

Ultra-fast sulphur grain boundary segregation during hot deformation of nickel

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Abstract

Sulphur grain boundary segregation during hot-compression of nickel (5.4 wt. ppm S) is monitored using Auger electron spectroscopy and wavelength dispersive X-ray spectroscopy. The deformation conditions (temperature/deformation rate) investigated are: 550 °C/0, 550 °C/3 × 10⁻⁵ s⁻¹, 550 °C/3 × 10⁻⁴ s⁻¹ and 450 °C/3 × 10⁻⁵ s⁻¹. It is shown that plastic deformation accelerates the kinetics of sulphur grain boundary segregation by a factor of ~10³ to a few 10⁵, depending on the deformation conditions. Very high levels of segregation (~0.8 monolayer of sulphur) are obtained after very low deformation (~5%). In addition a linear dependence of the segregation level with time and deformation is demonstrated. The segregation kinetics during plastic deformation is proportional to the deformation rate and almost independent of temperature. Several metallurgical mechanisms are discussed and confronted with the experimental results: dislocations dragging, pipe diffusion, dislocation collection/diffusion and acceleration by excess vacancies. It appears that the models developed in this work on the basis of the two latter mechanisms (dislocation collection/diffusion and acceleration by excess vacancies) predict the experimental data correctly.

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1. Introduction

The detrimental effect of sulphur 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]:

$$\frac{X}{X_{Max} - X} = \frac{X_B}{1 - X_B} \exp\left(-\frac{\Delta G}{RT}\right) \quad (1)$$

where X is the solute grain boundary concentration, X_{Max} is the solute grain boundary concentration at saturation, X_B is the bulk solute concentration, ΔG is the GBS 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. We have recently studied the temperature dependence of equilibrium GBS of sulphur in nickel [4]. Quite unexpectedly, the segregation free energy ΔG was found to be almost independent of temperature: $\Delta G = -93.9$ kJ mol⁻¹. X_{Max} was determined as well in that study. We found: $X_{Max} = 0.97$ monolayer = 65.8 ng cm⁻².

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

$$X = X_0 + \frac{4X_B\sqrt{Dt}}{\sqrt{\pi}} \quad (2)$$

where X_0 is the solute grain boundary concentration in the initial state, D is the solute bulk diffusion coefficient (cm² s⁻¹) at the annealing temperature and t is the annealing time. In Eq. (2), the bulk solute concentration X_B is expressed in cm⁻³ or g cm⁻³ (number of atoms or mass of solute per unit volume) and the grain boundary (GB) concentration,

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X , is in cm^{-2} or g cm^{-2} . The sulphur bulk diffusion coefficient D in nickel has been determined by Allart et al. [4] at 550 °C and 750 °C, in good agreement with the data obtained by Vladimirov et al. [5] from measurements undertaken at higher temperature (800 to 1200 °C).

The validity of Eq. (2) is restricted by the following assumptions: the GBS must be well below its equilibrium level (which corresponds to “short” annealing time); in the initial state, the bulk solute concentration X_B is assumed homogeneous in the material; the solute diffusion coefficient D is assumed to be constant in time and homogeneous in space. In cases where these assumptions are not fulfilled, the time dependence of segregation in the transient regime can be determined from the Darken–du Plessis approach (see Refs. [6,7] for a detailed description) that can be implemented numerically using the finite element or finite difference method. This approach has been successfully tested in various complicated situations of interface segregation [8,9].

This paper deals with sulphur GBS during hot deformation of pure nickel and deliberately focuses on low levels of deformation, so as to avoid dynamic recrystallization. GBS is expected to be accelerated during hot deformation because of the excess defects (dislocations and vacancies). Very few papers in the literature have been dedicated to the investigation of interface segregation during hot deformation, or even during annealing of deformed metals. Segregation of sulphur to the surface of cold-worked nickel annealed at 315 °C has been investigated in Refs. [10,11]. These studies have demonstrated a strong accelerating effect of plastic deformation on the surface segregation kinetics that was accounted for essentially by the fast solute diffusion in the dislocation network. However, the effect of the excess vacancies created by plastic deformation is to be considered as well. Assuming that sulphur is a substitutional solute in nickel (which is very likely considering the high activation energy of sulphur diffusion in nickel, 218.6 kJ mol⁻¹ [5]), its diffusion coefficient is proportional to the vacancy concentration [12]. This argument of accelerated diffusion by excess vacancies in deformed metals has been proposed in several papers dealing with GBS [13,14] or precipitation [15].

