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MEASUREMENT OF EQUILIBRIUM AND NONEQUILIBRIUM SEGREGATION
BY X-RAY MICROANALYSIS*

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ABSTRACT

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X-ray microanalysis in an analytical electron microscope is a proven technique for the measurement of solute segregation in alloys. Solute segregation under equilibrium or nonequilibrium conditions can strongly influence material performance. X-ray microanalysis in an analytical electron microscope provides an alternative technique to measure grain boundary segregation, as well as segregation to other defects not accessible to Auger analysis. The utility of the technique is demonstrated by measurements of equilibrium segregation to boundaries in an antimony containing stainless steel, including the variation of segregation with boundary character and by measurements of nonequilibrium segregation to boundaries and dislocations in an ion-irradiated stainless steel.

INTRODUCTION

Segregation of solute atoms can occur at defects in crystalline materials under both equilibrium and nonequilibrium conditions and can result in degradation of the physical, chemical, and mechanical properties. Temper embrittlement in ferritic alloys is associated with the segregation of arsenic, phosphorus, etc., to grain boundaries. Sensitization of austenitic stainless steels is related to chromium depletion at grain boundaries associated with the precipitation of chromium carbides. Though Auger spectroscopy is often employed to study such segregation, some alloys cannot be fractured intergranularly in situ and thus cannot be studied in this fashion. X-ray microanalysis in an analytical electron microscope (AEM) provides an alternative technique to measure grain boundary segregation in such cases, as well as segregation to other defects not accessible to Auger analysis. X-ray microanalysis in an AEM has been shown to be a powerful technique for the measurement of solute segregation in alloys [1-4]. In addition, the complementary information available from AEM allows the characterization of both the defects and the segregation.

The high-temperature creep deformation of a 16 at. % Cr, 14 at. % Ni stainless steel with and without ~0.4 at. % Sb added has been studied [5]. The antimony results in a threefold decrease in the elongation-to-fracture and a threefold increase in the density of intergranular cracks formed during creep deformation compared to the antimony-free material. Whereas antimony segregation to boundaries was suspected for the degradation in mechanical properties, Auger spectroscopy could not be applied as the material could not be fractured intergranularly in situ. The degree of segregation was measured by x-ray microanalysis in an AEM and related to the boundary character. From such correlations, a more basic understanding of segregation and grain boundary embrittlement will develop.

The radiation response of metallic alloys is strongly dependent on specific solute elements. Void swelling, embrittlement, and phase instability

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limit materials performance in nuclear reactors. A modified type 316 stainless steel, LS1A, which exhibits high resistance to swelling under ion irradiation, has been developed. The high fluxes of irradiation-produced point defects can induce fluxes of specific solute atoms toward or away from point defect sinks, such as dislocations, voids, and grain boundaries [6]. As radiation-induced segregation (RIS) continues, sufficient solute concentrations can develop locally to exceed the matrix solubility limit. Subsequent phase instability of the matrix results in precipitate formation. Detailed measurements of the solute profiles near grain boundaries, dislocations, and stacking faults will add to our understanding of the operative mechanisms for radiation-induced segregation and phase instability.

EXPERIMENTAL

Table I gives the composition of the two stainless steels studied: SS-Sb, the antimony-containing steel, and LS1A, the modified type 316 steel. The SS-Sb was solution annealed at 1000°C for 1 h, whereas the LS1A was solution annealed at 1050°C for 1 h. The SS-Sb material was aged at temperatures from 500 to 827°C for times up to 100 days. The LS1A was irradiated in the solution-annealed state with 4 MeV Ni ions at temperatures from 525 to 725°C to doses <600 dpa (displacements per atom), as part of a larger study [7].

