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The C-regime measurements of grain boundary diffusion of silver in copper Σ5 (310) bicrystal

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For the first time, grain boundary diffusion of a solute is measured in a single grain boundary in the C kinetic regime after common Harrison's classification. The radiotracer technique is used to determine the ^{110m}Ag diffusion coefficients in Cu Σ5 (310) [0 0 1] bicrystal along and perpendicular to the [0 0 1] misorientation axis. The anisotropy of grain boundary diffusion increases slightly with decreasing temperature. However, it remains moderate, within a factor of two to three for the temperature interval studied.

Keywords: Copper; Grain boundary; Grain boundary diffusion; Grain boundary segregation

The relationship between microscopic mechanisms of grain boundary (GB) diffusion and grain boundary structure represents not only a fundamental problem, but is of essential engineering importance, too. Its solution requires, in particular, the determination of diffusion coefficients for single grain boundaries with precisely characterized structures, i.e. with specified misorientation and inclination parameters.

So far, diffusion along single and precisely characterized grain boundaries was investigated only in the B-type kinetic regime after Harrison [1], see e.g. the handbook on GB diffusion data [2]. Alongside the most sensitive radiotracer method [3–6], the electron probe X-ray microanalysis [7,8] and secondary ion mass spectrometry [9,10] techniques were applied. These studies provided the values of the triple product $P = s \cdot \delta \cdot D_{gb}$ of the grain boundary diffusion coefficient D_{gb}, the effective (diffusional) GB width δ and the GB segregation coefficient s ($s = 1$ for self-diffusion in pure metal), but not the GB diffusion coefficient itself [11].

The state of the art in this field is well represented by the works of Herzig and co-workers [12,13], which highlight the importance of a precise and full characterization of the GB misorientation and inclination parameters in order to systemize the diffusion data. For example, the GB diffusivity of Au in Cu demonstrates a very narrow cusp near the perfect Σ5 misorientation and the triple product P corresponds to the diffusivity of random high-angle GBs at 1–2 degrees deviation from the exact Σ-misorientation. The existence of a twist component of the misorientation and especially the appearance of a network of secondary dislocations affect the measured triple product strongly, resulting in specific "shoulders" on the misorientation dependence of P [4]. It is completely unknown which quantity – D_{gb}, s, δ or their combination – controls such specific misorientation dependence of P.

Relatively recently, GB diffusion measurements in polycrystalline materials became feasible under the C kinetic conditions using radioactive isotopes ([14]; for an overview, see e.g. [15]). This method allows direct determination of the grain boundary diffusion coefficients D_{gb} since the tracer atoms probe GBs only, without any leakage to the crystalline interior. However, all such studies have hitherto been carried out exclusively on polycrystalline materials, mainly due to the extremely involved requirements to detect the tiny amounts of tracer atoms located in the grain boundaries.[2]

New and unprecedented information can be gained by the GB diffusion measurements in the C regime on precisely characterized bicrystals. The radiotracer technique represents the most suitable method for this due to its extreme sensitivity and the fact that section-averaged information is gained.

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[2] This problem can be by-passed by increasing the number of GBs, as in the case of nanocrystalline materials. The issue of thermal stability of the nanocrystalline structure during measurements then becomes of prime importance [16].

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In the present paper, diffusion of ^{110m}Ag along the copper Σ5 (310) grain boundary is studied along and perpendicular to the [0 0 1] misorientation axis. The radiotracer technique is applied to investigate solute diffusion at the true dilution limit of the tracer concentrations. The GB diffusion coefficients of a single grain boundary are measured in the true C-type kinetic regime for the first time. That has enabled the direct determination of the anisotropy of the grain boundary diffusion coefficient.

