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Influence of boron on void swelling in model austenitic steels

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Abstract

Model austenitic steels based on Fe–15Cr–16Ni with additions of 0.25Ti, 500 appm B, or 0.25Ti–500 appm B were irradiated in FFTF/MOTA over a wide range of dose rates at ~400 °C. In addition to the effect of dose rate on swelling, it was desired to study the effect of boron addition to produce variations in He/dpa ratio. A strong effect of dose rate was observed, so strong that the relatively small distances separating the boron-free and doped alloys introduced a complication into the experiment. For specimens irradiated within the core, boron addition had no significant effect. For irradiations conducted near or outside the core edge, swelling appeared to be either enhanced or decreased by boron. The variability was a consequence of a strong dose rate effect overwhelming the influence of boron and helium. It is shown that helium exerted little influence relative to other important factors in these alloys.
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1. Introduction

Natural boron contains ~20% of ^{10}B, which has a high but spectrally dependent cross section for (n,α) reactions. Boron additions thus increase both the helium and He/dpa ratio during neutron irradiation. Helium is known to assist void nucleation and often to accelerate the onset of swelling [1], especially if void nucleation is relatively difficult. However, the neutron flux/spectrum across the core of a fast reactor like FFTF (Fast Flux Test Facility) changes significantly with position, a situation which also produces variations in He/dpa ratios and dose rates.

In order to determine the influence of dose rate and helium production on swelling, specimens of simple austenitic steels with and without additions of 500 appm natural boron were irradiated close to each other in the FFTF/MOTA (Materials Open Test Assembly). The results for the boron-doped alloys are presented in this paper and compared with those of the boron-free alloys reported earlier [2,3].

2. Experimental procedure

Detailed descriptions of experimental procedures were presented elsewhere [2], and are only briefly reviewed here. Fe–15Cr–16Ni–500 appm B, Fe–15Cr–16Ni–0.25Ti–500 appm B, as well as the boron-free alloys were prepared from high purity Fe, Cr, Ni, Ti and B by arc-melting. No precipitates were observed by microscopy in unirradiated specimens, even though 500 appm boron exceeds the solubility limit at the 1050 °C annealing temperature [4,5]. The final specimens were 3 mm diameter microscopy disks of 0.2 mm thickness. Three to four nominally identical specimens of each alloy were stacked together.

The specimens were irradiated in sealed, helium-filled packets (6.4 cm long, 4 mm wide cylinder) for either one or two consecutive cycles over a wide range of dose rates (8.9×10^{-9}–1.7×10^{-6} dpa/s) at different axial locations. Many alloys were in each packet, requiring some small distance (~1.5–2.0 cm) between each of the two base alloys and their boron-doped counterparts. The

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cumulative doses at the packet centerline ranged from 0.23 to 67.8 dpa. Irradiation temperatures were actively controlled to ±5 °C, with each capsule maintained at a base temperature in the range 387–444 °C. Irradiation conditions and helium levels are shown in Table 1. Helium arises from three processes, high energy reactions with all Fe, Cr, Ni isotopes, the two-step $^{58}Ni(n,\gamma)^{59}Ni(n,\alpha)^{56}Fe$ sequence and $^{10}B(n,\alpha)^{7}Li$. The latter two contributions respond primarily to low energy neutrons and the resultant He/dpa ratio increases strongly in the softer spectra found out of core, while the high energy contribution to He/dpa decreases near the core edge and beyond, as calculated for each position by Greenwood and Garner [6].

Post-irradiation immersion density measurements were used to determine bulk swelling, followed by TEM observation with 200 kV.

3. Results

Fig. 1 shows the homogeneously distributed cavity microstructures observed at 28.8 dpa and 424–430 °C of boron-free and boron-doped Ti-modified alloy. Cavity densities are somewhat higher in the boron-doped alloy, with concurrent smaller average size. There is no precipitation, although the cavity surfaces of the boron-doped alloy appear to be accumulating some deposit. The swelling of nominally identical specimens is very reproducible, but there appears to be somewhat less swelling in the boron-doped alloy, ~21.5% vs. ~18.3%. It would be a mistake, however, to assume that boron addition alone decreased swelling.

Fig. 2 shows the swelling of the full set of specimens. If we focus on the two boron-free alloys, it is clearly observed that lower dose rates strongly increase swelling by shortening the incubation dose for the onset of steady-state swelling, while the steady-state swelling rate of 1%/dpa is not affected by dose rate [2,3]. For the

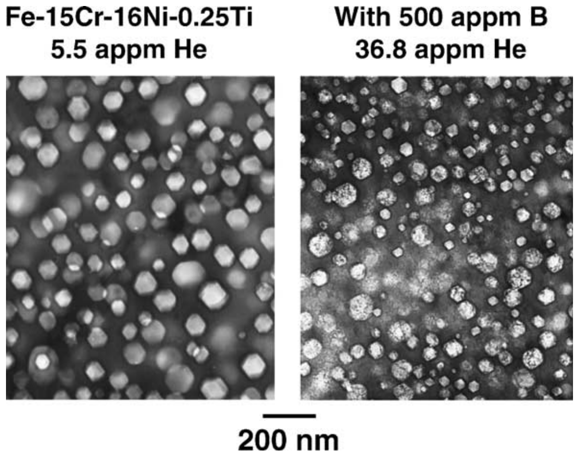

Fig. 1. Comparison of cavity microstructures produced by irradiation in MOTA-2A & 2B at 28.8 dpa and temperatures of 430 and 424 °C, respectively. Boron addition caused an increase in cavity density, an apparent slight decrease in average swelling and a mottled appearance of the cavities.

