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Orientation Dependence of ^{195}Au and ^{64}Cu Diffusion along Symmetric [001] Tilt Grain Boundaries in Cu

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Abstract

Under identical experimental conditions the grain boundary (gb) diffusion product $P=s\delta D_{gb}$ of ^{195}Au in Cu along a series of 12 different symmetric [001] tilt boundaries, exactly characterized by the Kossel–technique, with tilt angles near to the ideal $\Sigma = 5\Theta = 36.9°$ (310) CSL–boundary ($\Delta\Theta = 6°$) was measured as a function of temperature and tilt angle. In the temperature range of (0.48–0.78) T_m(Cu) the orientation dependence P(Θ) shows a characteristic cusp not exactly at but slightly below the ideal Σ=5 CSL–gb for all investigated temperatures. The reason for this apparent result is discussed.
The activation enthalpy Q_{gb} of Au gb diffusion shows a strong orientation dependence at sufficiently low temperatures. With increasing temperature a negative deviation from a straight Arrhenius behaviour is observed and the orientation dependence of Q_{gb} disappears. This result indicates to a temperature induced change in the gb structure.

Introduction

Numerous theoretical and experimental work on the structure and structure–dependent properties of gbs, like energy or diffusion, has been done in the past. For low–angle boundaries, the Read–Shockley model [1] had very early brought about a satisfactory, structure–related understanding of the way in which the properties of a gb vary with its misorientation. Attempts to develop a similar understanding for high–angle gbs produced only partially encouraging results but no complete success. As an example, the experimental investigations on the misorientation dependence of diffusion in <001> tilt boundaries are leading to contradictory results so far. Since several authors [2] [3] established a relatively continuous behaviour of the misorientation dependence (which can be described on the basis of the structural unit model [4] [5]), other authors [6] found well–pronounced cusps for gbs with a high density of coincidence site lattice points ($1/\Sigma$). Therefore it's still an open question whether gbs with low Σ show cusps due to their good crystallographic matching of the adjacent crystals. In most cases measurements as well as calculations are too widely spaced to reveal really narrow cusps.
The present paper reports on detailed measurements of gb self– and impurity diffusion along symmetric [001] tilt gb's close to one special boundary, the $\Sigma = 5, \Theta = 36.9°$ (310) [001] tilt boundary. According to theoretical predictions [7] [5] [8] as well as experimental observations [9] this special boundary with a low Σ consists of only one structural unit, the so–called 'capped trigonal prism'. The measurements were performed along a series of 12 different symmetric [001] tilt boundaries with tilt angles $33.21° \leq \Theta \leq 39.26°$ as a function of temperature and tilt angle using the high sensitive radiotracer method combined with serial sectioning technique as the most accurate method for gb diffusion measurements.

Experimental details

High purity Cu–bicrystals of two different original Cu materials were grown by using the Bridgman method. Subsequently the Kossel technique was applied to determine the exact crystallographic orientation. As an advantage of this technique not only the tilt angle Θ could be determined within an error of a few hundreths of a degree, but unavoidable small deviations (2nd tilt component perpendicular to the [001] tilt axis, named Θ', and a small twist component, named Φ) from an exact [001] tilt orientation, also. The deviations Θ' and Φ did not exceed one degree for most of the bicrystals. Both tasks, the growth of the bicrystals and their crystallographic characterisations were performed in Chernogolovka.

