

A NEW MODEL FOR THE DETERMINATION OF GRAIN BOUNDARY DIFFUSIVITIES

Reçu le 17/05/2000 - Accepté le 08/12/2001

Abstract

A new model, based on a surface saturation technique, is suggested to determine grain boundary diffusivity of impurities. The model is applied to the Ni-S system that is of great practical interest. The initial saturation of nickel grain boundaries with sulphur is obtained by annealing at a temperature which satisfies the thermodynamics criterion for surface saturation. In order to reduce the annealing time, dynamic (non-equilibrium) segregation is induced by carrying out the anneal on cold worked nickel ($\epsilon = 0.2$ true strain). Both the grain boundaries and the surface were saturated after only 24 hours of annealing at a temperature as low as 450°C. The heat treatment of the cold rolled material was carried out inside the vacuum chamber of an Auger Electron Spectrometer (AES). The diffusivity, as obtained from the slope of the linear parts of the kinetics curves recorded by the AES, is found to be given by the relationship $D = 2.7 \times 10^{-9} \exp(-58.700/RT) \text{ m}^2\text{s}^{-1}$ in the temperature range 450 to 700°C.

Key words: model, grain boundary diffusivity, sulphur, nickel, saturation.

Résumé

Un nouveau modèle basé sur une technique de saturation de la surface est proposé pour la détermination des coefficients de diffusion intergranulaire des impuretés. Le modèle est appliqué au système nickel – soufre qui a une grande importance pratique. La saturation des joints de grains en soufre est obtenue en effectuant un recuit à une température répondant aux conditions thermodynamiques de saturation de la surface. Afin de réduire le temps de recuit nécessaire, les cinétiques de ségrégation sont obtenues sur un matériau laminé à froid, c'est-à-dire dans des conditions hors d'équilibre. La surface et les joints de grains ont été ainsi saturés en moins de 24 heures de recuit à une température aussi basse que 450°C. Le recuit est effectué dans l'enceinte d'un spectromètre Auger RIBER à miroir cylindrique. La pente des parties linéaires des cinétiques de ségrégation obtenues par spectrométrie Auger permettent d'obtenir le coefficient de diffusion du soufre dans le nickel dans le domaine de température de 450 à 700°C, à partir du modèle suivant: $D = 2.7 \times 10^{-9} \exp(-58.700/RT) \text{ m}^2\text{s}^{-1}$.

Mots clés: modèle, coefficient de diffusion, intergranulaire, soufre, nickel, saturation.

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ملخص

يهدف هذا البحث إلى إيجاد علاقة رياضية تمكن من حساب معامل الانتشار للشوائب عبر حواف الحبيبات للمواد المعدنية الصافية ويتعلق الأمر هنا على وجه الخصوص بتغلغل شائبة الكبريت داخل معدن النيكل. قمنا بتشبيح حواف حبيبات النيكل بالشائبة المذكورة عن طريق معالجة حرارية لعينات من النيكل تعرضت قبل ذلك لعملية درفلة أدت إلى تخفيض حقيقي في السمك مقداره 0.2. تمت هاته المعالجة الحرارية في درجات حرارة مختلفة تتراوح بين 450 و 700°م، داخل الغرفة المفرغة لمطياف أوجيه (Auger). تستغل المنحنيات البيانية الممثلة لسرعة انسياب ذرات الكبريت المستنتجة من أطياف أوجيه وذلك باستخدام ميول الأجزاء الخطية منها لحساب معامل انتشار ذرات الكبريت عبر حواف حبيبات النيكل باستخدام العلاقة المستنتجة التالية:

$$D = 2.7 \times 10^{-9} \exp(-58.700/RT) \text{ m}^2\text{s}^{-1}.$$

الكلمات المفتاحية: نموذج، معامل الانتشار، حواف الحبيبات، الكبريت، النيكل، تشبيح.

Sulphur atoms segregate to the free surface and to the grain boundaries when nickel is annealed, with the reduction in free energy associated with segregation to the surface being more important than that associated with grain boundary segregation [1]. This creates a driving force that tends to convert grain boundary segregation to free surface segregation. This is exploited in this work to deduce grain boundary diffusivities from surface segregation kinetics. The same approach is reported to have been exploited to show that sulphur diffuses along the grain boundaries while antimony comes directly from the bulk when these elements segregate in a Ni-Sb alloy [2]. A model yielding grain boundary concentration in terms of surface segregation kinetics is also reported in the literature [5].