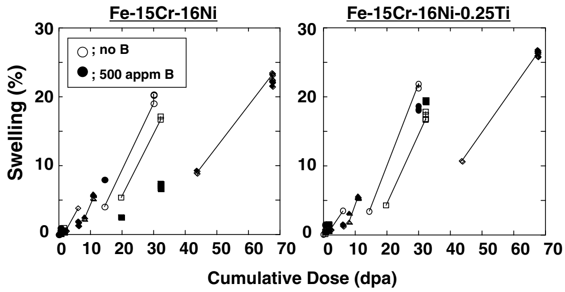

Fig. 2. Influence of 500 appm boron additions (solid symbols) on total swelling of the ternary and Ti-modified alloy. Note that the data at 67.8 dpa, with and without boron, are overlapping for both alloys, demonstrating that boron addition does not affect swelling for irradiations conducted within the core, where negligible dose rate gradients exist.

Table 1
Irradiation conditions

Dose rate, dpa/s		Dose, dpa		Temperature, °C		appm He without B		appm He with 500 appm B	
2A	2B	2A	2A & 2B	2A	2B	2A	2A & 2B	2A	2A & 2B
1.7×10^{-6}	1.4×10^{-6}	43.8	67.8	427	408	9.0	15.5	34.4	56.7
7.8×10^{-7} [a]	9.5×10^{-7}	20.0 [a]	32.4	390	387	6.6	10.9	30.2	47.6
5.4×10^{-7}	8.4×10^{-7}	14.0	28.8	430	424	3.1	5.5	23.1	36.8
3.1×10^{-7} [b]	3.0×10^{-7}	8.05 [b]	11.1	411	410	1.8	3.2	48.5	65.7
9.1×10^{-8}	2.1×10^{-7}	2.36	6.36	430	431	0.45	0.70	21.8	34.0
2.7×10^{-8}	6.6×10^{-8}	0.71	1.87	434	437	0.23	0.35	14.1	22.6
8.9×10^{-9}	2.2×10^{-8}	0.23	0.61	436	444	0.013	0.021	6.5	11.1

[a] 6.0×10^{-7} dpa/s and 15.6 dpa for 2 cycles-irradiation specimens.
[b] 2.2×10^{-7} dpa/s and 5.69 dpa for 2 cycles-irradiation specimens.

lowest dose rate, the incubation doses can be very low, as low as <1.0 dpa, demonstrating that the void nucleation can easily occur at very low doses in these alloys.

This finding of strong dose rate effects introduces a severe complication into the experiment. The distance separation of the boron-free and doped alloys introduces a gradient in dose rate and spectra that is much larger in impact than anticipated when the experiment was designed. Since there was no record of which end of the packet was on top, there can be either a positive or negative increment of dose rate between the boron-free and doped alloys when the packet resides in a dose rate gradient near the core edge or outside the core. It should be noted that the results suggest that boron can decrease or increase swelling in capsules that straddle a dose rate gradient. It is observed that the steeper the gradient the greater the disparity in swelling.

For irradiations conducted within the core with negligible gradients in dose rates, however, there is essentially no significant difference in swelling with boron addition. Based on these findings we conclude that the boron additions do not significantly change swelling for either of the ternary or Ti-modified alloy, at least at this temperature range and over the range of He/dpa ratios studied.

4. Discussion

This relative insensitivity to boron and the helium and lithium it produces probably reflects the fact that void nucleation is relatively easy in these simple alloys under these irradiation conditions, and the impact of extra helium is small compared to other factors that influence nucleation. This latter point can be tested using the microstructural data.

Helium atoms are believed to stabilize small cavities by providing a gas pressure and thereby reducing vacancy evaporation from vacancy clusters [1]. The vacancy concentration in equilibrium with a cavity is given by

$$C_v^0 = C_v^{\mathrm{eq}} \exp\left\{ \left(\frac{2\gamma}{r} - P_{\mathrm{He}} \right) \frac{\Omega}{kT} \right\},$$

where C_v^{eq} is the thermal vacancy concentration, r is the cavity radius and γ is the surface energy, assumed to be 2.0 J/m^2, P_{He} is the helium pressure within the cavity, Ω is the atomic volume, T is the temperature in Kelvin, and k is the Boltzmann's constant. The average helium pressure in cavities, $\overline{P}_{\mathrm{He}}$, can be related to the total helium concentration, C_{He} in the materials, assuming negligible amounts of helium in solution. This relationship follows from the gas law and can be written as

$$\overline{P}_{\mathrm{He}} \cdot \frac{\Delta V}{V} = 6.566 \cdot R \cdot T \cdot z \ [\mathrm{MPa}].$$

Here $\Delta V/V$ is the swelling, R the gas constant, and z the compressibility ratio, which is larger than 1 only for very high pressures.

