Radiotracer Diffusion of Ni and Ag in Ag and Ni Grain Boundaries and Oriented Ag/Ni Interphase Boundaries

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Abstract

Grain boundary and interphase boundary diffusion has been investigated in the system Ag/Ni using the radiotracer serial sectioning technique. Ni segregation in Ag grain boundaries is strongly temperature dependent leading to the conclusion that Ni atoms are located mainly in the bulk planes adjacent to the grain boundary. From interphase boundary diffusion measurements in (110) oriented Ag/Ni interphase boundaries it can be deduced that the structure of this interphase boundary is incoherent.

Introduction

Diffusion in grain boundaries (GB) and interphase boundaries (IB) is strongly affected by their structure and chemistry. In this work the influence of both factors has been investigated. First, segregation of ^{63}Ni in Ag GBs was studied by comparative measurements in the type-B and –C kinetic regime. These results were necessary [1] for the evaluation of IB diffusion coefficients of ^{110m}Ag diffusion in (110) oriented IBs of Ag/Ni bycrystals. Moreover, ^{110m}Ag GB diffusion in Ni polycrystals was measured.

To study the influence of the orientation of the single crystals forming an IB, it is prerequisite to produce bycrystals with well defined sharp interfaces. Therefore a system with low mutual solid solubility of the IB forming components and a miscibility gap in the phase diagram is favourable, e.g. the systems Ag-Ni. The ratio of the lattice constants a_{Ag}/a_{Ni} is almost exactly 7:6. For cube-on-cube oriented bycrystals of Ag and Ni this leads to a coincidence of every 6th Ag with every 7th Ni atom (Fig.1) in the interplane. The misfit between these coincident atoms is equalised by misfit dislocations and relaxation. The misfit dislocations form a superlattice being parallel to the orientation of the Ag and Ni single crystals and with a periodicity of $6a_{Ag}$. For a (110) oriented IB this leads to an anisotropic density of misfit dislocations, which in <100>-direction is higher (by a factor $2^{1/2}$) than in <110>-direction. In previous investigations on the IB diffusion of Ag in Ag/Cu IBs it has been shown, that a higher density of misfit dislocations leads to a faster IB diffusion [2].
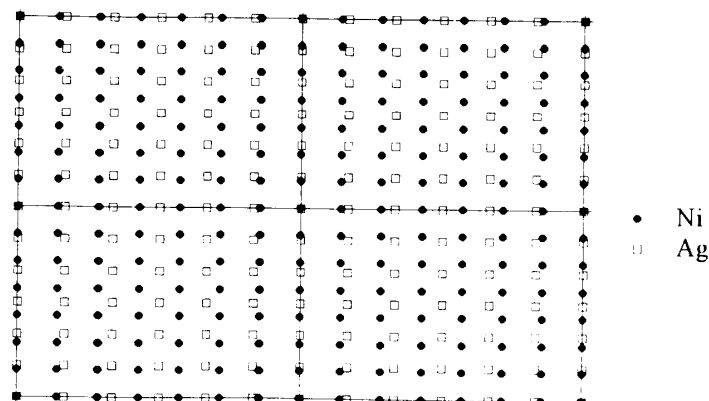

Fig. 1:
Onview on the
unrelaxed structure
of a (110) IB in Ag/Ni

• Ni
▫ Ag

Experimental procedure

Ag and Ni samples, single- and polycrystals, were produced from high purity (5N) ingots. Single crystals of Ag and Ni were grown from the melt and slices of 4 mm were cut with (110) surface orientation. The single crystals were etched, polished and diffusion-bonded with cube-on-cube orientation. From these bycrystals samples were cut perpendicular to the IB with <100> or <110> orientation of the surface.

All samples were pre-annealed at the temperature of the later diffusion annealing. The radiotracer materials, ^{63}Ni and ^{110m}Ag, were evaporated onto the samples. All annealings were performed under high vacuum ($p \approx 10^{-3}$ Pa). The sectioning of the diffusion profiles was done on a microtome; the slices were dissolved and their radiation detected with a high sensitive Liquid Scintillation Counter (LSC).

