-irradiation deformation does not integrate the effect of the irradiation *during* irradiation. Hence, we have begun a program to address the role of *in-situ* deformation during irradiation. To date, we have completed a first draft of a design for a constant extension rate facility to be attached to the target chamber of the Tandatron accelerator. The facility will allow for the deformation of the sample in a constant extension rate tensile (CERT) test mode during irradiation at temperature. The sample temperature will be controllable between 300 and 500°C and the strain rate range will be from $1 \times 10^{-8} \text{ s}^{-1}$ to $1 \times 10^{-6} \text{ s}^{-1}$ under a displacement rate from $1 \times 10^{-6} \text{ dpa/s}$ to $1 \times 10^{-5} \text{ dpa/s}$. Temperature monitoring will be accomplished using a pyrometer and a series of tests of the response time, accuracy and repeatability have just been completed on a unit in house. The temperature control system, environment control system and straining system have all undergone preliminary design and are ready for finalization. This ratio of deformation rate to displacement rate is similar to that experienced in the swelling of control rod tubes in reactor and therefore captures the proper relation of deformation rate to irradiation damage rate.

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Table 1: Chemical composition of the high purity stainless steel alloys as reported by GE and analyzed by electron microprobe.

Alloy (*)	Cr	Ni	Mn	Mo	Si	C	N	P	S
UHP (945)									
GE wt. % [at. %]	19.2 [20.4]	9.03 [8.5]	1.11 [1.11]	<0.005 [<0.003]	0.03 [0.06]	0.0046 [0.021]	0.0031 [0.012]	<0.005 [<0.009]	0.005 [0.0086]
probe wt. % [at. %]	19.5 [20.72]	9.43 [8.88]	1.11 [1.11]	-	0.05 [0.09]	-	-	0.006 [0.01]	-
24/24 (1151)									
GE wt. % [at. %]	23.9	23.4	0.98	0.03	0.02	0.005	0.001	0.007	0.005 [<0.009]
probe wt. % [at. %]	24.6 [26.2]	23.8 [22.4]	1.39 [1.4]	0.002 [0.001]	0.06 [0.12]	-	-	-	-
20/24 (1155)									
GE wt. % [at. %]	18.7	24.4	1.14	0.03	<0.005	0.003	-	<0.005 [<0.009]	0.005 [<0.009]
probe wt. % [at. %]	19.4 [20.7]	23.8 [22.5]	1.35 [1.4]	0.006 [0.003]	0.06 [0.12]	-	-	-	-
15/24 (1177)									
GE wt. % [at. %]	14.7	23.9	1.12	0.03	<0.005	<0.005	-	<0.005 [<0.009]	<0.005 [<0.009]
probe wt. % [at. %]	15.3 [16.3]	23.1 [21.9]	1.27 [1.3]	<0.001	0.06 [0.12]	-	-	-	-

* Balance iron

Table 2: Summary of the grain boundary compositions (at%) of the UHP, 15/24, 20/24 and 24/24 alloys after irradiation

with 3.2 MeV protons to 1 dpa as determined via Auger. Errors are given as the standard deviation of the mean.

Alloy	Irradiation temperature	number of irradi batches	number of samples	number of meas.	Iron	Chromium	Nickel	Phosphorus	Sulfur	Silicon
UHP (from [5])	400°C	3	5	31	69.9±0.7	17.2±0.7	12.9±0.3	ND	ND	ND
24/24	400°C	1	2	23	49.2±0.6	13.2±0.4	37.7±0.6	ND	ND	ND
	200°C	1	1	10	50.7±0.2	23.3±0.3	23.4±0.3	ND	ND	ND
20/24	400°C	1	2	20	53.0±1.1	11.6±0.6	35.4±1.2	ND	ND	ND
15/24	400°C	1	2	17	50.3±1.0	10.0±0.7	39.7±1.4	ND	ND	ND

ND: not detected

Table 3: Summary of the CERT test performed in water.

Alloy	Irrad. batch number	Irrad. temp.	CERT test number	CERT test water conduct. ($\mu\text{S}/\text{cm}$)	UTS (*) (MPa)	% elong. at failure	% IG cracking in irradiated region	no. of cracks in irradiated region
UHP	9	400°C	14	0.5	350	13	80-100	13
	10	200°C	15	0.5	310	10	80-100	8
	11	400°C	16	1	320	12.5	80-100	24
24/24	9	400°C	14	0.5	460	29	-	none
	11	400°C	16	1.0 for 12%, 3.2 for rest	470	30	-	none
20/24	9	400°C	14	0.5	410	30	-	none
	10	200°C	15	0.5	410	27	-	none
15/24	9	400°C	14	0.5	430	28	-	none
	10	200°C	15	0.5	390	23	-	none
	11	400°C	16	1.0 for 12%, 3.2 for rest	370	27	< 20	1

Tests conducted in 288°C water, 2 ppm oxygen conc., at noted conductivity, and initial strain rate of 3.6 E-7/s

* UTS reflects bulk sample properties, not irradiated region.

Figure 1. Change in grain boundary composition, as determined by Auger electron spectroscopy, following irradiation with 3.2 MeV protons at 400°C to 1 dpa.

Figure 2. Stress-strain curves for the UHP and xCr/24 Ni alloys irradiated at 400°C (unless noted), then strained in water at 288°C, 0.5 μS/cm conductivity, (unless noted), 2 ppm dissolved oxygen concentration, at an initial strain rate 3.6 x 10⁻⁷ s⁻¹. The conductivity was increased in fig. 2c from 1 μS/cm to 3.2 μS/cm after the test was interrupted.

Figure 3. Depletion of grain boundary chromium from the bulk concentration due to RIS, as measured by AES; all samples irradiated with 3.2 MeV protons at 400°C (closed symbols) or 200°C (open symbols) to 1 dpa. Data from Winfrith SGHWR 20Cr/25Ni/Nb neutron irradiated alloy (approx 1.5 dpa) shown for comparison [1]; data obtained via STEM-EDS rather than AES.

Fig. 4. Number of cracks vs. elongation at failure with samples in this study shown as points, and the range found in previous work shown as shaded regions. Samples were irradiated with 3.2 MeV protons at 400°C, (or 200°C if identified with L.T.), to 1 dpa, then CERT tested at a strain rate of $3.6 \times 10^{-7} \text{ s}^{-1}$ in 288°C, 2 ppm O_2 water. Closed symbols indicate a conductivity of 0.5 $\mu\text{S}/\text{cm}$ during the CERT test, while open symbols indicate a conductivity of 1.0 $\mu\text{S}/\text{cm}$ for the first 12% elongation, then 3.2 $\mu\text{S}/\text{cm}$ for the remaining elongation.

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