The specimens, cut from the bicrystals, were preannealed first at 1173 K and furthermore under the conditions (temperature T and time t) of the intended diffusion anneals in order to achieve equilibrium gb segregation of spurious impurities and to proove the stability of the gb. Carrier free ^{195}Au (half-life 183 days) and ^{64}Cu (half-life 12.7 h) were used for the diffusion experiments. The radiotracer was dropped onto the sample surfaces from an acid solution. Subsequently the measurements were performed in the temperature range of (780 – 1030) K. Sealed in quartz tubes under purified argon atmosphere ($\approx 10^2$ Pa), 6–8 samples, different in Θ, were diffusion annealed at each temperature simultaneously. This procedure allowed for absolute identical experimental conditions, which were necessary to compare results from specimens with different misorientations in a range of a few hundreths of a degree. Standard sectioning technique [10] and measuring the tracer concentration in a liquid scintillation counter completed the experimental work. Typical diffusion profiles are shown in figure 1.
The gb product $P = s\delta D_{gb}$ (segregation factor s≡1 for gb self–diffusion and $2 \leq s \leq 6$ for Au in Cu [11]; $\delta \equiv 0.5$ nm ≡ gb width; D_{gb} ≡ gb diffusion coefficient) was determined from the profiles using Suzuoka's equation for gb diffusion from an instantaneous source [12].

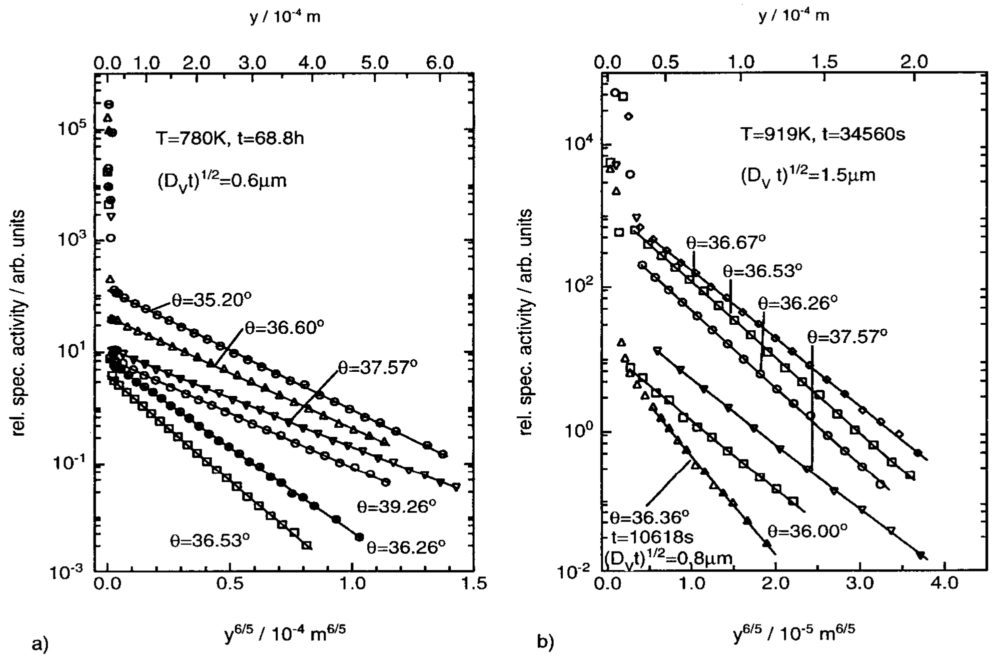

Fig. 1a, b: Penetration profiles of ^{195}Au (a) and ^{64}Cu (b) in symmetric [001] Cu tilt gb's.

Results and discussion

The results of this study are given in figures 2 and 3. It is seen that P shows the same characteristic orientation dependence for gb self– as well as for gb impurity diffusion of Au in Cu. Due to the short half-life of ^{64}Cu the P(Θ) dependence was only measured once at a comparatively high temperature. The qualitatively identical orientation dependence and the small segregation factors of Au in Cu prove that ^{195}Au is a meaningful substitute for the non handsome ^{64}Cu–tracer. Furthermore this orientation dependence is independent of the purity of the used Cu–material (fig. 2a). Both facts clearly show that segregation effects cannot hold as arguments to explain the observed sharp variations in P.