MODEL AND EQUATIONS

Let us consider a grain boundary emerging at the surface and having an initial sulphur concentration of C_{Gb}^0 . Assuming that the grain boundaries are the only source of sulphur and that the initial surface concentration is zero, the solution to Fick's second equation can be written as follows:

$$C_{Gb}(x,t) = C_{Gb}^0 \operatorname{erf} \left(\frac{x}{2\sqrt{D_{Gb}t}} \right). \quad (1)$$

The surface flux is therefore given by:

$$J = -D_{Gb} \frac{\partial C_{Gb}}{\partial x} \Big|_{x=0} = \frac{D_{Gb} C_{Gb}^0}{\sqrt{\pi D_{Gb} t}}. \quad (2)$$

The total amount of diffusing specie accumulated on the surface is hence

given by:

$$Q(t) = S_{Gb} \int_0^t J dt = 2G_{Gb}^0 \sqrt{\frac{D_{Gb}t}{\pi}} S_{Gb}, \quad (3)$$

where S_{Gb} is the area of the grain boundary network crossing the surface and t the annealing time.

Bearing in mind that $Q(t)$ is also equal to the concentration at the surface, the following, time dependant, expression can be obtained for surface concentration:

$$C_{surf} = 2 \frac{S_{Gb}}{S_{surf}} C_{Gb}^0 \sqrt{\frac{D_{Gb}t}{\pi}}. \quad (4)$$

This expression can be rewritten as follows:

$$D_{Gb} = \left(\frac{C_{surf}}{\sqrt{t}} \right)^2 \left(\frac{S_{surf}}{S_{Gb}} \right)^2 \frac{\pi}{4C_{Gb}^0{}^2}. \quad (5)$$

S_{Gb}/S_{surf} is given by [4]:

$\frac{S_{Gb}}{S_{surf}} = \frac{2\delta}{d}$, where δ is the thickness of the grain boundary and d the mean intercept dimension of the grain.

The initial conditions are set as follows: the grain boundary sulphur concentration corresponding to saturation is taken to be 9.26×10^{21} at/cm³ and d is taken to be 0.5 nm. The initial surface concentration is, as mentioned before, taken to be nil.

EXPERIMENTAL WORK

The material studied is Ni 270 of Wiggins alloys (UK), the chemical composition of which is given in table 1.

Element	B	C	Co	Fe	Mn	O	P	S	Ti
Content (weight ppm)	<10	70	<10	30	20	21	5	0.5	0.2

Table 1: Chemical composition of Ni 270.

Prior to deformation, the samples were homogenised for 5 h at 850°C in a sealed quartz capsule under a residual atmosphere of pure argon and then quenched into water. This treatment produced a fully recrystallized material of uniform fine grain size of about 100 µm. The homogenised material was subsequently cold rolled to a true strain, ϵ , of 0.8 ($\epsilon = \ln[e_0/e]$, where e_0 and e are the thickness of the sample before and after deformation respectively).

Specimens of dimensions (5x1.2x0.5 mm³) were cut from the cold-rolled sheets using a low-speed diamond saw, and then mechanically polished to 1 µm diamond surface finish. Subsequently, they were electrolytically polished using a solution of ethanol (70 ml) + water (12 ml) + 2-butoxyethanol (10 ml) + perchloric acid (8 ml), at a potential of 3 V for 20 s. A surface layer of about 5 µm was removed with this polishing process and the influence of mechanical polishing was thus avoided.

Surface segregation was studied by Auger Electron Spectroscopy (A.E.S) in a C.M.A RIBER ISA model ASC

2000 analyser. The sample was spot welded to a strip of resistively heated tantalum inside the A.E.S vacuum system. The temperature was measured with a thin wire (50 µm) thermocouple spot welded to the sample. Such a device allowed the temperature to reach 450°C within 20 seconds. The residual pressure was maintained below 5.10^{-8} Pa. The operating conditions were: 3 keV primary energy, 0.1 µA primary beam current, 1 µm beam diameter. The recording of the spectra was done in the differential mode $dN(E)/d(E)$. The sulphur peak (152 eV) was normalised with respect to the nickel peak (848 eV). Taking the atomic density of a polycrystalline surface of nickel to be 10.54×10^{18} at.m⁻² [3], the superficial concentration of sulphur can be obtained from the following expression [3]:

$$C_{surf}^S = \alpha \frac{H_S}{H_{Ni}} 10.54 \times 10^{18} \quad (\text{at.m}^{-2}) \quad (6)$$