With the measured values for swelling, the average helium pressures in the cavities were calculated, and the results are shown in Fig. 3. Fig. 3 also shows the average surface tension for the observed cavities, $2\gamma/r$. It is seen that for all irradiation conditions in this study, the helium pressure is always much lower than the surface tension of the cavities, even for the boron-doped alloys. The difference is at least two orders of magnitude or more even at the lowest dose rates for which the helium pressures are the highest. The difference becomes even larger with increasing dose and dose rate. This clearly shows that the helium pressures are always negligible throughout the entire irradiation history in these experiments. The increase of helium by boron addition is not sufficient to oppose the surface tension of the cavities. Therefore, boron additions do not strongly change the swelling, and the cavities are in fact voids even in the boron-doped alloys.

These results also support the idea that the void nucleation does not always require helium [7]. There are many ion-irradiation or electron-irradiation experiments where voids form without helium. In neutron irradiation experiments, one would expect aggregations of helium atoms into bubbles and conversion of bubbles into voids to assist initiation of swelling. This may be true under conditions when helium atoms are generated faster than voids, such as irradiations at higher temperatures or irradiations of swelling-resistant materials. However, when void nucleation can easily occur, as in our model alloys, it is seen that helium is not required for void

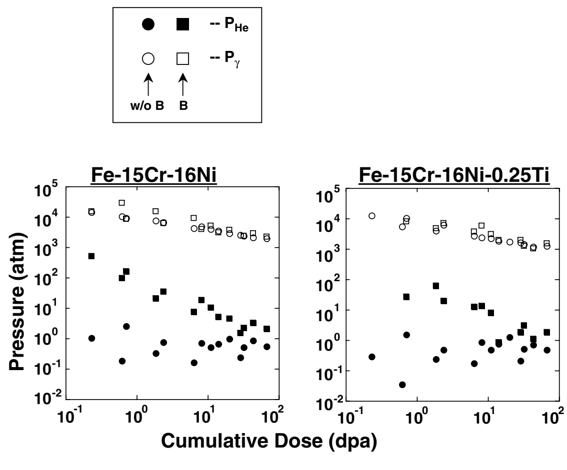

Fig. 3. Calculated helium pressures in cavities (P_{He}) for boron-doped (solid squares) and for boron-free (solid circles) alloys are compared with the calculated surface tension of cavities (P_γ) for boron-doped (open squares) and boron-free (open circles) alloys.

nucleation, and increases of helium have little influence. It remains an open question for other alloys and commercial steels whether helium generation by (n, α) reactions is ultimately found to be an important aspect of void swelling.

In Fig. 1 the void density increased even though the swelling decreased with boron addition. This appears then to be only a reflection of the increased helium level, but it must not be forgotten helium is not the only consequence of boron addition. Boron doping can lead to boride formation and generation of lithium [5]. Lithium has also been shown to affect void nucleation. We note that most of the boron still remains, either as ^{11}B or unburned ^{10}B. The solubility of boron within γ-Fe is estimated to be $<10^{-4}$ appm at the irradiation temperature of ∼400 °C, and <30 appm at the annealing temperature of 1050 °C. These estimates are based on extrapolating the data obtained at higher temperatures of 910 and 1150 °C [4]. It is apparent that boron is in super-saturation prior to and during the irradiation. The activation energy for boron migration in γ-Fe is estimated to be 0.91 eV [8], and is significantly less than the activation energy for vacancy migration [9]. Therefore, as voids form in the early stages of irradiation, boron can easily diffuse and segregate to void surfaces. The micrograph of the boron-doped alloy in Fig. 1 shows the existence of visible islands on the void surfaces, which we interpret as possible segregation of boron or borides. We consider this to be the most likely cause of the mottled appearance of the voids in the boron-doped alloys.

Remarkably, however, the swelling is not strongly changed at ∼400 °C, and the sensitivity to dose rate is preserved even when boron may be present or segregated to the void surfaces.

5. Conclusion

In very simple model austenitic alloys that initiate swelling relatively easily, the transient regime preceding the onset of steady-state swelling can be strongly affected by irradiation variables such as dose rate. Boron addition tends to increase the void density somewhat, but the presence of helium is not always a major determinant of the duration of the transient regime. In experiments where flux-spectra variations are significant, extra care must be taken in the separation of the concurrent influence of two variables such as dose rate and helium/dpa ratio.

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