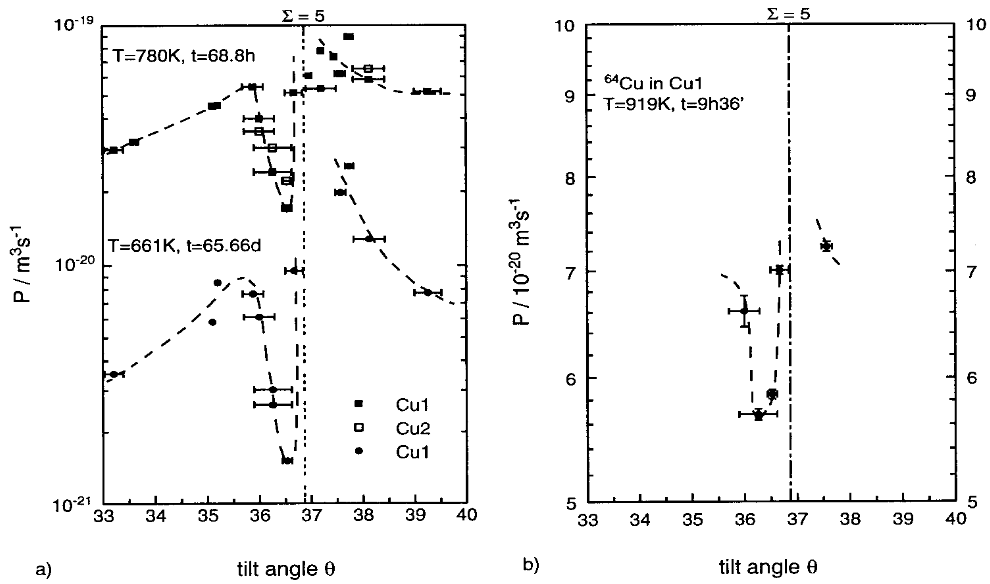

Fig. 2a,b: Orientation dependence of gb diffusion product P(Θ) for different temperatures. a) ^{195}Au in Cu [001] tilt gbs; b) ^{64}Cu in Cu [001] tilt gbs. The given errors of Θ refer to the variation in the tilt angle along the whole original bicrystal of 10–20 cm length.

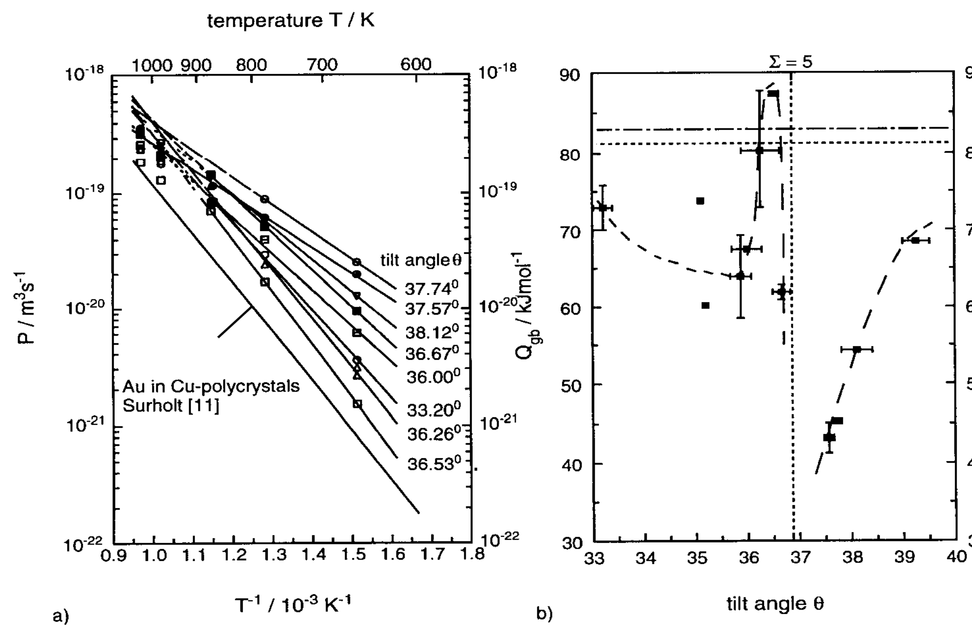

Fig. 3a, b: Arrhenius diagram of the gb diffusion product P for different bicrystals (a) and orientation dependence of the activation enthalpy Q_{gb} (b) for sufficiently low temperatures.