A bicrystal with dimensions of $6 \times 20 \times 200$ mm^3 containing the Σ5 (310) [0 0 1] grain boundary was grown using high-purity copper (5N8) from precisely oriented seeds in a high-purity graphite container in a purified argon atmosphere by a horizontal scheme of the Bridgman method. The misorientation parameters of the bicrystal were measured by the Kossel technique [17] using X-ray microdiffraction. The main misorientation angle, $\theta = 36.3^\circ$, as well as the deviations from the ideal tilt misorientation, i.e. the "second tilt" angle $\psi = 1.1^\circ$ and the twist angle $\phi = 0.3^\circ \div 0.5^\circ$, were determined to an accuracy of ± 0.04 to $\pm 0.06^\circ$. More details of the production of bicrystals with pre-determined misorientation parameters are given in Ref. [18].

Two kinds of disc-shaped specimens were cut from the bicrystal by spark erosion with the basis plane normal and parallel to the [0 0 1] misorientation axis.

The ^{110m}Ag radioisotope was produced by neutron irradiation of natural silver chip at the GKSS research reactor (Geesthacht, Germany). A droplet of the highly diluted ^{110m}Ag solution was deposited onto the polished surface of each specimen and dried. The specimens were evacuated in silica ampoules to a residual pressure of less than 10^{-4} Pa, sealed and annealed. After annealing treatment, the samples were reduced in diameter to remove the effect of lateral and/or surface diffusion. At each temperature, the two samples for investigation of diffusion along and perpendicular to the misorientation axis were annealed together to allow the direct comparison of the measured diffusivities.

The penetration profiles of ^{110m}Ag were determined by the serial sectioning technique using an SM2500E (Leica) microtome. Further experimental details are similar to those in Refs. [19,20]. A well-type intrinsic Ge γ-detector with a very low background (less than 10^{-2} counts per second in the corresponding energy window) equipped with an automatic sample changer was used. The counting time per section lasted 10 h or more to provide a good statistic and supply reliable data.

The kinetic regime of GB diffusion is determined unambiguously by the value of Le Claire's parameter $\alpha = s\delta/2\sqrt{D_\mathrm{v}t}$ [1,11,21]. Here D_v is the bulk diffusion coefficient taken here from the investigation of Barreau et al. [22]. Taking into account typical experimental uncertainties of about 15%, the condition $\alpha > 2$ defines the C kinetic regime and $0.1 < \alpha < 2$ corresponds to the transition regime between the B and C kinetics. Therefore, the values of s and δ have to be initially known for the penetration profiles to be analysed.

The segregation factor of Ag in Cu GBs measured on polycrystalline samples for random high-angle GBs [19] was used as an initial estimate of the s values in the Σ5 bicrystal.

The effective diffusional GB width δ was determined directly in a series of GB self-diffusion measurements in polycrystalline materials and a consistent value of $\delta \approx 0.5$ nm was found (see e.g. [14,15,23]). In the present investigation, it is assumed that the GB width is the same for self- and solute diffusion. The atomistic simulation of Σ5 (210) GB in Cu and Cu–Ag alloys have shown that this is a reliable approximation and a notable variation of the GB structure width occurs only at temperatures close to the melting point [24]. Accordingly, it is reasonable to assume that the diffusion GB width δ is approximately constant in our temperature range. Moreover, we assume that δ does not depend on the diffusion direction. In the following, the estimate $\delta = 0.5$ nm is used.

Using these estimates, the experiments were designed to be performed in the C kinetic regime with $\alpha \geqslant 2$ at $T \leqslant 575$ K. The temperature T and time t of the annealing treatments together with other relevant experimental parameters are listed in Table 1. The expression

$$D_\mathrm{gb} = \frac{1}{4t}\left(-\frac{\partial \ln \bar{c}}{\partial y^2}\right)^{-1} \tag{1}$$

is used to determine the GB diffusion coefficients, D_gb, from the profiles obtained in the C regime.

