Full length article

Grain boundary diffusion and segregation of ^{57}Co in high-purity copper: Radiotracer measurements in B- and C-type diffusion regimes

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ABSTRACT

Grain boundary diffusion of ^{57}Co in high-purity polycrystalline copper is investigated using the radio-tracer technique in Harrison's B- (850–1150 K) and C-type (550–950 K) kinetic regimes. The triple product $P = s \cdot \delta \cdot D_{gb}$ (s is the segregation factor and δ the grain boundary width) and the grain boundary diffusion coefficient D_{gb} of Co in Cu are determined to obey the Arrhenius laws with the activation enthalpies of $Q_{gb} = 66.2$ kJ/mol and $H_{gb} = 100.9$ kJ/mol, respectively. Using the experimental estimate of δ, $\delta \cong 0.5$ nm, Co is found to segregate strongly at Cu grain boundaries and the corresponding segregation factor follows an Arrhenius dependence with the segregation enthalpy of $H_s = -34.7$ kJ/mol. Co-diffusion experiments with the ^{57}Co and ^{110m}Ag isotopes support a 'sub-interface'-type of grain boundary segregation of Co in Cu.

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1. Introduction

Radiotracer measurements of solute grain boundary (GB) diffusion in a polycrystalline solid are typically performed in true dilute limit conditions and, as a result, equilibrium solute segregation can be determined [1]. The key idea is to combine the GB diffusion experiments with a solute in both Harrison's B and C type conditions [2] for the same polycrystalline material. At low temperatures and/or relatively short annealing times (Harrison's C regime) the tracer diffuses dominantly along GBs, there is practically no bulk diffusion, and the GB diffusion coefficient, D_{gb}, can directly be measured. At relatively high temperatures and/or longer annealing times (Harrison's B regime) the tracer diffuses fast along GBs with a subsequent leakage into the adjacent grain interiors which is characterized by the corresponding bulk diffusion length $\sqrt{D_v t}$ (D_v and t are the bulk diffusion coefficient and the diffusion time, respectively). The latter has to be significantly larger than the GB width δ remaining smaller than the grain size d. As an exact solution of such diffusion measurement, the so-called triple product

$$P = s \cdot \delta \cdot D_{gb} \qquad (1)$$

can be evaluated [3]. Here the pertinent solute segregation factor s is determined as the ratio between the solute concentrations in the GB, c_{gb}, and in the adjacent bulk, c_v

$$s = \left.\frac{c_{gb}}{c_v}\right|_{x=\pm\delta/2} \qquad (2)$$

and δ is the diffusional GB width, respectively. Here x is the coordinate perpendicular to the grain boundary which in Fisher's model [4] is considered as a homogeneous slab of the thickness δ.

Combining the B- and C-type regime measurements, the product of the solute segregation factor, s, and the diffusional GB width, δ, can be determined as:

$$s \cdot \delta = \frac{P}{D_{gb}} \qquad (3)$$

The combination of the B- and C-type regime measurements for GB *self-diffusion*, when the solute segregation factor $s = 1$, allows an experimental determination of the diffusional GB width δ. The GB self-diffusion measurements over very large temperature intervals in NiO [5], pure Ag [6,7], Ni [8,9], Fe [10], α-Ti [11] and in a nano-crystalline γ-FeNi-alloy [12–14] provided a temperature independent value of about 0.5 nm (within the limits of experimental uncertainties) for the diffusional GB width. Using this value of δ, the solute segregation factor s can be determined from Eq. (3), assuming that the GB width negligibly depends on the type of tracer atoms [15]. A pre-requisite of the application of the approach,

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Eqs. (1)–(3), is the stability of the same GB structure and an absence of any structure transition in the whole temperature interval of the GB diffusion measurements [15]. In the case of a GB structure transition, a kink in the corresponding Arrhenius dependencies can be observed [17,18].

So far, the GB diffusion of different solutes − Au [19], Ag [20,21], Se [22], Ge [23], Bi [24], Ni [25,26], Fe [27,28] and Cu self-diffusion [29] − in the same high-purity copper (99.9998 wt%) has been measured and the corresponding segregation factors have been determined. The investigation of Ni grain-boundary diffusion in 5N Cu depending on the sulfur content and pre-annealing treatments by Tôkei et al. [26] verifies the importance of using the same high-purity matrix in order to determine the intrinsic diffusion and segregation properties. Note that GB diffusion of Ag in Cu was investigated using Auger electron spectroscopy and applying the Hwang-Balluffi method [21] and the results are similar to those determined by the radiotracer technique [20].

It seems that presently Cu is the most intensively investigated metal with respect to grain boundary diffusion and segregation. A further example is pure Al of nominally the same purity but different origin in which GB diffusion of different solutes − i.e. Fe [30], Zn [31–33], and Ga [34] − has been investigated using the radiotracer technique or electron probe micro-analysis (predominantly in the B-type kinetic regime).

