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HETERO PHASE BOUNDARIES IN THE SILVER-NICKEL SYSTEM

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RESUME

Les relations d'orientations préférées de joints de grains entre phases hétérogènes ont été déterminées dans le système argent/nickel en utilisant la méthode de rotation de sphères selon Gleiter. La comparaison avec d'autres études de rotation de sphères démontre une grande similarité entre les systèmes étudiés jusqu'à présent, inclus les systèmes métaux sur oxydes et sur alcalihalogènes. En tout, 33 types d'orientations ont été trouvés; ils peuvent être réduits à 10 types de joints de grains "élémentaires", si "facetting" et "twinning" aux joints sont admis. Dans presque tous les systèmes l'orientation la plus dominante est celle de cube-sur-cube. L'analyse de joints préférés "élémentaires" démontre qu'ils ne sont pas conformes au "Lock-in" ou au modèle conventionnel de coïncidence, mais qu'ils peuvent être compris comme joints de coïncidence avec un rayon de tolérance très étendu. On suppose que celle "coïncidence" étendue ne pourrait pas être déraisonnable pour des paires de matériaux avec lieu faible entre les phases.

ABSTRACT

Using Gleiter's sphere rotation technique, the orientation relations of preferred heterophase boundaries have been determined in the system silver/nickel. Comparison with other sphere rotation studies shows great similarities between all systems studied so far, which include metals on oxides and on alkali halides. In all, 33 orientation types have been found; these can be reduced to 10 "elementary" boundary types if facetting and twinning at the boundary are admitted. In almost all systems, cube-on-cube is the most dominant orientation. Analysis of the preferred "elementary" boundaries shows that they do not conform to the lock-in or to the conventional coincidence model, but that they could be understood as coincidence boundaries with a considerably extended tolerance radius. It is suggested that such "extended coincidence" might not be unreasonable for pairs of materials with weak interphase bonding.

INTRODUCTION

For boundaries between crystals of the same material, the relation between the structure or the crystallography of the boundaries and their specific energy has been investigated in considerable depth. For heterophase boundaries, the state of knowledge is still rather rudimentary. In particular, most of the empirical information concerns boundaries between very unlike materials such as metals against oxides or alkali halides, and little information is available for boundaries between mutually insoluble metals. The pair silver/nickel is a good representative of this category. This paper describes experiments on Ag/Ni boundaries following the "sphere rotation" concept proposed by Herrmann et al. (1)

EXPERIMENTAL

Heterophase boundaries between silver and nickel were formed by sintering about 10^7 monocrystalline silver spheres of $\sim 2\mu\text{m}$ diameter onto a nickel (110) substrate. During sintering (45 hrs at 900°C), the spheres rotate so as to assume orientations of low

specific phase boundary energy. The relative frequencies of the final orientations are determined, using an x-ray texture goniometer, by recording the Ag{111} pole figure. The pole intensities reflect the population densities of the various boundary orientations which are assumed to be proportional to their specific energies.

Except for special orientations, each silver sphere gives four {111} reflexes, some of which may coincide with reflexes due to other orientations. Any such coincidences have to be deconvoluted to extract the true orientation distribution from the pole figures. In the present case, all observed poles could be accounted for by eight different sphere orientations (each of which was manifested by the required four poles). These orientations are listed in table I.

Table I. Orientation relationships for Ag-Ni boundaries derived from X-ray pole figures:

Nr.	Parallel planes		Parallel directions *		angle $\langle 011 \rangle_{Ag} \wedge \langle 011 \rangle_{Ni}$	intensity
	Ag	Ni	Ag	Ni		
I	(011)	(011)	[100]	[100]	0°	very strong
II	(211)	(011)	[$\bar{1}\bar{1}\bar{1}$]	[100]	55°/[01 $\bar{1}$]	medium
III	(411)	(011)	[$\bar{1}\bar{2}\bar{2}$]	[100]	71°/[01 $\bar{1}$]	weak
IV	(511)	(011)	[$\bar{2}\bar{5}\bar{5}$]	[100]	74°/[01 $\bar{1}$]	medium
V	(611)	(011)	[$\bar{1}\bar{3}\bar{3}$]	[100]	77°/[01 $\bar{1}$]	very weak
VI	(011)	(011)	[4 $\bar{1}\bar{1}$]	[100]	71°/[011]	medium
VII	(811)	(011)	[01 $\bar{1}$]	[100]	90°/[011] + 10°/[01 $\bar{1}$]	medium
VIII	(111)	(011)	[01 $\bar{1}$]	[100]	90°/[011] + 35°/[01 $\bar{1}$]	weak

* All orientations occur in equivalent pairs, of which only the first is stated here.

DISCUSSION

The most prominent orientation by far is the "cube-on-cube" *) type, which is also found with equal prominence in the systems Au/MgO, Cu/MgO, Au/LiF, Au/NaCl, Au/KCl (2), both in sphere rotation experiments and in thin film epitaxy, e.g. (3-8). It occurs also in the system Ag/NaCl (9), but with lower frequency.

