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A multi-technique investigation of sulfur grain boundary segregation in nickel

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The grain boundary segregation (GBS) of sulfur in nickel was studied using Auger electron spectroscopy (AES) and wavelength-dispersive X-ray spectroscopy (WDS), and a linear correlation between the two techniques was demonstrated. The kinetics and thermodynamic parameters of sulfur GBS were determined. The discrepancy between the AES/WDS results obtained here and those from a previous study on the same material undertaken using secondary ion mass spectroscopy was interpreted in terms of the selection of grain boundary type by the sample preparation method.

Keywords: Interface segregation; Auger; WDS; EPMA; SIMS

The detrimental effect of sulfur grain boundary segregation (GBS) on the mechanical properties of nickel and nickel alloys has been documented in several experimental studies [1,2]. The temperature dependence of equilibrium solute GBS obeys the well-known Langmuir–McLean equation [3]:

$$\frac{X}{X_{Max}-X}=\frac{C_V}{1-C_V}\exp\left(-\frac{\Delta G}{RT}\right), \tag{1}$$

where X is the solute grain boundary (GB) concentration, X_{Max} is the solute grain boundary concentration at saturation, C_V is the bulk solute concentration, ΔG is the grain boundary segregation free energy (J mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) and T is the temperature (K). In Eq. (1), X can be expressed as a fraction of a monolayer or as a mass (or a number of atoms) of solute per unit grain boundary area. Only two experimental studies have been dedicated to the determination of the thermodynamic parameters (ΔG and X_{Max}) of sulfur GBS [4,5]. However, the values published in these studies must be considered with caution. The reliability of the ΔG value proposed by Larère et al. [4] can be seriously questioned since it was obtained "by supposing that at 700 °C, the maximum equilibrium segregation is at least 95% of the saturation value". However, no measurement of sulfur GBS supporting that assumption is presented in that work. Mulford et al. [5] have determined $\Delta G = 72.8$ kJ mol^{-1} from Auger measurements undertaken on specimens equilibrated at several different temperatures in the range 500–900 °C. However, they used nickel containing a bulk concentration of sulfur $C_V = 75$ at. ppm, which is very likely to be above the limit of solubility, at least in the temperature range 500–700 °C [6]. This means that the term C_V is not accurately known in that study.

The kinetics of GBS during isothermal annealing obeys the McLean kinetic equation [3]:

$$X = X_0 + \frac{4C_V\sqrt{Dt}}{\sqrt{\pi}}, \tag{2}$$

where X_0 is the solute grain boundary concentration before the annealing treatment to induce segregation, D is the solute bulk diffusion coefficient (cm^2 s^{-1}) at the annealing temperature and t is the annealing time. In Eq. (2), the bulk solute concentration, C_V, is expressed in cm^{-3} or g cm^{-3} (number of atoms or mass of solute per unit volume) and the GB concentration, X, is in cm^{-2} or g cm^{-2}. The sulfur bulk diffusion coefficient has been determined by Vladimirov et al. [7] using a radiotracer depth profiling technique on Ni crystals in the temperature range 800–1200 °C.

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For the last 50 years, Auger electron spectroscopy (AES) has been the most widely used technique for the quantification of GBS [8,9]. The analysis is undertaken on an intergranular fracture surface, and since AES is highly sensitive to surface contamination, the specimen has to be fractured in situ, i.e. inside the ultrahigh-vacuum (UHV) chamber of the spectrometer. GBS measured using AES is expressed as a fraction of a monolayer [8,9]. Over the last five years, new experimental techniques have been proposed for the quantitative analysis of GBS. Nowakowski et al. [10] have demonstrated the possibility of quantitative determination of GBS using wavelength-dispersive X-ray spectroscopy (WDS) in a scanning electron microscope (SEM). Like AES, WDS analysis is undertaken on an intergranular fracture surface. However, in contrast to AES, the specimen can be fractured ex situ, as it has been shown that WDS is practically insensitive to surface contamination. The WDS technique is, however, limited to systems with very low solute concentrations in the bulk. GBS as measured using WDS is expressed as a mass (or a number of atoms) of solute per unit surface in the grain boundary.