Results and discussion

Grain Boundary diffusion of ^{63}Ni in Ag polycrystals. Measurements were performed in Harrisons type-B and -C kinetics. In the B-kinetic regime superposition of grain boundary diffusion (D_{GB}) and volume diffusion ((D) into the adjacent bulk makes it impossible to calculate the GB diffusion coefficient D_{GB} independently. From type-B measurements on GB solute diffusion only the triple product $s\delta D_{GB}$ can be evaluated, with s being the GB segregation coefficient and δ the GB width:

$$s \cdot \delta \cdot D_{GB} = 1.308 \cdot \left(\frac{D}{t}\right)^{1/2} \left(-\frac{\partial \ln \bar{c}}{\partial y^{6/5}}\right)^{-5/3} \tag{1}$$

Measurements were performed in the range 821 K to 989 K. The detected decrease in the tracer concentration $\bar{c}$ was up to 4 decades (Fig.2a). In the type-C kinetic regime this decrease was only about 1-2 decades due to the negligible bulk diffusion from the GB (Fig.2b). In such a condition the
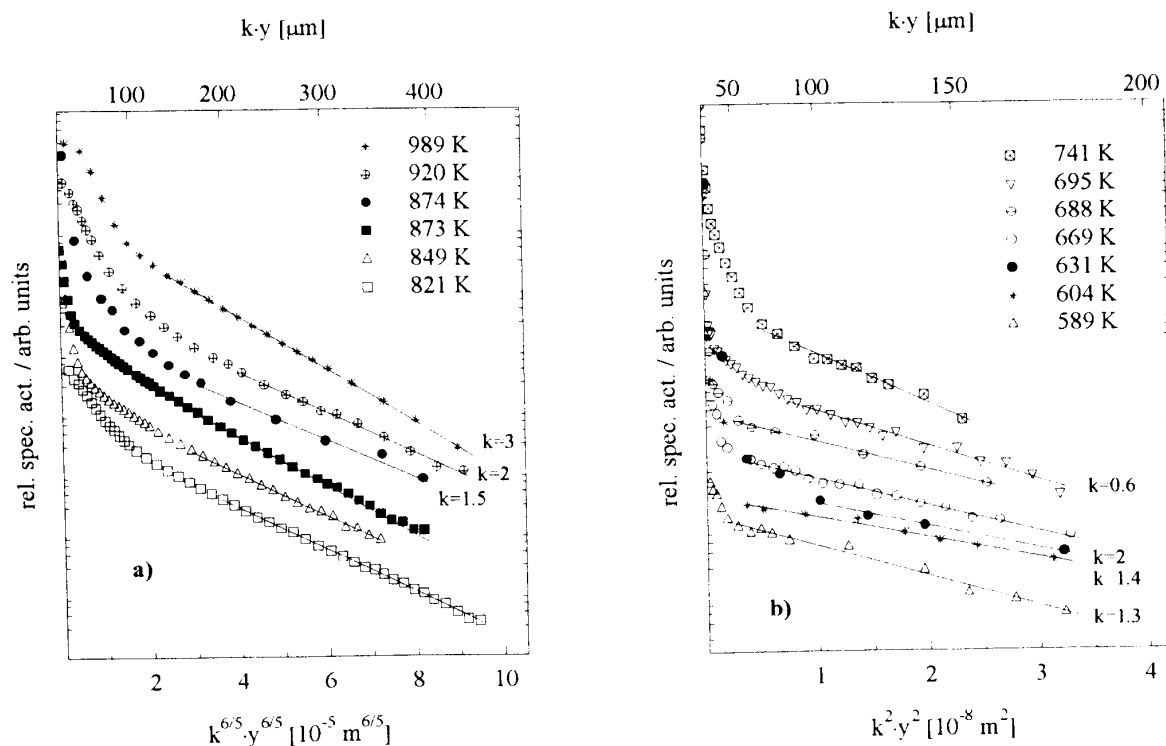

Fig.2: GB diffusion of ^{110m}Ag in Ni polycrystals according to different kinetic regimes
a) type-B   b) type-C

GB diffusion coefficient D_{GB} can directly be calculated from the slope $\partial \ln \bar{c} / \partial y^2$. The resulting Arrhenius relations for [63]Ni GB diffusion in Ag polycrystals are:

$$s \cdot \delta \cdot D_{GB} = 1.9 \cdot 10^{-15} m^3 s^{-1} \cdot \exp\left(-69.2 kJmol^{-1} / RT\right).$$