The other seven orientations in table I, which are much less populated than the cube-on-cube type, also have correspondences among the other systems studied by the sphere-on-plate technique, or by epitaxy experiments. The occurrence of these boundary orientations in very different systems strongly suggests the existence of some general principle governing the architecture of low energy heterophase boundaries.

However, when the observed boundaries are analyzed in terms of the density of near coincidences (10), or of configurations allowing lock-in between rows of atoms in the planes adjacent to the boundary (2), it is found that neither of these two models can account for the selection of the observed orientations as low energy boundaries. (The analysis, which is published elsewhere (11), considers the density of "nearly coincident" sites - within a tolerance radius of 2.5% of an atomic diameter - on both sides of an unrelaxed boundary between perfect half-crystals of the two materials, and the strain required to bring the two lattices into perfect coincidence at the corners of the "near coincidence" cells is also taken into consideration.) In particular, the cube-on-cube boundary has decidedly lower coincidence density and lower density of lock-in configurations than boundaries which are formed with much lower frequency.

*)used here for all boundaries with zero rotational misorientation between the two lattices, regardless of the inclination of the boundary plane.

Conversely, when analysing the geometry of all theoretically possible boundaries of moderately simple crystallography, one finds boundaries which have much more favourable coincidence density or lock-in configurations than any of those observed in the experiment.

Thus we are forced to conclude that the often-invoked principles of "near coincidence" or "lock-in", when applied in their customary form, cannot correctly predict the boundary types which are formed when nature is left to its own preferences. This is similar to the conclusion of Sutton and Balluffi (12) in a recent analysis of the crystallography of a large variety of observed homo- and heterophase boundaries. Likewise, it is impossible to account for the boundaries formed in the Ag/Ni system in terms of the excess volume model (13, 14) or in terms of a model based on the minimisation of the total surface energy of the spheres (15).

The x-ray pole figure technique defines the orientation relation between the bulks of the substrate and of the sphere, and in deriving the boundary structure it is normally assumed that the boundary plane is identical to the plane of the substrate surface. If the possibilities of faceting of the boundary plane and of twinning in the material adjacent to the boundary (fig. 1) are admitted, many apparently complicated boundaries can be reduced to the cube-on-cube type. The remainder are found to have a common characteristic in that either the $\{111\}$ or the $\{211\}$ plane of a $\Sigma=3$ twin of the one material faces a low index plane such as $\{100\}$ or $\{011\}$ of the other (fig. 2). The occurrence of such "half-twin configurations" is noted here in a purely phenomenological sense. No physical explanation can be given at this time for this "half-twin configuration", but it seems to have at least heuristic value: of the 33 different boundary configurations that occur in all the systems which have been studied by sphere-on-plate experiments, 15 can be described as variants of the "half-twin"-type, and 18 as variants of the cube-on-cube type. Under "variants", we subsume faceting of the boundary, twinning of the material adjacent to it, various boundary planes $[(100), (110), (111)]$ in the cube-on-cube orientation, and various rotational displacements of the one crystal against the other in the boundary plane (fig. 3). This reduces the plurality of observed (macroscopic) orientation types to a basic set of only 10 (microscopic) boundary orientation types (cf. Table II).

Table II. Crystallographic characterization of the basic set of boundary orientation types:

Nr.	Parallel planes	Parallel directions*
1.	cube-on-cube	
2.	$(111)_s \parallel (100)_p$	$[01\bar{1}]_s \parallel [01\bar{1}]_p$
3.	$(211)_s \parallel (100)_p$	$[01\bar{1}]_s \parallel [01\bar{1}]_p$
4.	$(111)_s \parallel (011)_p$	$[01\bar{1}]_s \parallel [01\bar{1}]_p$
5.	$(211)_s \parallel (011)_p$	$[01\bar{1}]_s \parallel [01\bar{1}]_p$
6.	$(011)_s \parallel (100)_p$	$[01\bar{1}]_s \parallel [01\bar{1}]_p$
7.	$(100)_s \parallel (100)_p$	$[01\bar{1}]_s \parallel [010]_p$
8.	$(111)_s \parallel (100)_p$	$[01\bar{1}]_s \parallel [010]_p$
9.	$(211)_s \parallel (100)_p$	$[01\bar{1}]_s \parallel [010]_p$
10.	$(111)_s \parallel (011)_p$	$[01\bar{1}]_s \parallel [100]_p$

* The subscripts s and p refer to planes and directions in the lattices of the spheres and plates.

Although we have to bear in mind that some of these microscopic boundary types remain hypothetical until checked by electron microscopy, they form, at the moment, the simplest set of elementary boundary configurations from which the whole range of observed orientations might be constructed. Therefore it is of interest to examine

Fig. 1

Microtwinning and facetting of the $(11\bar{1})_{Au} \parallel (111)_{LiF}$, $[01\bar{1}]_{Au} \parallel [01\bar{1}]_{LiF}$ boundary to form cube-on-cube boundaries.