In the temperature range of (0.48–0.78)T_m(Cu) the orientation dependence P(Θ) shows a characteristic cusp not exactly at but slightly below the ideal Σ=5 CSL–gb. This cusp becomes more pronounced with decreasing temperature. A critical look to the misorientation of the used bicrystals reveals that the shift of the cusp seems to be apparent only and might be due to the unusual high twist component ($\Phi = 1.85°$) and its impact on the diffusivity of the sample with $\Theta = (36.67 \pm 0.17)°$. Here, Φ is more than one degree larger than the average twist component of the other bicrystals. This supports the idea that the additionally inserted secondary gb–screw–dislocations [13] seem to enhance the gb diffusion drastically. On the other hand, small tilt deviations Θ' show no comparatively significant influence on P. Similar results were recently found in calculations by Nomura et al. [14]. They reported an unusual fast diffusion along localized primary screw dislocations in small angle twist boundaries.
For all investigated bicrystals the temperature dependence of P does not show a straight line but a more or less pronounced downward curvature for the Arrhenius plot, fig. 3a. The average activation enthalpy Q_{gb} of P is decreasing with increasing temperature. This fact could be taken as a first direct indication for temperature induced structural changes in these tilt boundaries. For sufficiently low and for sufficiently high temperatures the P(T) dependence can be approximated by a straight Arrhenius–line. In the low temperature part P_0 and Q_{gb} again show a characteristic orientation dependence. This is consistent with the P(Θ) results: the gb's with low P–values show high activation enthalpies and vice versa (fig. 3b). At the same time a huge variation of Q_{gb} of more than 40 kJmol^{-1} is found within an tilt angle interval of only 1°. Such huge variations in Q_{gb} cannot be explained within the existing models for high angle gbs.
On the other hand the Arrhenius parameters determined from the high temperature data of P(T) do not show any characteristic orientation dependence. Here, relatively low values of about $P_0 \approx 10^{-17} m^3 s^{-1}$ and $Q_{gb} \approx 40 kJmol^{-1}$ are estimated with no significant variation in the measured misorientation interval. This might be the second indication for temperature induced structural changes in the tilt boundaries: due to characteristic ordered structure of the tilt boundaries only well defined atomic jumps occur which determine the gb diffusion in the low temperature range. With increasing temperature the gb's become more random and diffusion is determined by the same atomic jump process(es) for all gb's.

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References

[1] W. T. Read and W. Shockley: Phys. Rev. **78** 275 (1950).
[2] J. Sommer, C. Herzig, S. Mayer and W. Gust: Defect and Diffusion Forum **66-69** 843 (1989).
[3] Q. Ma and R. W. Balluffi: Acta metall. mater. **41** 133 (1993).
[4] A. P. Sutton: Phil. Mag. A **46** 171 (1982).
[5] A. P. Sutton and V. Vitek: Trans. R. Soc. Lond. A **309** 1, 37 und 55 (1983).
[6] A. N. Aleshin, B. S. Bokshtein and L. S. Shvindlerman: Sov. Phys. Solid. State **19** 2051 (1977).
[7] M. F. Ashby, F. Spaepen and S. Williams: Acta metall. **26** 1647 (1978).
[8] R. W. Balluffi and P. D. Bristowe: Surf. Sci **144** 28 (1984).
[9] F. Cosandey, S.-W. Chan und P. Stadelmann: Metall. Trans. A **21a** 2299 (1990).
[10] J. Sommer and Chr. Herzig, J. Appl. Phys. **72**, 2758 (1992).
[11] T. Surholt, Yu. M. Mishin and Chr. Herzig, Phys. Rev. B **50**, 3577 (1994).
[12] T. Suzuoka, J. Phys. Soc. Japan **19**, 839 (1964).
[13] T. Schober and R. W. Balluffi: Phil. Mag. **21** 109 (1970).
[14] M. Nomura and J. B. Adams: J. Mater. Res. **7** 3202 (1992).