In this expression C_{surf}^S is the surface concentration of sulphur (in at.m⁻²), H_S and H_{Ni} are the peak to peak heights of sulphur (152 eV) and nickel (848 eV) and $\alpha = 0.48$ is a constant of the Auger analyser.

Substituting in equation (5) above, this latter can be rewritten as follows:

$$D_{Gb} = \left(\frac{H_S/H_{Ni}}{\sqrt{t}} \right)^2 \alpha^2 (10.54 \times 10^{18})^2 \left(\frac{S_{surf}}{S_{Gb}} \right)^2 \frac{\pi}{4C_{Gb}^0{}^2}. \quad (7)$$

D_{Gb} can therefore be calculated from the slope of the H_S/H_{Ni} versus \sqrt{t} curve.

RESULTS AND DISCUSSION

The segregation kinetics against \sqrt{t} are shown in figure 1. The rise towards saturation is linear enabling the slope to be easily determined. The values of D_{Gb} are given in table 2, together with values of the bulk heterodiffusion constant obtained from the literature [5]. The grain boundary diffusivity is nearly 10^6 times the bulk diffusivity at low temperature (450 and 500°C). This is in good agreement with other results reported in the literature [6,7].

Figure 2 shows an Arrhenius plot which yields values of 0.61 eV and 2.45×10^{-9} m²s⁻¹ for the activation energy and the pre-exponential factor, D_0 , respectively, in the temperature range 450 to 700°C. Although the value of the activation energy seems to be very low, it is of the same order of magnitude as for sulphur in Cu and in Ag (0.84 eV [8] and 0.8 eV [9] respectively). The low value may be due to the relatively low temperatures of this study. The activation energy has been found elsewhere [10] to tend towards decreasing values with decreasing temperature.

The very low value of the diffusivity at 800°C is probably due to a desegregation phenomenon taking place at this temperature. It can therefore be concluded that the model put forward in this work is only valid for temperatures not exceeding 700°C.

Temperature (°C)	450	500	550	600	700	800
D_{Gb} (m^2s^{-1})	1.0×10^{-13}	3.6×10^{-13}	7.4×10^{-13}	4.5×10^{-13}	1.8×10^{-12}	1.2×10^{-12}
D_B (m^2s^{-1})	2.2×10^{-20}	2.3×10^{-19}	1.8×10^{-18}	1.1×10^{-17}	2.5×10^{-16}	3.1×10^{-15}

Table 2: Grain boundary diffusivity values corresponding to a temperature range from 450 to 800°C.

