RADIATION-INDUCED SEGREGATION IN ALLOY X-750

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ABSTRACT

The microstructural and microchemical evolution of an Alloy X-750 heat under neutron irradiation has been studied in order to understand the origin of irradiation-assisted stress corrosion cracking. Both clustering of point defects and radiation-induced segregation (RIS) at interfaces and boundaries have been observed. Although no significant changes in the precipitate structure were observed, boundaries exhibited additional depletion of Cr and Fe and enrichment of Ni.

INTRODUCTION

Alloy X-750 is a γ' -strengthened nickel-base alloy that is frequently used in nuclear power systems because of its excellent corrosion resistance and mechanical properties [1]. However, under neutron irradiation, Alloy X-750 can be susceptible to irradiation-assisted stress corrosion cracking (IASCC) [2]. Both conventional transmission electron microscopy and high spatial resolution analytical electron microscopy (AEM) in a field emission gun scanning transmission electron microscope (FEG-STEM) were used to characterize the microstructural and microchemical evolution of Alloy X-750 under neutron irradiation in order to evaluate the importance of RIS in IASCC.

EXPERIMENTAL

The Alloy X-750 material (see Table 1 for alloy composition) was in the HTH commercial heat treatment (1h at 1121°C + air cooling + 20h at 704°C). Specimens for AEM were prepared from both unirradiated control material and material irradiated at 360°C to a fluence of 2.3×10^{20} n/cm² (E > 1 MeV), which is estimated to produce ~0.4 displacements per atom (dpa).

Table 1 Alloy Composition (wt%, *trace elements in wt ppm)

Ni	Cr	Fe	Ti	Nb	Al	C	Si	Mo	B*	P*	S*
71.8	15.3	8.05	2.61	0.96	0.75	0.041	0.07	0.02	28	20	3

Analytical electron microscopy was performed in a Philips EM400T/FEG (field emission gun) operated in the scanning transmission mode with a probe diameter of ~1.4 nm (FWHM). For a 1-dimensional integration, more than 90% of the probe current is contained within ~1 nm of the probe center (i.e., the critical dimension for 1-dimensional profiles at interfaces). The AEM was equipped with facilities for both energy dispersive X-ray spectrometry (EDS) and parallel-detection electron energy-loss spectrometry (PEELS)[3]. Composition profiles were acquired in two different ways; all EDS and some PEELS profiles were acquired as individual spot analyses, whereas the majority of the PEELS profiles were acquired as spectrum lines with short (~10 s) acquisition times per point. The quoted compositions are as measured; no attempt has been made to deconvolute the grain boundary versus matrix contributions. In addition, the concentrations measured by PEELS for the elements detected (typically Ti, Cr, Fe, and Ni) were normalized to 100 wt%, leading to a slight overestimate of their concentrations. X-ray microanalysis was generally performed in foil thicknesses ~50 nm, where the spatial resolution for X-ray microanalysis (probe size plus beam broadening) was estimated from Monte Carlo simulations to be ~6 nm. The spatial resolution for PEELS should be slightly better (3-4 nm), as a result of the weaker influence of beam broadening. Large-area analyses

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as a function of foil thickness indicated the presence of a thin, Cr-enriched surface oxide, which resulted in slightly elevated Cr levels. Repeated measurements for similar large-area regions gave standard deviations of 0.5-0.8 wt% Cr for EDS and ~1 wt% Cr for PEELS.

RESULTS

Unirradiated Alloy X-750 Control Material

Typical microstructure of the unirradiated X-750, including fine (~20 nm) intragranular γ' precipitates along with several intergranular phases is shown in Figures 1 and 2 (Table 2 gives the measured compositions for these phases). Two forms of intergranular precipitation were observed with roughly equal frequency; some grain boundaries exhibited $M_{23}C_6$ and γ' precipitates (e.g., Fig. 1), whereas others exhibited $M_{23}C_6$ and a mixed precipitate containing both $M_{23}C_6$ and τ $M_{23}B_6$ boride (Fig. 2). This precipitate had overall electron diffraction patterns consistent with the $M_{23}C_6$ structure. Some regions exhibited a composition (>85 Cr, ~3 Fe, ~7 Ni) consistent with $M_{23}C_6$, whereas other regions exhibited a distinctly different composition (~7 Ti, ~2 Fe, ~2 Cr, ~2 Nb, and >80 Ni). Convergent beam electron diffraction indicated that the Cr-rich and Ni-rich regions exhibited very similar, parallel-oriented diffraction patterns. Both regions of the mixed precipitate were oriented parallel to one of the adjacent grains in a cube-on-cube relation, similar to that observed for $M_{23}C_6$ precipitates.