This paper focuses on the effect of deformation rate and temperature on the kinetics of sulphur GBS in nickel during hot deformation, before recrystallization. The experimental data obtained from Auger electron spectroscopy (AES) and wavelength dispersive X-ray spectroscopy (WDS) measurements are discussed and modelled on the basis of several possible metallurgical mechanisms.

2. Material and techniques

The material used in this study is ultra-high-purity nickel from Aperam. A 6 kg cast was prepared with controlled additions of sulphur. A sulphur bulk concentration of 5.4 wt. ppm was measured using glow discharge mass spectroscopy (GDMS). The material was provided

as plates 3 mm in thickness, annealed at 900 °C. The average grain size is 260 μm .

Compression specimens (20 × 6 × 3 mm) were cut from the nickel plates. Using a DY26 tensile apparatus from Adamel (MTS), the specimens were compressed along the 6 mm side at temperatures of 450 °C or 550 °C and at deformation rates of $3 \times 10^{-5} \text{ s}^{-1}$ or $3 \times 10^{-4} \text{ s}^{-1}$. The actual deformation ε was determined from $\varepsilon = \ln(h_i/h_f)$. h_i and h_f are the specimen heights before and after compression, respectively. h_i and h_f were measured using a micrometer with an accuracy of 10 μm . The deformation range investigated in this study is a few percent only to avoid dynamic recrystallization during compression. The typical stress needed to reach 5% of deformation is 50 MPa at 550 °C and 150 MPa at 450 °C. After compression, a notched microtensile specimen was cut from each specimen to allow AES or WDS analysis of the grain boundaries.

The kinetics of sulphur GBS during simple annealing at 550 °C (without deformation) was also measured in this work. The specimens were first annealed at 550 °C under high vacuum for different times. Sulphur GBS was then measured by either AES or WDS.

AES measurements were undertaken using a MAC2 cylindrical spectrometer from Riber. Each specimen analysed was first fractured at ~ -120 °C using a tensile apparatus inside the UHV preparation chamber ($\sim 5 \times 10^{-10}$ mbar) of the spectrometer. One half of the broken specimen was then transferred to the analysis chamber ($\sim 10^{-9}$ mbar). About 30 GB facets were analysed for each specimen. Spectra were acquired in the derivative mode from 30 to 900 eV. In any condition tested, sulphur was the only segregated element detected at grain boundaries. For example, Fig. 1 shows the fracture surface of a specimen compressed at 550 °C/ $3 \times 10^{-5} \text{ s}^{-1}$ to a deformation level of 2.5%, as well as a typical AES spectrum from that specimen.

The sulphur GBS quantification was achieved using the Seah equation [16]:

$$X = \frac{2}{1 - \exp\left(-\frac{a}{\lambda \cos \beta}\right)} \frac{\frac{H_S}{S_S}}{\frac{H_S}{S_S} + \frac{H_{Ni}}{S_{Ni}}} \quad (3)$$

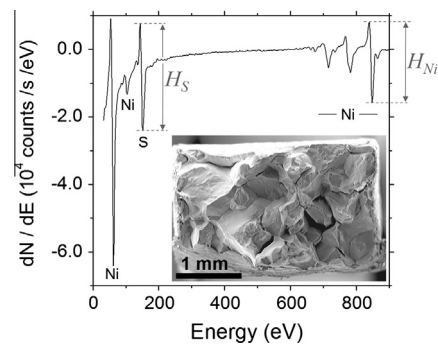


Fig. 1. Typical AES spectrum from a specimen compressed at 550 °C/ $3 \times 10^{-5} \text{ s}^{-1}$ to a deformation level of 2.5%, and corresponding intergranular fracture surface. H_S and H_{Ni} denote the peak heights used for the quantification of grain boundary segregation (see Eq. (3)).

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