Table I. Alloy Composition (at. %)

	Fe	Cr	Ni	Si	Mn	Sb	Mo	Ti	C
SS-Sb	68.12	16.06	14.22	0.79	0.20	0.46	--	0.03	0.12
LS1A	63.85	17.41	12.88	2.07	2.06	--	0.99	0.17	0.37

Analyses were performed in a Philips EM400T equipped with a high brightness field-emission source and a 6585 STEM unit, an EDAX 9100/70 system, and a Gatan double-tilt beryllium cooling holder. X-ray microanalysis was performed in the STEM mode, for which measured probe sizes of 1–2 nm were achieved. Measurements were performed at –185°C to minimize contamination. Strong, low-order diffracting conditions and zone-axis orientations were avoided to minimize the complicating effects of channeling and coherent bremsstrahlung peaks. Measured peak intensities were corrected for silicon escape peaks ($\text{CrK}_\alpha/\text{SiK}_\alpha/\text{SbL}_\alpha$), overlap peaks ($\text{Mn}/\text{K}_\alpha/\text{CrK}_\beta$), and the "hole count" spectrum [8]. Compositions are quoted in atomic percent for elements with atomic number $Z > 11$.

The use of the cooling holder resulted in an increased specimen drift rate relative to the room-temperature stage, thus degrading the spatial resolution attainable by the technique. The probe could be maintained on boundaries with relative ease by monitoring the intensities of two reflections in the diffraction pattern, one from each grain. Performing analyses away from the grain boundary or on other defects required frequent interruptions for repositioning of the probe. In regions where the composition was changing rapidly with distance, the specimen drift resulted in larger fluctuations in apparent composition than observed at grain boundaries or in regions where composition was reasonably constant.

RESULTS

Equilibrium Segregation in SS-Sb

Figure 1 illustrates typical energy dispersive x-ray spectroscopy (EDXS) measurements near a high-angle grain boundary [Fig. 1(a)] in a SS-Sb specimen aged five days at 827°C. Comparing the matrix spectrum [Fig. 1(b)] to that with the probe (~2 nm diameter) on the grain boundary [Fig. 1(c)], there is

Fig. 1(a). High-angle boundary in SS-Sb specimen aged for five days at 827°C. Similar thickness regions of EDXS analyses (~ 2 nm probe) indicated. (b) EDXS spectrum in matrix. (c) EDXS spectrum on the grain boundary. Spectra are scaled to give equal height FeK_{α} peaks.

a twofold increase in the apparent antimony level at the boundary. Table II gives the apparent compositions (averaged over the excited volume) of the matrix and the grain boundary. At 827°C, the results indicate segregation of antimony to and depletion of iron from the boundary. The average of repeated analyses is given along with the standard deviation.

TABLE II. Apparent EDXS Compositions

	Average Composition $\pm$ Standard Deviation, at. %					
	5 days, 827°C		99 days, 500°C			
	Matrix	Grain Boundary	Matrix	Grain Boundary	Twin Coherent	Twin Incoherent
Sb	0.34 ± 0.03	0.67 ± 0.03	0.40 ± 0.02	1.26 ± 0.03	0.37 ± 0.03	0.78 ± 0.02
Cr	17.40 ± 0.12	17.81 ± 0.17	18.02 ± 0.21	12.07 ± 1.06	17.40 ± 0.18	16.88 ± 0.21
Fe	68.32 ± 0.12	67.40 ± 0.25	67.64 ± 0.36	67.61 ± 0.10	68.88 ± 0.10	67.04 ± 0.45
Ni	13.94 ± 0.14	14.12 ± 0.19	13.94 ± 0.18	19.06 ± 0.96	13.35 ± 0.15	15.30 ± 0.22