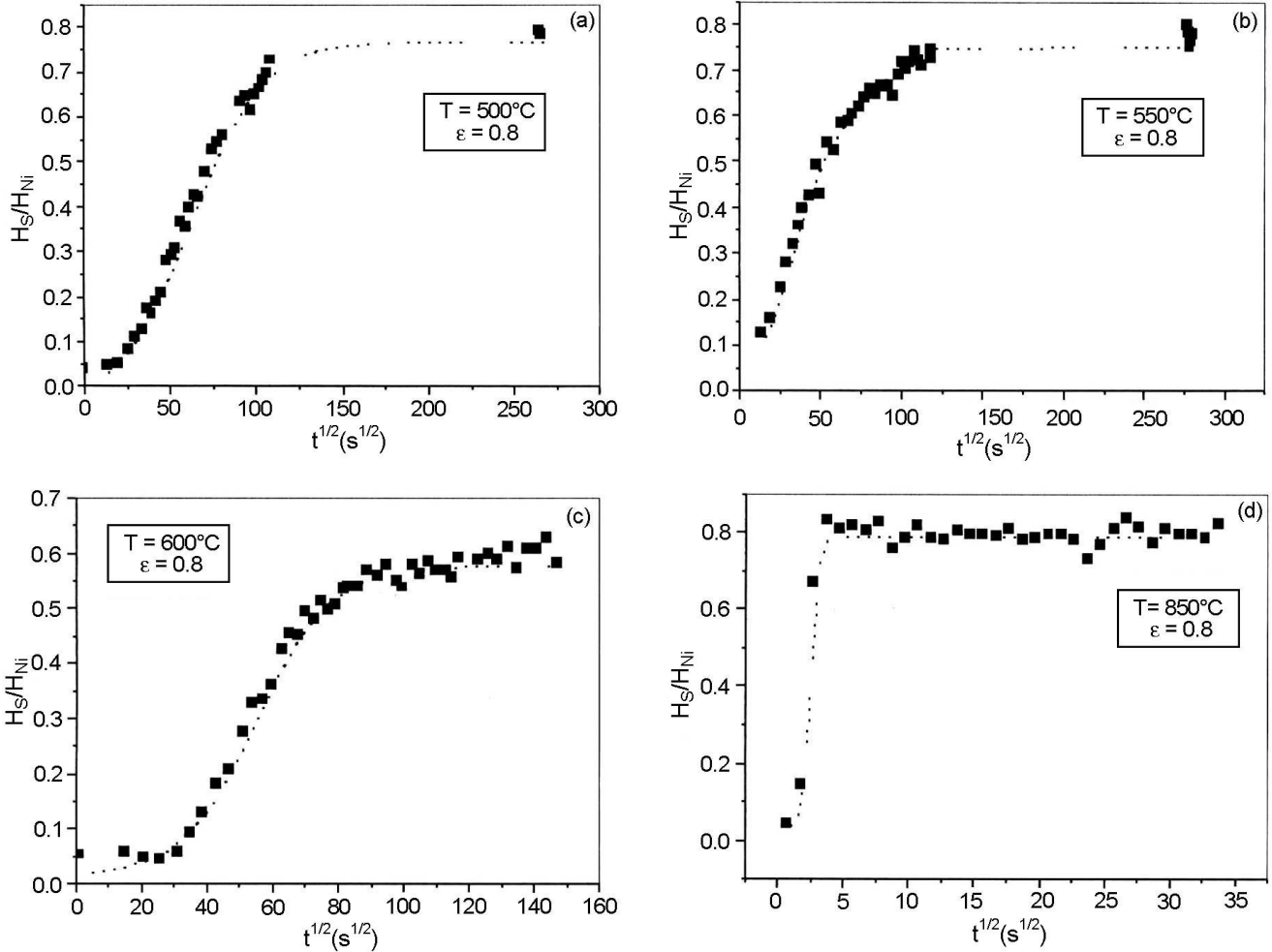


Figure 1 (a) to (d): Segregation kinetics, presented in the form of peak heights ratios (H_S/H_{Ni}), determined at 500, 550, 600 and 850 °C for the material deformed to 0.8 true strain.

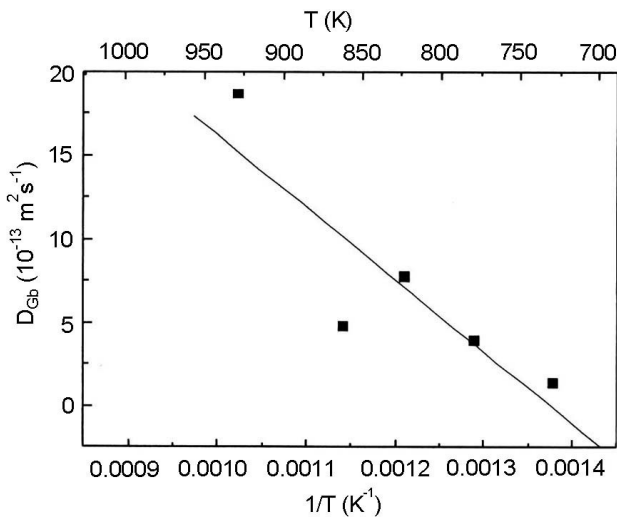


Figure 2: Arrhenius plot of D_{Gb} against temperature. The value at 800°C (1073K) has been disregarded.

CONCLUSION

The model presented in this work enables the determination of the grain boundary diffusion coefficient from kinetic measurements carried out on bulk samples.

Special techniques such as thin foils are not required. It is however applicable only to those systems where the solute segregates to both the grain boundaries and the surface.

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