(2)

$$D_{GB} = 3.1 \cdot 10^{-6} m^2 s^{-1} \cdot \exp\left(-110.1 kJmol^{-1} / RT\right).$$

(3)

From the comparison of D_{GB} (multiplied with $\delta = 0.5nm$) with $s\delta D_{GB}$ (Fig.3) the segregation factor s was evaluated :

$$s = 1.2 \cdot \exp\left(40.9 kJmol^{-1} / RT\right).$$

(4)

The characteristic features of the present results are : the strong segregation (segregation enthalpy $H_S=40.9$ kJ/mol) and the slow GB diffusion of Ni in Ag as compared with the Ag GB self-diffusion [3]. These facts can be explained by the high surface tension σ_{Ni} of Ni, which is remarkably higher than that of Ag, and by a repulsive vacancy–Ni solute interaction. From this it can be concluded that Ni does not segregate in the GB core, but in the adjacent bulk planes [4].

Grain Boundary diffusion of [110m]Ag in Ni polycrystals. Measurements were performed in the type-B kinetic regime from 973 to 1253 K. The profiles were of the same quality as for GB diffusion of [63]Ni in Ag polycrystals (Fig.2a). The Arrhenius relation is :

$$s \cdot \delta \cdot D_{GB} = 5.6 \cdot 10^{-15} m^3 s^{-1} \cdot \exp\left(-120.5 kJmol^{-1} / RT\right).$$

(5)

The values of $s\delta D_{GB}$ for Ag GB diffusion in Ni (Fig. 4) are higher than those of Ni GB self diffusion [5], while the activation enthalpy is nearly the same. The very low solid solubility of Ag in Ni is expected to lead to a strong Ag segregation in Ni GBs. Taking this into account, it can be estimated that the Ag mobility in Ni GBs is less than that of Ni.
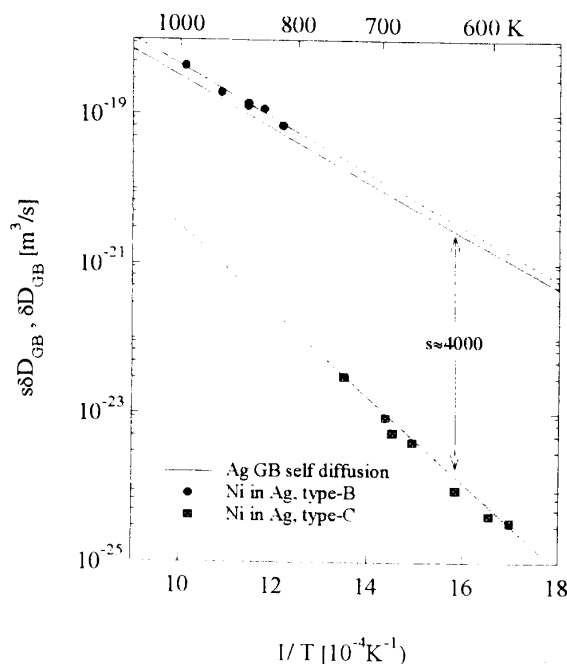

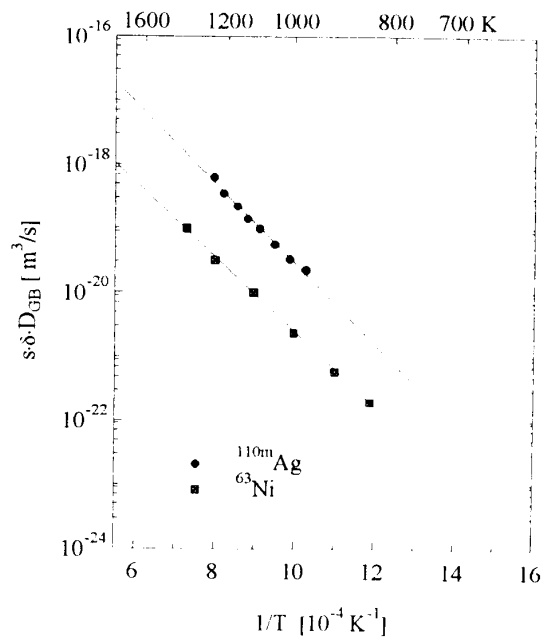Fig. 3: Arrhenius plot of $s\delta D_{GB}$ (upper) and δD_{GB} (lower curve)