Comparing all solutes studied, the ferromagnetic impurities like nickel and iron represent a special case of solutes with relatively small atomic radii and high surface energies with respect to those of pure copper. However, nickel and iron differ significantly concerning their solubility in Cu − nickel is completely miscible (a miscibility gap is though suspected at low temperatures) and iron is almost immiscible. While for Ni in Cu a moderate but distinct segregation has been established [25], the case of Fe diffusion and segregation in Cu turned out to be quite intricate and even formal C-type profiles were measured at high temperatures in the B regime [27,28]. It was proposed that at higher temperatures GB diffusion-induced Fe coverage of a GB core in Cu provokes grain boundary instability with respect to lateral shifts by several atomic planes that induces Fe-rich layers in the adjacent grains [28]. As a consequence the Cu matrix is over-saturated locally and this fact changes the kinetics of the GB penetration which complicates measurements under B-type kinetic conditions [28].

The present paper aims to investigate GB diffusion and segregation of another ferromagnetic impurity, namely of cobalt, in the same high-purity copper. Cobalt is similar to Ni and Fe in many respects, it has a smaller atomic radius and a higher surface energy as those of Cu and is almost immiscible with it [35]. Actually, investigations of Co segregation in Cu-Co-alloys were performed [36], but the segregation behaviour of Co in GBs of high-purity polycrystalline copper remains unknown. Itckovich et al. [37] already tried to investigate GB diffusion of Co in Cu using an electron probe micro analysis, however, no Co GB diffusion flux could be detected. In view of the similarity of the Fe−Cu and Co−Cu systems, similar segregation behaviors may potentially be expected. However, a fundamental difference is found with a strong temperature dependence of Co GB segregation, whereas Fe segregation in the same Cu material is practically temperature-independent.

2. Experimental procedure

2.1. Sample preparation

Copper of the nominal purity 5N8 was used (which corresponds to the material A used for the copper self-diffusion investigation in Ref. [29]). The preparation procedure of the cylindrical samples of about 10 mm in diameter and 3 mm in thickness was equivalent to the procedure described in Ref. [25]. One face of the specimen was polished by a standard metallographic procedure to a mirror-like quality. In order to recover the defects introduced by the preparation procedure, the specimen was sealed in a silica tube under a purified (5N) Ar atmosphere and annealed at 1023 K for 24 h. After this pre-diffusion annealing each sample was further annealed at the temperature of the intended diffusion treatment for at least the double duration (in order to achieve equilibrium GB segregation of all spurious impurity elements inherent in the material and to minimize grain growth during the subsequent solute tracer diffusion experiment). After each step of the preparation procedure the samples were etched carefully with nitric acid.

The average grain size was about 200 μm, which is appropriate for GB diffusion measurements in the B-type regime. For the C-type regime measurements, the grain size was reduced to about 60−80 μm applying mechanical deformation to about 20% before the above described thermal treatment.

2.2. Radiotracer experiments

The radiotracer ^{57}Co (half-life 271.7 d) was available as a HCl solution. To achieve the required specific activity of the tracer material, the solution was highly diluted with double-distilled water. The tracer solution (with the total activity of about 12 kBq) was applied on the polished sample surface and dried. Under a purified Ar atmosphere the samples were sealed into silica tubes and subjected to the diffusion annealing in a temperature range of 550−1150 K for the chosen durations. The temperatures were measured and controlled with a Ni-NiCr thermocouple to an accuracy of ±1 K. After the diffusion annealing, the samples were reduced by about 2 mm in diameter in order to remove the effects of lateral and surface diffusion. The penetration profiles were determined by parallel mechanical sectioning using a microtome and weighting the sections using a microbalance.

The isotope ^{57}Co decays after capturing an electron into an excited state of the isotope ^{57}Fe and after emitting γ-radiation the isotope ^{57}Fe turns into a stable state [38]. In order to measure the activity of each section a germanium detector was used.

Additionally, a Co/Ag co-diffusion experiment has been performed. A ^{110m}Ag tracer solution (half-life 249.8 d) with an activity of approximately a half of that of the ^{57}Co tracer was used. The ^{110m}Ag isotopes decay with emission of mainly 658 and 885 keV γ-quanta [50], which can easily be distinguished from the ^{57}Co decays, γ-peaks at 122 and 136 keV, by an available germanium detector with a 16 K multi-channel analyzer.

3. Experimental results

The way to analyze the GB penetration profiles depends crucially on the kinetic regime in which the measurements are performed. The key parameter is the value of the Le Claire parameter α [2] (which is generally unknown for solute diffusion):

$$\alpha = \frac{s\delta}{2\sqrt{D_v t}} \tag{4}$$

This parameter relates the effective GB width, $s \cdot \delta$, with the corresponding diffusion length in the grain volume, $2\sqrt{D_v t}$. According to the present knowledge [15], $\alpha > 1$ corresponds to Harrison's C-type regime (lower temperatures and/or shorter diffusion times) and $\alpha < 0.1$ corresponds to the B-type regime (higher temperatures and/or longer diffusion times), while the interval $0.1 < \alpha < 1$ represents the transition regime BC (for a theoretical estimate of the limits of diffusion regimes see also Ref. [16]). In the