Figure 1 represents the ^{110m}Ag penetration profiles plotted in the coordinates of $\ln \bar{c}$ vs. y^2, where $\bar{c}$ is the layer concentration of solute atoms and y is the penetration depth. The GB diffusion-related parts of the penetration profiles are seen to be linear in such coordinates that is a "fingerprint" of the C regime [11]. Figure 1 suggests that the GB diffusion measurements in a bicrystal are indeed feasible even in the C regime. One can see that the penetration of Ag atoms in Cu

Table 1. Experimental parameters of ^{110m}Ag GB diffusion in Cu Σ5 (310) [0 0 1] bicrystal. T is the diffusion temperature, t the diffusion time, D_gb the diffusion coefficient. $\alpha^* = \delta/2\sqrt{D_\mathrm{v}t} = \alpha/s$. The diffusion direction is referred to the main tilt axis [0 0 1] of the bicrystal. s^* represents an estimate of the Ag segregation factor and k is the correction factor for the diffusivities measured in the transition regime between the C and B kinetics (see text).

T (K)	t (10^4 s)	Diffusion direction	α^*	D_gb	s^*	k
534	121	$\parallel$	9.4×10^{-2}	8.97×10^{-16}	442	
		$\perp$		3.00×10^{-16}	1324	
555	121	$\parallel$	4.1×10^{-2}	1.98×10^{-15}	361	
		$\perp$		1.43×10^{-15}	500	
575	121	$\parallel$	2.0×10^{-2}	4.71×10^{-15}	256	
		$\perp$		1.53×10^{-15}	787	
675	25.9	$\parallel$	2.1×10^{-3}	7.80×10^{-14}	131	2.1
		$\perp$		4.73×10^{-14}	217	1.6

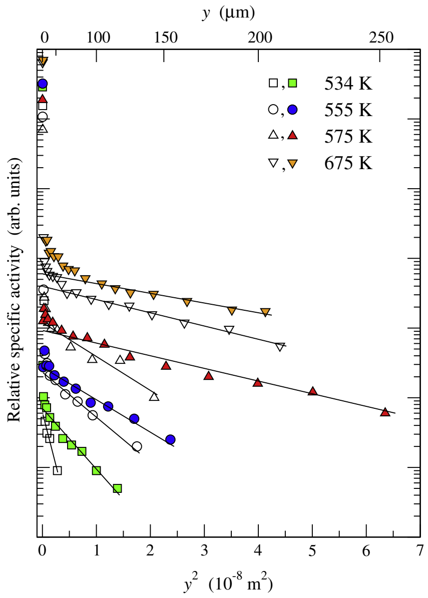

Figure 1. The penetration profiles of ^{110m}Ag diffusion in the Cu Σ5 (310) [0 0 1] bicrystal. The profiles are shifted vertically for a convenient comparison. The same shift was applied to the profiles measured at the same temperature both parallel (solid symbols) and perpendicular (open symbols) to the misorientation axis.

Σ5 (310) [0 0 1] GB is somewhat larger parallel to the tilt axis than that perpendicular to it (Fig. 1).

It should be noted here that the Cu bicrystals grown by the Bridgman method contain a certain amount of grown-in dislocations (the density of $10^{10} - 10^{11}$ m^{-2}) and mosaic cell boundaries (50–100 µm large cells, with the total variation of the misorientations within 0.03°), which could potentially affect the measured penetration profiles. However, the simple estimates verify that the corresponding dislocation density is too small to provide a measurable contribution to the direct diffusion transport from the sample surface or to affect the tracer leakage from the high-angle GB. In the latter case, the dislocation densities of about 10^{15} m^{-2} are required to violate the C-type conditions [25,26].

Using Eq. (1), the diffusion coefficients, D_{gb}, were determined. They are presented in Table 1 and plotted in the Arrhenius coordinates in Figure 2.