PEELS light element analysis indicated that the chromium-rich phase contains carbon with little or no boron; whereas the nickel-enriched phase contains boron with little or no carbon. This analysis identified the Ni,Ti-enriched phase as the τ boride ($M_{23}B_6$) which is isostructural with $M_{23}C_6$. This observation agrees with a similar report by Kruger et al. [4] of the formation of τ boride in close association with a non-boron-containing carbide (M_7C_3) in Ni-16 Cr-9 Fe-C-B heats. The formation

Fig. 1 Grain boundary in control material exhibiting an essentially continuous precipitate layer of predominantly $M_{23}C_6$ (C) with some γ' interspersed (arrowed).

Fig. 2 Grain boundary in control material exhibiting mixed particles of $M_{23}C_6$ carbide and τ ($M_{23}B_6$) boride. Defocused image (inset) permits differentiation of $M_{23}C_6$ (smooth contrast, arrowed) and $M_{23}B_6$ (mottled contrast).

of these mixed-phase particles is probably linked through cooperative growth of the two precipitates, as one precipitate accepts elements which the other rejects (i.e., Cr and C versus Ni, Ti, and B). As a result of the close structural similarity, the τ boride forms cube-on-cube with the $M_{23}C_6$ and appears as a single, homogeneous precipitate under most diffracting conditions. However, slight defocussing of the image permits the different regions to be visualized in the TEM mode (inset in Fig. 2), where the τ phase appears mottled and the $M_{23}C_6$ phase exhibits more uniform contrast.

Though $M_{23}C_6$ was the dominant intergranular phase in the unirradiated material, the volume fraction of the τ boride phase was estimated to be no more than 10-20% of that for $M_{23}C_6$ precipitates, based on the frequency of $M_{23}C_6/M_{23}B_6$ precipitates and the relative proportion of $M_{23}B_6$ in the mixed precipitates. In general, the grain boundaries decorated with either $M_{23}C_6$ or mixed $M_{23}C_6/M_{23}B_6$ precipitates were wavy, because of the preferential growth of the precipitates into the non-cube-on-cube oriented grain.

Twenty-six composition profiles were measured at grain and phase boundaries in the unirradiated X-750 material to identify pre-existing elemental distributions possibly associated with intergranular precipitation. In addition, both EDS and PEELS were performed to identify possible segregation of impurity elements (e.g., B, N, Si, P, S) to various interfaces/boundaries. No boron (or sulfur) was detected at precipitate-free grain boundaries or interphase boundaries in the unirradiated material, except for τ borides. Composition measurements near an unmixed $M_{23}C_6$ precipitate are summarized in Fig. 3. There were wide variations for multiple measurements made at the same distance from the phase boundary (PB), but at different positions parallel to the boundary. Measurements were grouped on the basis of low (solid curves) or high (dotted curves) Ti levels. High Ti levels generally coincided with high Al and Nb levels and low Cr and Fe levels. Possibly the high-Ti regions contain γ' phase, as $M_{23}B_6$ does not incorporate Al. The high-Ti curves exhibit a region near the boundary enriched in Ti, Nb, (and Al) and depleted in Cr and Fe. However, the low-Ti curves do not exhibit such a region. If the low-Ti curves represent the actual γ composition, then there is little depletion of Cr or Fe within 20 nm of the boundary. Similar results were measured using PEELS.

Beam broadening and the incident probe size result in biasing of the apparent matrix composition near a phase boundary toward that of the adjacent phase. This explains the increased chromium levels near (≤ 10 nm) $M_{23}C_6$ precipitates. Any chromium depletion closer to the boundary would tend to be masked by this effect. Therefore, $M_{23}C_6$ interphase boundaries are especially poor locations to quantify localized RIS effects on chromium; whereas τ boride and γ' phase interfaces are poor locations to quantify titanium RIS effects. However, these boundaries can be utilized to detect RIS effects of elements which do not change by large amounts between the adjacent phases. Precipitate-free sections of grain boundaries between the large intergranular phases provide the best location for measuring RIS of both major and minor elements in the X-750 material.