Auger spectroscopy has shown that boundary segregation obeys the McLean's isotherm, which indicates that boundary enrichment increases as aging temperature decreases. However, no segregation was detected by EDXS for a specimen aged 12 days at 500°C. Auger spectroscopy on nickel-antimony binary alloys indicates that boundary composition reaches its maximum value after short aging times (< 1 day). Figure 2 indicates the reason EDXS may be unable to detect such increased segregation. At short aging times, the matrix adjacent to the grain boundary is depleted of solute atoms as they segregate to the boundary [Fig. 2(a)]. The width of the depleted zone is determined by the solute diffusivity and the aging time. If the excited volume is larger than the depleted zone, no segregation will be detected. With longer aging, the magnitude of the matrix depletion is reduced and the zone width increases, as solute atoms diffuse from the grain interiors to eliminate the diffusion profile in the matrix. To test this hypothesis, a specimen was annealed for 99 days at 500°C and checked for boundary segregation, which was observed. Table II gives the apparent compositions for the matrix and a high-angle boundary and indicates a threefold increase in antimony, an associated nickel segregation and chromium depletion at the boundary. The chromium depletion may be in response to the antimony-nickel segregation or may be associated with the observed grain boundary precipitation of a chromium-rich phase (probably M_{23}C_6 based on composition and unit cell size). Such chromium depletion has been observed to occur during sensitization of

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Fig. 2(a). Segregation of solute to grain boundary locally depletes matrix. (b) Longer aging allows solute to diffuse from grain interiors to eliminate diffusion gradient.

stainless steels. However, as the density of the chromium-rich precipitates is several orders of magnitude lower than that observed in sensitized steels, it seems likely that the observed chromium depletion is part of the equilibrium segregation.

Figure 3 gives the atomic ratios Ni/Fe and Cr/Fe as a function of distance from a second high-angle boundary in the material aged at 500°C for 99 days. Each data point represents a 10-s (1.7 nm) portion of an analog (continuous scan) line-scan across the boundary with a ~1.5-nm-diam probe. The high Ni/Fe points and low Cr/Fe points are located adjacent to the boundary and deviate by more than 4σ (standard deviation) from the average matrix composition. The point-to-point scatter of the matrix composition in this line-scan is that which would be expected on the basis of counting statistics. The width (FWHM) of the segregant profile at the grain boundary was estimated as 3.5 to 5 nm. The profile of a narrow segregant layer (1-2 interatomic spacings wide) would be broadened by several experimental factors: a finite probe size (~1.5 nm diameter), the distance moved by the probe during one channel of the scan (~1.7 nm), the projected width of the slightly tilted boundary

Fig. 3(a). High-angle grain boundary in SS-Sb aged 99 days at 500°C. (b) Ni/Fe, Cr/Fe atomic ratios as function of distance for line scan across boundary with ~1.5-nm-diam probe. High-nickel (low-chromium) points straddle the position of the boundary.

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(~1.2 nm), and specimen drift. From the relative size of the measured profile, it seems likely that the segregant layer is very thin (0.1–1 nm).

Table II also gives the apparent composition measured for coherent and incoherent twin boundaries in the material aged at 500°C for 99 days. The coherent twins show no significant segregation, whereas the incoherent twin boundaries show some intermediate degree of segregation. Although repeated measurements on a given boundary gave reproducible results, measurements on different boundaries gave wider variation in segregation. This variation is taken to reflect actual variation in segregation behavior as a function of boundary structure. Studies are in progress to further examine the relation between boundary character and degree of segregation.

Radiation-Induced Segregation in LS1A

An earlier study of radiation-induced segregation in ion-irradiated stainless steel has shown segregation of silicon and nickel to faulted dislocation loops [3]. However, as a result of the large probe size for AEM available at that time, the fine-scale structure of the segregation profile could not be distinguished. With the advent of higher resolution AEMs, the radiation-induced segregation in LS1A was again investigated. Figure 4 shows the solute profiles measured at a high-angle grain boundary in material irradiated to 1 dpa at 675°C. Silicon and nickel (undersized solutes) segregate strongly to the grain boundary [Fig. 4(b)], while chromium and iron (oversized solutes) are depleted at the boundary [Fig. 4(c)]. In addition, molybdenum and manganese (oversized solutes) are depleted at the boundary. The error bars plotted in Fig. 4 represent the scatter between repeated analyses. The larger bars in the region where composition is strongly dependent upon distance are the result of specimen drift, as mentioned earlier. The width of the segregation profile is significantly larger than that for the equilibrium segregation in SS-Sb and much larger than the probe size (~1.5 nm). As such, the measured profile is a good representation of the radiation-induced segregation profile. The width of the profile varies for the different solutes.