In Figure 2 the diffusion coefficients of Ag in Cu Σ5 bicrystal are compared to those in high-purity polycrystalline copper. It is obvious that diffusion of Ag in the Cu Σ5 bicrystal under investigation is slower than that in general high-angle GBs. On the other hand, our preliminary measurements in the B kinetic regime revealed that the values of the triple product $P^b = s^b \cdot \delta \cdot D^b_{gb}$ in the Σ5 bicrystal[3] are at least not smaller than those in polycrystalline copper, $P^p = s^p \cdot \delta \cdot D^p_{gb}$, i.e. $P^b \geqslant P^p$. The relationship $D^b_{gb} < D^p_{gb}$ suggests that Ag segregates much more strongly to the special Σ5 GB than to random high-angle GBs in polycrystalline copper, $s^b > s^p$. Thus, the values of α were underestimated using s^p as an initial guess. We have calculated $s^* = P^p/(\delta \cdot D^b_{gb})$ using P^p from Ref. [19] and the preliminary data indicate that $s^b \geqslant s^*$. This circumstance allows to analyze the penetration profiles at $T = 675$ K as measured in the transition regime between the B and C kinetics. It is known that the measured diffusion coefficients underestimate the real ones in such a case [11]. We have determined the correction factors k according to the approach described in Ref. [23] and the resulting diffusivities at $T = 675$ K are listed in Table 1.

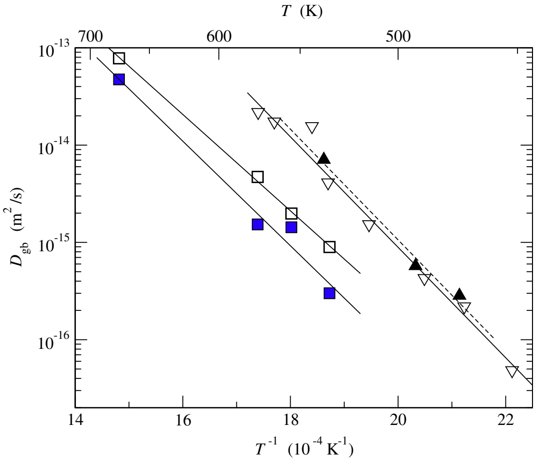

Figure 2. The GB diffusion coefficients of Ag in the Cu Σ5 (310) [0 0 1] bicrystal measured parallel (open squares) and perpendicular (filled squares) to the tilt axis in comparison to those in polycrystalline pure Cu (triangles down [19]) and Cu–0.2 at.%Ag alloy (triangles up [27]).

Assuming linear dependencies of GB diffusion in the Arrhenius coordinates, the following relations are derived:

$$D^{\parallel}_{gb} = \left(1.73^{+18.3}_{-1.58}\right) \times 10^{-6} \times \exp\left\{-\frac{(94.8 \pm 12)\text{kJmol}^{-1}}{RT}\right\}\text{m}^2\text{s}^{-1}, \qquad (2)$$

and

$$D^{\perp}_{gb} = \left(4.30^{+90}_{-4.20}\right) \times 10^{-6} \times \exp\left\{-\frac{(102.9 \pm 18)\text{kJmol}^{-1}}{RT}\right\}\text{m}^2\text{s}^{-1} \qquad (3)$$

In Figure 3, the published data on self-diffusion in Cu [4] and Ag [28] Σ5 (310) [0 0 1] GBs (divided by the effective GB width $\delta = 0.5$ nm) are plotted together with the present results in the Arrhenius coordinates. The reduced temperature, T_m/T, is used, with T_m being the melting temperature.

The anisotropy of diffusion in a Σ5 bicrystal has previously been investigated for Ag self-diffusion [28]. The anisotropy was within a factor of two, and increased slightly with increasing temperature (Fig. 3). The present data for Ag diffusion in Cu Σ5 (310) [0 0 1] bicrystal reveal a slightly larger anisotropy which decreases with rising temperature – diffusion along the tilt axis is a factor of two to three faster than that perpendicular to it. This likely to be related to the higher density of parallel "open channels" along the [0 0 1] misorientation axis in the structure of the Σ5 (310) GB in Cu, which offer attractive sites for segregation of oversized Ag atoms. An atomistic simulation confirms the existence of the parallel "open channels" in a relaxed structure of Σ5 (310) [0 0 1] GB in Cu [29]. Note, that the parallel "open

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[3] These measurements are still in progress.