Figure 4 is a composition profile measured by PEELS at a section of grain boundary (GB) which appeared free of precipitates. The γ matrix compositions are relatively constant to within ~ 10 nm of the boundary. Depletion of Cr to ~ 7 wt% and enrichment of Ti to ~ 6 wt% occur at the boundary. X-ray microanalysis at a similar, apparently precipitate-free, grain boundary segment indicated similar depletion of Cr and Fe and enrichment of Nb, Al, and Ti. This enrichment may indicate the unobserved presence of a thin precipitate enriched in these three elements (i.e., γ' phase). If either τ boride or γ' phase are present, each excess atom of titanium detected in such a case is associated with approximately 9 excess nickel atoms. It is more this large excess of nickel in the absence of chromium and iron, rather than the excess titanium and niobium, that results in decreased chromium and iron levels. In order to select precipitate-free matrix measurements, a maximum 1 wt% Ti level is used as a cutoff criterion. Table 2 gives the average chromium level measured at all boundaries and at non- $M_{23}C_6$ interfaces that met the 1 wt% Ti criterion.

X-ray microanalysis of several grain and interphase boundaries indicated a correlation of Ti and Nb enrichment with a slight (< 1 wt%), but consistent segregation of phosphorus. The phosphorus was associated with the boundary layer and measurements at ± 5 nm did not exhibit any higher P level than non-GB points. No statistically significant enrichment of P was detected for boundaries with low (< 2 wt%) Ti levels. For boundaries exhibiting phosphorus segregation, the average phosphorus excess

Fig. 3 Composition profile measured by EDS at the interface of an intergranular $M_{23}C_6$ precipitate in the control material.

Fig. 4 Composition profile measured by PEELS at a grain boundary (GB) in the control material which locally appeared free of precipitates.

Table 2 Average Chromium Levels at Boundary [wt% (number of profiles)]

	Unirradiated (≤ 1 wt% Ti)		Irradiated (≤ 1 wt% Ti)	
	All	Non	All	Non
EDS	13.0 (4)	13.3 (3)	11.0 (7)	11.0 (7)
PEELS	15.5 (7)	15.8 (4)	13.0 (29)	11.5 (16)

(i.e., above apparent matrix levels) $\delta \sim 0.3$ wt%, slightly above the detection limit. It is possible that the phosphorus is associated with equilibrium segregation, as has been observed in stainless steels [5]. A second possible explanation is a co-segregation of Ti and P to the Ti-enriched phase(s) that form at many grain boundaries and interfaces. Of all the boundaries examined in the unirradiated X-750 material, only one exhibited excess silicon ($\delta \sim 0.2$ wt%).

As enrichment of Ti and Nb was detected at a number of grain and interphase boundaries, all PEELS spectra were analyzed for the presence of nitrogen. Only one boundary was found that indicated detectable levels of nitrogen. Nitrogen levels of ~ 1.3 wt% (~ 5 at.%) were exhibited within 5 nm of the boundary, an extent similar to the region enriched in Ti and Nb. The presence of a thin, stoichiometric TiN precipitate at the boundary would account for all the titanium detected. Bajaj et al. [2] reported a low number density of large, film-like platelets (2 μm diameter and < 1 nm thick) enriched in Ti and Nb at interfaces in extraction replicas of the same unirradiated X-750 material. Based on electron diffraction, they concluded that these precipitates were nitrides or carbonitrides.

Irradiated Alloy X-750 Material

No major change in the precipitate microstructure was apparent after neutron irradiation. Both faulted dislocation loops (5-25 nm diameter) and isolated cavities (1.5-8 nm diameter) were present. There was no significant association of the observed cavities with grain or interphase boundaries. It has been shown previously that the dislocation loops are present only in matrix γ' precipitates and result in internal antiphase boundaries [2]. No boron was detected, except at τ borides. In addition, no sulfur segregation was observed at grain or phase boundaries.

An EDS composition profile across a τ boride/matrix interface is shown in Fig. 5. The presence of boron, as well as the absence of carbon and nitrogen, in the precipitate was confirmed by

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Fig. 5 Composition profile measured by EDS at a τ $M_{23}B_6$ /matrix interface in the irradiated material.