Fig 4 : Arrhenius plot of [110m]Ag GB diffusion compared with GB self-diffusion in Ni [5]
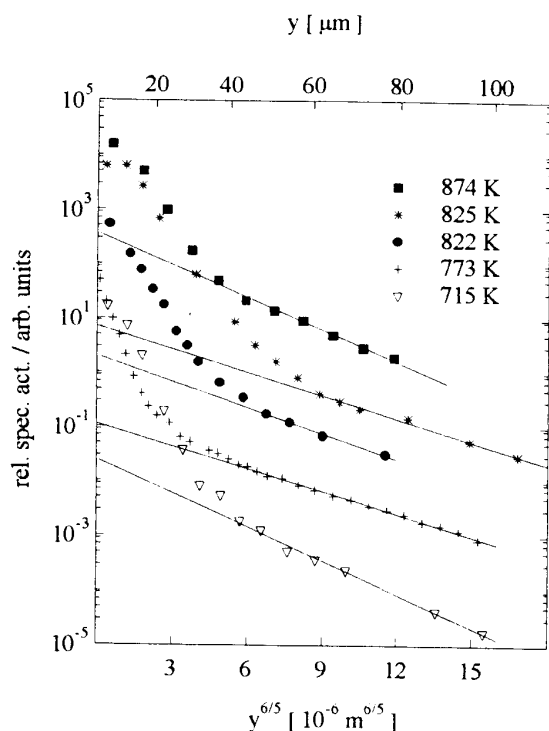
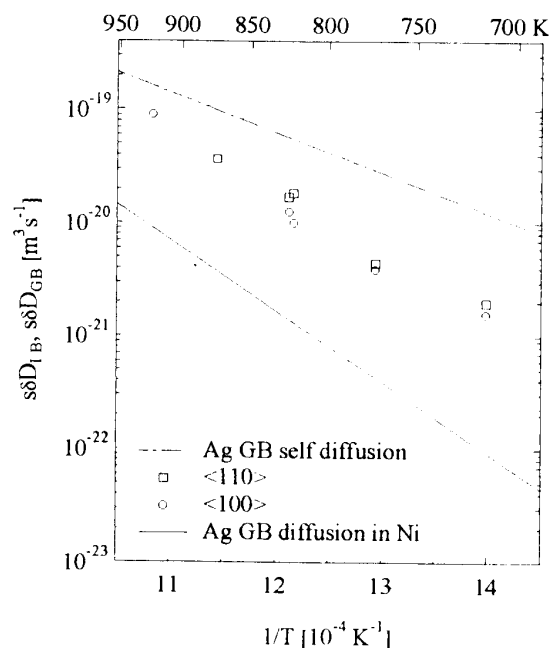Fig. 5: Penetration profiles for IB diffusion of ^{110m}Ag in Ag/Ni (110) bycrystals.

Fig. 6 : Arrhenius plot of ^{110m}Ag IB diffusion in Ag/Ni bycrystals and comparison with GB diffusion of Ag in Ag and Ni.

IB diffusion of ^{110m}Ag in (110) oriented Ag/Ni IB. Measurements were performed from 715 K to 923 K (Fig.5). In [1] it was shown that IB diffusion coefficients can be evaluated e.g. from the Suzuoka solution if the volume diffusion coefficient is replaced by an effective volume diffusion coefficient D_{eff} depending on volume diffusion and segregation of the tracer material in both bycrystal materials. In the case of Ag diffusion in Ag/Ni bycrystals the quantitative evaluation of D_{eff} is more simple, because it turns out that the terms related to diffusion of Ag in Ni can be neglected.

From the Arrhenius plot (Fig. 6) it can be seen that in the presently investigated IB nearly no diffusional anisotropy can be observed. Diffusion of ^{110m}Ag in <100>-direction is equal to or even slower than in <110>-direction which is in disagreement to the results found in Ag/Cu IBs []. This can be explained by the larger misfit in lattice constants of Ag/Ni when compared with Ag/Cu leading to an incoherent structure of the IB in the present case because of a very high misfit dislocation density. Thus, at higher temperatures a completely incoherent IB appears to be more favourable than a semi-coherent structure of the (011) Ag/Ni phase boundary.

References

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