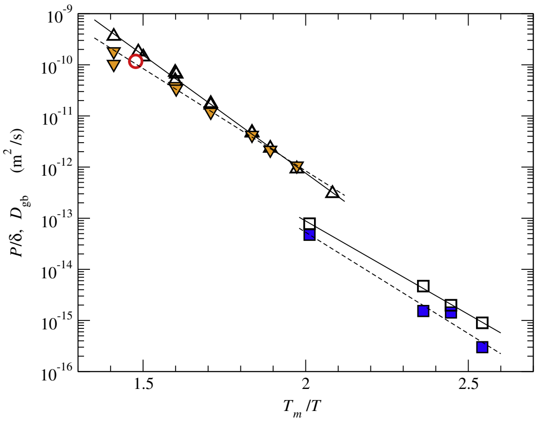

Figure 3. Diffusion anisotropy in the tilt Σ5 (310) [0 0 1] GBs for Ag in Cu (squares, the present work) and Ag in Ag (triangles [28]) plotted against the reduced temperature, T_m/T. Here T_m is the corresponding melting point of the metal. For comparison, the Cu self-diffusion coefficient in the Σ5 (310) [0 0 1] GB [4] is presented (circle). GB diffusivities measured perpendicular (filled symbols and dashed lines) and parallel (open symbols and solid lines) to the tilt axis are plotted. The GB self-diffusivities P measured for Ag [28] and Cu [4] are divided by the GB width, taken as $\delta = 0.5$ nm for convenient comparison with the present results.

channels" characterize low-Σ CSL tilt GBs, whose fraction in real polycrystals is small.

The rates of GB self-diffusion of Cu and Ag in the tilt Σ5 (310) GBs [4,28] are very similar when plotted against the reduced temperature (Fig. 3). This result indicates a common diffusion mechanism in this GB structure. On the other hand, extrapolating the Ag self-diffusion data (Fig. 3) to lower temperatures, relatively slower rates of Ag solute diffusion in the Cu Σ5 (310) [0 0 1] GB are seen. The trapping of Ag atoms at the cites near the "channels" may lead to a partial blocking of suitable sites for Ag diffusion. In such a case, one may expect diffusion jumps along alternative paths and even new GB diffusion mechanisms related to the new path. Thus, GB diffusion along the misorientation axis occurs mainly via several different types of diffusion jumps. Their relative contribution should depend on temperature due to the temperature dependence of segregation. A deviation from linear Arrhenius dependence is then expected. Therefore, the activation enthalpy may represent an effective value, the magnitude of which lies between the activation enthalpies of the two types of jump. Actually, the activation enthalpy of 95 kJ mol^{-1} for Ag diffusion in Cu Σ5 (310) [0 0 1] GB parallel to the tilt axis (Eq. (2)) lies between the activation enthalpy for the interstitialcy mechanism (about 50 kJ mol^{-1}), being the main mechanism, and the activation enthalpy for an alternative vacancy mechanism (about 110 kJ mol^{-1}), which were found for self-diffusion in Σ5 (310) [0 0 1] GB in Cu by atomistic simulations [29,30]. The activation enthalpy of 101 kJ mol^{-1} for Ag diffusion in Cu Σ5 (310) GB perpendicular to the tilt axis (Eq. (3)) is close to that (about 110 kJ mol^{-1}) found in Refs. [29,30] for the vacancy mechanism being the principal mechanism for self-diffusion in Cu Σ5 (310) GB in this direction.

The enthalpies of Ag GB diffusion in polycrystalline Cu (108.6 kJ mol^{-1}) [19] and in the Cu–0.2 at.%Ag alloy (108.8 kJ mol^{-1}) [27] are close to the activation enthalpy of Ag diffusion perpendicular to the tilt axis of the Cu Σ5 (310) [0 0 1] GB (see Fig. 2). This could be related to a small fraction of GBs having "open channels" in their structure in the Cu and Cu–0.2 at.%Ag alloy polycrystals. This suggests that the vacancy mechanism provides Ag diffusion in Cu Σ5 (310) [0 0 1] GB perpendicular to the tilt axis and diffusion of Ag in general GBs in polycrystalline Cu and Cu–0.2 at.%Ag alloy.