The possibility of quantitative determination of GBS by secondary ion mass spectroscopy (SIMS) using a NanoSIMS system has also been recently demonstrated by Christien et al. [11,12]. The NanoSIMS ion microprobe uses a highly focused (~50 nm) Cs^+ primary ion beam and a high-resolution magnetic sector mass spectrometer. The analysis of GBS using NanoSIMS is undertaken on a polished cross-section of bulk material, in contrast to AES and WDS where the analysis is done on a fracture surface. This is a major advantage as it allows the analysis of all the grain boundaries that intersect the polished surface, not only those that can be fractured as is the case for AES and WDS. As the lateral resolution of NanoSIMS is far above the GB width, the beam broadening effect is taken into account in the quantification procedure [11,12]. As for WDS, GBS measured using NanoSIMS is expressed as a mass (or a number of atoms) of solute per unit area of grain boundary.

The objective of this paper is the determination of the kinetics and thermodynamics of sulfur GBS using AES and WDS. A comparison with the data obtained in previous studies [11,12] using NanoSIMS on the same material is then presented.

The material used in this study is ultrahigh-purity nickel from Aperam. A 6 kg cast was prepared with controlled additions of sulfur. A sulfur bulk concentration of 5.4 wt. ppm was measured using glow discharge mass spectroscopy. The material was provided as 3 mm thick plates, annealed at 900 °C. The average grain size was 260 μm.

AES measurements were undertaken using a MAC2 cylindrical spectrometer from Riber. Each specimen analyzed was first fractured at approximately −120 °C using a tensile apparatus inside the UHV preparation chamber (~5×10^{-10} mbar) of the spectrometer. One half of the broken specimen was then transferred to the analysis chamber (~10^{-9} mbar). About 30 GB facets were analyzed for each specimen. Sulfur was the only segregated element detected at grain boundaries. Sulfur GBS is quantified using the Seah equation [8]:

$$X = \frac{1}{1-\exp\left(-\frac{a}{\lambda\cos\beta}\right)} \frac{\frac{H_S}{S_S}}{\frac{H_S}{S_S}+\frac{H_{Ni}}{S_{Ni}}}, \tag{3}$$

where X is the sulfur GB concentration expressed as a fraction of a monolayer, λ is the sulfur Auger electron attenuation length, a is the thickness of the segregation layer ($\lambda \approx 2a$ in our case [13]), β is the average emission angle ($\beta = 45°$ in our case), H_S and H_{Ni} are the sulfur and nickel peak heights measured on the derivative spectrum at 152 and 848 eV, respectively, and S_S and S_{Ni} are the sulfur and nickel sensitivity factors, respectively. Following the approach described in Ref. [14], S_S and S_{Ni} have been measured on our spectrometer using FeS_2 and FeNi 36% (Invar) standard materials, respectively, giving $S_S = 13.76$ and $S_{Ni} = 1.53$. The standard deviation of the sulfur concentration measured on different GB facets of the same specimen was about 35% of the mean value. There are several possible contributions to this significant variation. The first is that the sulfur equilibrium GB concentration depends on the grain boundary character and is consequently different from one grain boundary to another. The second possible contribution is the fact the sulfur is split randomly (not equally) on both sides of the fracture surface. Furthermore, it has been demonstrated in Ref. [15] that another very important contribution is the variation of the emission angle from one GB facet to another (at least in the spectrometer used in this study), which was not taken into account for each individual GB facet. Even with these experimental perturbations, the overall sulfur GBS in the specimen can be determined accurately by replicating the analysis on a large number of GB facets (here, about 30 for each specimen) and calculating the average value. Using this methodology, the statistical uncertainty (repeatability) on the overall sulfur GBS measured in one particular specimen using AES is reduced to less than 10%, which corresponds to a maximum inaccuracy of a few per cent of a monolayer.

WDS measurements were undertaken using an Inca Wave spectrometer from Oxford Instruments in a high beam current Merlin SEM from Carl Zeiss. Each specimen to be analyzed was fractured ex situ on a conventional tensile machine in a liquid nitrogen container. One half of the broken specimen was then transferred into the SEM chamber (~10^{-6} mbar) for WDS analysis. 15 GB facets on average were analyzed for each specimen using a beam voltage of 20 kV and beam currents ranging from 350 to 450 nA. The sulfur GBS was quantified using the following equation [10]:

$$X = 2K\frac{I}{I_{Std}}\cos\theta - X_V, \tag{4}$$

where X is the sulfur GB concentration expressed as a mass of sulfur per unit surface (ng cm^{-2}), K is a constant taking account of the element analyzed (sulfur), the chemical composition of the substrate (pure nickel), the X-ray line chosen for analysis (K_α), the beam voltage used (20 kV) and the composition of the standard material (FeS_2). The determination of K for this system (256100 ng cm^{-2}) is detailed in Ref. [10]. I and I_{Std} (counts s^{-1} nA^{-1}) are the intensities of the sulfur K_α line measured on the grain boundary facets of the specimen