Fig. 6 Composition profile measured via PEELS at a grain boundary (GB) in the irradiated material, which locally appeared free of precipitates.

subsequent PEELS. Near the interface, low Cr and Fe levels and elevated levels of Ni, Ti, and Nb are observed as a result of excitation of the τ boride. Using the ≤ 1 wt% Ti cutoff for γ -only measurements, a chromium depletion to 12 wt% was indicated for this interface, slightly lower than the average value (13.3 wt%) for non- $M_{23}C_6$ boundaries in the unirradiated material. Slight segregation of silicon ($\delta \sim 0.4$ wt%, δ is excess above matrix levels) and phosphorus ($\delta \sim 0.4$ wt%) were observed at this interface, as well as at others boundaries. These excess values are near, but greater than the detection limits for Si and P.

There were three basic classes of apparently precipitate-free grain boundary segments observed in the irradiated material; those exhibiting high levels of Ti, Nb, and N near the boundary, those exhibiting high levels of Ti and Nb (as in Fig. 4 above), and those exhibiting little enrichment of Ti and Nb. The first class was attributed to the presence of film-like titanium nitrides at various boundaries, as discussed above. Nitrogen was not detected at $M_{23}C_6$ interfaces, although it was detected at some τ boride interfaces. The second boundary class was attributed to the presence of either thin γ' or τ boride at the boundary. X-ray microanalysis of some Ti+Nb-enriched boundaries also indicated slight (<0.5 wt%) phosphorus co-enrichment, though without PEELS data the boundaries could not be assigned to class 1 or 2. An PEELS composition profile at grain boundary segment from the third class is shown in Figure 6. Depletion of Cr and Fe to 9 and 7 wt%, respectively, and enrichment of Ni to 83 wt% were exhibited. Ti levels were 1-2 wt% with no maximum at the boundary. The average Cr concentration for 16 PEELS profiles at non- $M_{23}C_6$ interfaces in the irradiated material was 11.5 wt%, significantly greater depletion than for the unirradiated material (15.8 wt%). Table 2 gives average chromium levels from EDS and PEELS for both all boundaries and for only non- $M_{23}C_6$ interfaces. The difference in minimum chromium level at non- $M_{23}C_6$ interfaces between the control and the irradiated materials as measured by PEELS is 4.3 wt%, larger than that measured by EDS (2.3 wt%). This difference may in part reflect the better spatial resolution of PEELS because of the reduced influence of beam broadening.

CONCLUSIONS

The current AEM investigation of both unirradiated and irradiated X-750 materials has led to a number of major conclusions. In addition to matrix γ' and intergranular γ' and $M_{23}C_6$, a third intergranular τ boride ($M_{23}B_6$), isostructural with $M_{23}C_6$ and enriched in boron, was identified in mixed $M_{23}C_6/M_{23}B_6$ precipitates. There was also evidence for the presence of interfacial TiN at both grain boundaries and τ boride interfaces. A defocused imaging technique was found that

distinguished the τ boride from $M_{23}C_6$. The copious intergranular precipitation, especially of $M_{23}C_6$, made the measurement of localized composition changes quite challenging. However, a slight degree of chromium depletion was observed both at grain and interphase boundaries in the unirradiated material. Radiation-induced segregation (RIS) produces more pronounced chromium depletion and nickel enrichment in narrow (~ 10 nm) zones at the same boundary types in the irradiated material. The utilization of a 1 wt% Ti cutoff limit was required to reproducibly measure this segregation as a result of the inability to visually detect the γ' phase and TiN in the analyzed volume. RIS results in a slight enrichment of silicon. However, the observed segregation of phosphorus appears to arise from a pre-existing equilibrium segregation of phosphorus present in the unirradiated material. This segregation may occur as cosegregation with titanium and nitrogen associated with the presence of (Ti,Nb)N in the unirradiated material. However, additional PEELS on extraction replicas from the unirradiated material is needed to confirm this speculation. As a result of beam broadening effects, there is poor sensitivity for measuring the segregation of an element at a phase boundary where the concentration of that element takes a large step change. Therefore, $M_{23}C_6$ interphase boundaries are especially poor locations to quantify segregation of chromium. Similarly, τ boride and γ' phase interfaces are poor locations to quantify titanium segregation effects. No boron was detected in either the unirradiated or irradiated material, except within τ borides.

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