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[1] L.G. Harrison, Trans. Faraday Soc. 57 (1961) 597.
[2] I. Kaur, L. Kozma, W. Gust, Handbook of Grain and Interphase Boundary Diffusion Data, Ziegler, Stuttgart, 1989.
[3] J.T. Robinson, N.L. Peterson, Surf. Sci. 31 (1972) 586.
[4] E. Budke, Chr. Herzig, S. Prokofjev, L.S. Shvindlerman, Defect Diffus. Forum 156 (1998) 21.
[5] E. Budke, Chr. Herzig, S. Prokofjev, L.S. Shvindlerman, Mater. Sci. Forum 207–209 (1996) 465.
[6] T. Surholt, D.A. Molodov, Chr. Herzig, Acta Mater. 46 (1998) 5345.
[7] A.N. Aleshin, B.S. Bokshtein, L.S. Shvindlerman, Sov. Phys. Sol. State 19 (1977) 2051.
[8] A.N. Aleshin, S.I. Prokofjev, Poverkhn. Fiz. Khim. Mekh. 9 (1986) 131, in Russian.
[9] W. Gust, M.B. Hintz, A. Lodding, R. Lucik, H. Odelius, B. Predel, U. Roll, J. Phys. Colloques 46 (1985) C4–C475.
[10] S.M. Schwarz, B.W. Kempshall, L.A. Giannuzzi, F.A. Stevie, Acta Mater. 50 (2002) 5079.
[11] I. Kaur, Y. Mishin, W. Gust, Fundamentals of Grain and Interface Boundary Diffusion, Wiley, Chichester, 1995.
[12] E. Budke, T. Surholt, S.I. Prokofjev, L.S. Shvindlerman, Chr. Herzig, Acta Mater. 47 (1999) 385.
[13] C. Minkwitz, Chr. Herzig, E. Rabkin, W. Gust, Acta Mater. 47 (1999) 1231.
[14] J. Sommer, Chr. Herzig, J. Appl. Phys. 72 (1992) 2758.
[15] S.V. Divinski, Chr. Herzig, J. Mater. Sci. 43 (2008) 3900.
[16] S. Divinski, H. Rösner, G. Wilde, in: G. Wilde (Ed.), Nanostructured Material, Elsevier, London, 2009, pp. 1–50.
[17] J. Bauch, J. Brechbühl, H.J. Ullrich, G. Meinl, H. Lin, W. Kebede, Cryst. Res. Technol. 34 (1999) 71.
[18] S.I. Prokofjev, B.B. Straumal, I.N. Zorin, Zavodskaya Laboratoriya 50 (1984) 45, in Russian.
[19] S.V. Divinski, M. Lohmann, Chr. Herzig, Acta Mater. 49 (2001) 249.
[20] S.V. Divinski, J. Ribbe, G. Schmitz, Chr. Herzig, Acta Mater. 55 (2007) 3337.
[21] A.D. Le Claire, Br. J. Appl. Phys. 14 (1963) 351.
[22] G. Barreau, G. Brunel, G. Cizeron, P. Lacombe, C.R. Acad. Sci. (Paris) C270 (1970) 516.
[23] S.V. Divinski, G. Reglitz, G. Wilde, Acta Mater. 58 (2010) 386.
[24] P.L. Williams, Y. Mishin, Acta Mater. 57 (2009) 3786.
[25] L. Klinger, E. Rabkin, Acta Mater. 47 (1999) 725.
[26] S.V. Divinski, J. Geise, E. Rabkin, Chr. Herzig, Z. Metallknd. 95 (2004) 945.
[27] S.V. Divinski, M. Lohman, Chr. Herzig, Interface Sci. 11 (2003) 21.
[28] J. Sommer, Chr. Herzig, T. Muschik, W. Gust, Acta Metall. Mater. 43 (1995) 1099.
[29] M.R. Sørensen, Y. Mishin, A.F. Voter, Phys. Rev. B 62 (2000) 3658.
[30] A. Suzuki, Y. Mishin, Interface Sci. 11 (2003) 131.