Fig. 4(a). High-angle grain boundary in LS1A ion-irradiated to 1 dpa at 675°C. Arrows indicate position of line scan. (b) Silicon and nickel profiles. (c) Iron and chromium profiles. Error bars indicate standard deviation for multiple analyses. Arrowed bars at right of graphs indicate error based on counting statistics.

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An additional feature is the presence of a local minimum or maximum in the solute profile at a finite distance from the grain boundary as atoms rejected from the boundary region pile up. This behavior is most clearly exhibited by iron, where the local maximum occurs at ~ 20 nm, but is also evident for chromium and silicon. This local extrema point arises because the segregation process can only affect the composition out to a distance related to $(D_i t)^{1/2}$, where D_i is the diffusivity of the i -th species and t is time. Iron, being the slowest diffusing species in stainless steel, exhibits the closest extrema point (~ 20 nm). On the other hand, chromium, being $\sim 3\times$ faster diffusing, shows a smaller maximum at ~ 50 nm.

Figure 5 illustrates the radiation-induced segregation near a faulted, Frank loop formed by ion irradiation at 675°C to 1 dpa. The EDXS measurements were taken with the loop oriented edge-on. Figure 5(a) shows the loop tilted away from that orientation to illustrate several features: the loop is faulted and extends through the foil thickness; the dislocation segments remain at the inclined edges of the fault; and there is a localized thinning of the foil near the loop. Silicon and nickel segregate to the fault plane [Fig. 5(b)], while chromium and iron (and manganese and molybdenum) are depleted at the fault plane [Fig. 5(c)]. The profiles are all asymmetric, with solute enrichment (or depletion) extending further to the right from the fault plane than to the left. The region is somewhat wedgy, with the left-most point (~ 107 nm) in Fig. 5 being ~ 15 nm thick and the right-most point ($+107$ nm) being ~ 45 nm thick. This asymmetry does not arise from increased beam broadening or a surface film effect. The asymmetry may reflect the fact that the foil, in effect, samples different parts of the complex, three-dimensional segregation profile at the loop. In addition, the width of the iron-depleted region is narrower than the segregation profiles for silicon,

Fig. 5(a). Weak-beam dark-field image of near edge-on faulted dislocation loop in LS1A ion-irradiated to 1 dpa at 675°C . Arrowed line indicates position of line scan. (b) Silicon and nickel segregation to dislocation loop. (c) Iron and chromium depletion at dislocation loop. Error bars indicate standard deviation of multiple analyses. Arrowed bars near maxima (or minima) indicate error based on counting statistics.

nickel, and chromium. This behavior is consistent with iron being the slowest diffusing species.

The measured compositions at the bounding partial dislocations were similar to those measured on the center of the fault, possibly indicating little or no segregation at the dislocations. However, as the partial dislocations were not parallel to the electron beam, the excited volume sampled a very heterogeneous region, including dislocation, segregated fault, and possibly depleted matrix. Measurements made ~13 and ~27 nm outside the dislocation loop on the plane of the loop indicated that no segregation had occurred in that region.

In order to address the question of segregation to the bounding partial dislocation of a faulted loop, EDXS point analyses were performed in the vicinity of nearly face-on Frank loops (Fig. 6). The [111] normal to the fault plane was ~10° from the beam direction. Figure 6 gives, in six schematics of the loop, the atomic percent of Si, Fe, Ni, Mo, Cr, and Mn as a function of position relative to the dislocation loop marked A in the micrograph. Comparing the compositions for the seven positions running vertically, Si and Ni exhibit local maxima on the fault ~10 nm inside the dislocation; Cr, Fe, and Mn exhibit local minima at the same position, while Mo exhibits a minimum at the partial dislocation. The matrix outside the dislocation loop shows little deviation from the bulk composition. This is true in both the vertical and horizontal directions.