Fig. 2

"Half-twin" configuration: boundary $(111)_{Ag} \parallel (011)_{Ni}$, $[01\bar{1}]_{Ag} \parallel [01\bar{1}]_{Ni}$

Fig. 3

Two observed twist variants of a Ag/NaCl boundary:

- the simple cube-on-cube-type and
- a twist variant of this boundary (rotation of 45° around the plate normal)

Fig. 4

Illustration of the coincidence site density and the lattice misfit strain. The significance of the symbols is explained in the text.

their possible structures in some more detail. For example, how are we to understand the apparent preference for cube-on-cube boundaries in systems of such widely varying lattice misfit (1.3 to 35.1 %)? Does it perhaps indicate that the coincidence principle should be applied with a substantially extended tolerance radius?

An analysis was made of the microscopic boundary types for each of the material pairs in which they occur, each pair being characterized by different ratios of the lattice periodicities on the "sphere" and on the "plate" side of the boundary plane (fig. 4). To allow quantitative comparisons, the coincidence density of the heterophase boundary is characterized by the square root of the product of the coincidence densities on either side of the boundary plane,

$$1/\Sigma^* = 1/(\Sigma_1 \cdot \Sigma_2)^{1/2} \quad (1)$$

"Coincidence" is assumed to exist when two lattice points are within a tolerance width τ of each other. Obviously, the larger τ , the higher will be the coincidence density, but also the strain required to bring the two lattices to coincide exactly at the coincidence points; this strain is a measure of the misfit energy of the boundary, or of its geometrically necessary Burgers vector content. We characterize this strain by

$$\epsilon = (\epsilon_1^2 + \epsilon_2^2)^{1/2}, \quad (2)$$

$$\text{where } \epsilon_1 = 2\tau_1/(n_1a_1 + m_1b_1) \text{ and } \epsilon_2 = 2\tau_2/(n_2a_2 + m_2b_2), \quad (3)$$

and where τ_1 and τ_2 are the components of the misfit vector and n_1a_1 and n_2a_2 are the edges of the coincidence cell in one of the adjoining lattices, and m_1b_1 , m_2b_2 refer to the other lattice (cf. fig. 4).

Customarily, the tolerance limit for coincidence is taken as 0.02. In the boundaries under consideration, this results in unreasonably large coincidence cells for some of the highly populated cube-on-cube boundaries, with values of Σ^* of the order of several hundred or above one thousand. Such large coincidence cells (small coincidence densities) must be considered physically meaningless. In the case of homophase (grain) boundaries, low boundary energies have been found in the range $3 \leq \Sigma \leq 11$. For the set of "elementary" boundaries considered here, a value of $\epsilon = 0.064$ must be admitted in order to bring the maximum value of Σ^* down to 42, and $\epsilon = 0.215$ would be required to bring it down below 15 - but once we get below this point, we find that no boundaries are left with coincidence densities lower than $\Sigma^* = 6$ (fig. 5).

Fig. 5
Number of irreducible boundaries with Σ^* below stated ϵ

CONCLUSIONS

Two alternative conclusions can be drawn from this analysis:

(i) If large tolerance widths are considered unlikely, one has either to accept that no physical explanation is at hand for the formation of the 10 elementary boundary types which occur in all systems studied so far, or

(ii) if one is willing to experiment with an "extended coincidence" concept, one can ask whether the tolerance limit of 21% is reasonable in the light of other known facts. Somewhat misleadingly, lattice misfits are usually expressed as uniaxial strains, $\epsilon_1 = \tau_1/(n_1 a_1)$, neglecting the two-dimensional nature of misfit at interfaces. To make these customary values comparable to ours, they have to be multiplied by $\sqrt{2}$. The following facts may be recalled to put the idea of "coincidence" phase boundaries with such a large misfit into perspective:

(a) in monolayer epitaxy, coherency between substrate and film breaks down at a linear misfit of about 18%, which in our terms corresponds to $\epsilon = 25.4\%$ in two dimensions (16)

(b) the final breakdown of coherence at precipitate-matrix interfaces occurs at about the same level of misfit strain (17);

(c) a two-dimensional misfit of 21.5% would correspond to a density of misfit dislocations of one Burgers vector in 7 spacings. This is the density of a 6.7° small angle boundary, albeit with different Burgers vectors. Note that all the systems reviewed here have weak bonding between the phases ($98 - 238 \text{ mJ/m}^2$) (11); this will tend to delocalize the cores of misfit dislocations and reduce the strain energy. Recent TEM studies (18) on oxide/metal interfaces with misfit values approaching the limit postulated here have demonstrated the absence of long-range stress fields corresponding to localized interface dislocations.

We believe that such an extension of the coincidence concept may be worth further consideration, especially in the case of weak - though not vanishing - interphase bonding. It is hoped to gain further information from HREM and computer simulation studies.

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