The presence of a maximum (or minimum) in solute content just inside the faulted dislocation loop indicates that the partial dislocation has a higher degree of segregation than the fault. If there were no additional solute segregation at the dislocation line, the apparent composition would change from that characteristic of the bulk to that characteristic of the fault region. The apparent composition at the dislocation would be intermediate, as roughly equal volumes of segregated and "bulk" matrix would be excited. However, if there were additional segregation at the dislocation, local

Fig. 6(a). Nearly face-on faulted loop in LSIA ion-irradiated to 1 dpa at 675°C. (b)-(g) Schematic representation of solute concentration (atomic percent) in vicinity of Loop A for Si, Fe, Ni, Mo, Cr, and Mn, respectively.

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maxima for silicon and nickel (or local minima for the other solutes) would occur just inside the dislocation loop, as has been observed. The exact position of the extrema values depends on the diameter of the excited volume at the dislocation line, which in turn depends on the incident probe and beam broadening. Loop A in Fig. 6 was in a foil ~100 nm thick. In a second analysis in a 20-nm-thick region, the maximum segregation occurred within 5 nm of the partial dislocation. Quantification of the level of segregation at both the fault and the dislocation will require some detailed Monte Carlo simulations for the complex three-dimensional segregation field.

The radiation-induced segregation at dislocation loops appears to be the driving force for the phase instability of the matrix. The second phases which form, G and η (eta), are enriched silicon and nickel and have fcc Bravais lattices with large lattice parameters $a_0 \approx 1.1$ nm. G phase is a silicide analogous to $M_{23}C_6$ containing primarily silicon and nickel, whereas η phase is a carbide, rich in Si, Cr, Ni, and Mo. As the phase instability progresses, silicon and nickel are preferentially depleted from the matrix. As these elements are critical to swelling resistance and the precipitates act as heterogeneous nucleation sites for cavities, the swelling resistance is reduced.

CONCLUSIONS

It has been shown that x-ray microanalysis in an analytical microscope (AEM) is a powerful technique for segregation studies. Both equilibrium and nonequilibrium segregation processes can be studied, even for alloys or boundaries as defects not amenable to more conventional techniques. In addition, the associated AEM techniques provide supplemental microstructural or defect characterization. For antimony segregation in stainless steel, these studies indicate: (1) Co-segregation of antimony and nickel to boundaries and chromium depletion. (2) The segregation width is narrow. (3) The segregation depends on boundary character. For the radiation-induced segregation in LS1A, these studies indicate: (1) Undersized solute atoms segregate to defect sinks; oversized solutes are depleted at sinks. (2) Relative diffusivity of solutes is reflected in profiles. (3) Segregation is confined to the region of fault. (4) Highest levels of segregation occur at dislocations.

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REFERENCES

- [1] C. S. Pande, M. Suenaga, B. Vyas, H. S. Isaacs, and D. F. Harlings, *Scripta Met.* 11, 681 (1977).
- [2] E. L. Hall and C. L. Briant, *Met. Trans.* 15A, 793 (1984).
- [3] E. A. Kenik, *Scripta Met.* 10, 733 (1976).
- [4] J. R. Michael and D. B. Williams, *Met. Trans.* 15A, 99 (1984).
- [5] J. H. Schneibel, C. L. White, G. F. Peterson, and R. A. Padgett, *New Developments in Stainless Steel Technology*, p. 61, ed., R. A. Lula, ASM, Metals Park, OH (1985).
- [6] Reviewed in *J. Nucl. Mater.* 83, 1-237 (1979).
- [7] E. A. Kenik, *J. Nucl. Mater.* 85&86, 659 (1979).
- [8] J. Bentley, N. J. Zaluzec, E. A. Kenik, and R. W. Carpenter, *Scanning Electron Microscopy/1979*, II, p. 581, SEM, Inc., AMF O'Hare, IL 60666, (1979).

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