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ENERGY AND STRUCTURE OF INTERPHASE BOUNDARIES

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Abstract - The energy of interphase boundaries between noble metals (Au, Cu) and various ionic crystals (LiF, NaCl, KCl, MgO, Al_2O_3, mica) was investigated by means of the plate/sphere method. The results obtained suggest that the coincidence model is not applicable to describe the structure of interphase boundaries of low energy between noble metals and ionic crystals. The atomic structure of the low energy boundaries observed may be understood in terms of the proposed "lock-in model". Moreover the energy of interphase boundaries seems to be strongly dependant on the temperature. Measurements of the energy of Cu/MgO and Au/Al_2O_3 interphase boundaries at 550° C and 950° C indicate the existence of a transition from an energetically anisotropic boundary structure into an isotropic one.

Introduction

Whereas structural models of grain boundaries in metals (1), (2) and ceramic materials (3) are well developed, much less is known on the structure and properties of interphase boundaries. This paper reports measurements of low energy interphase boundaries between Au or Cu and various ionic crystals (LiF, NaCl, KCl, MgO, Al_2O_3, mica). The ionic crystals were selected in such a manner that the effects of lattice mismatch (varied between 1.3 and 35.1 %), the effect of lattice structure (cubic/cubic and hexagonal/cubic), chemical effects and the effect of the temperature could be studied systematically (4). About 10^7 isolated and crystallographically randomly oriented, small ($\sim 1\,\mu m$) spherical single crystals (metal) were sintered onto a flat single crystal substrate (ionic crystal) (5). In order to minimize the interfacial energy of the boundaries formed between the small crystals and the substrate, the spheres may rotate at elevated temperatures (550° C - 950° C) into orientation relationships of low energy. The resulting alignment of the crystals can be measured by the conventional methods of X-ray texture analysis.

Experimental Results

Interphase boundaries of low energy are characterized by the parallelism of low index lattice planes and close packed directions in both crystals (for detailed description see Ref. (4)).
The number of the experimentally found interphase boundaries of low energy is dependant on

- the lattice mismatch $(a_p - a_s) / a_p$, (a_p, a_s : lattice parameters of the plate p and the sphere s respectively)
  and the lattice structure
  $a_p - a_s$ small : many orientation relationships (Au/LiF up to 6)
  $a_p - a_s$ large : only the cube/cube orientation (Au/KCl)
  cub./hex. : partly no orientation relationship of low energy (Cu/Al_2O_3, Au/mica)

- chemical effects

  Ag/NaCl : nearly all spheres in the cube/cube orientation (5)

  Au/NaCl : very few spheres in the cube/cube orientation

  although the lattice constants of Ag and Au are nearly identical (< 0.2 % difference),

- the temperature

  Cu/MgO, Au/Al_2O_3 : at 950^o C no orientation relationship of low energy, at 550^o C special orientations

  Au/MgO : at all temperatures investigated (550^o - 900^o C) special orientations.

Discussion

1) Temperature = const. = 550^o C

The results obtained suggest that boundary models based on the coincidence concept are not applicable to interphase boundaries of low energy between metals and ionic crystals. For example, Fig.1 shows a schematic cross section through a coincidence boundary between Au and KCl. This boundary was not observed experimentally to be of low energy, whereas the highly symmetric cube/cube boundary was found to be energetically preferred (Fig. 2), although the interfacial mismatch is 35.1 %.

Fig.1

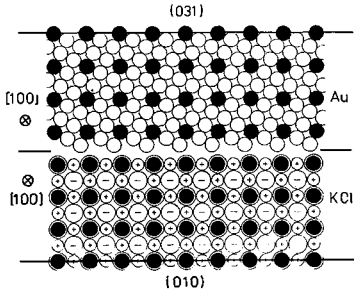

Fig.2

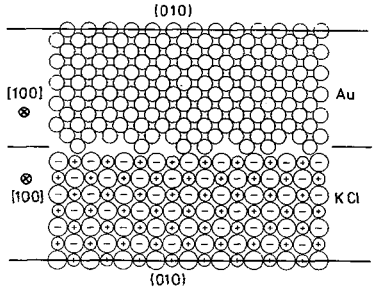

Fig. 1: Schematic cross section through a coincidence boundary between Au and KCl. The atoms (ions) at coincidence sites are indicated in black. This boundary was not observed to be of low energy.

Fig. 2: Schematic cross section through the low energy boundary observed between Au and KCl. The two crystals have the cube/cube orientation relationship ($(010)_{Au} \parallel (010)_{KCl}$ and $\langle 100 \rangle_{Au} \parallel \langle 100 \rangle_{KCl}$).

Also for systems with small lattice mismatch (e.g. 1.3 % Au/LiF) expected coincidence boundaries (Σ= 5, 7, 9, 11 etc.) did not result in low energy boundaries and the low energy boundaries observed did not correspond to high coincidence orientation relationships (4), (6). Assuming that the plane of the interphase boundary-between a metal and a ionic crystal lies parallel to the low energy (cleavage) plane of the ionic crystal (for example {100} for cubic crystals), the "surface" of the ionic crystal may be described in terms of a set of close packed rows of atoms separated by relatively deep "valleys". The experimentally observed low energy boundaries are identical with those configurations for which the closest packed rows of the atoms at the "surface" of the metal form a "lock-in configuration" with the valleys of the "surface" of the underlying ionic crystal.

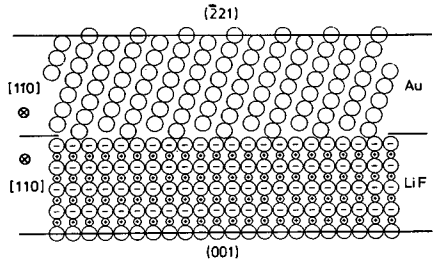

Fig. 3 :
"Lock-in" structure of one of the low energy boundaries observed between Au and LiF.

With increasing lattice mismatch the width of the "rows" and the "valleys" becomes gradually incompatible. So the number of low energy "lock-in" configurations decreases
Chemical effects and temperature effects are not incorporated in the lock-in model.

2) Temperature = variable (550^{o} C - 950^{o} C)

At 900^{o} C the boundary energies of the systems Cu/MgO and Au/Al_2O_3 became independent of the relative orientations of the Cu (Au) crystals with respect to the MgO (Al_2O_3) lattice. At lower temperatures (550^{o} C) special orientation relationships were found.

Low energy interphase boundaries can only exist, if the atomic boundary depends on the orientation of the two crystals on both sides. In other words, if the boundary is ordered, hence, the observed transition of the energetically anisotropic boundary structure to an isotropic one may be interpreted in terms of a order/disorder transformation of the structure of the interphase boundaries. Qualitatively, such a transformation may be understood in energetic terms as an effect of the entropy of the boundary, similar to phase transformations at free surfaces.

This transition was not observed in all systems investigated. For example the interphase boundaries between Au and MgO are ordered at all temperatures investigated (550^{o} C - 950^{o} C), whereas in the system Cu/Al_2O_3 no orientation relationships of low energy were found. This seems to be correlated with the lock-in model in the manner that systems with small mismatch (Au/MgO) are ordered up to high temperatures whereas systems with a large mismatch disorder at high temperatures (Cu/MgO, Au/Al_2O_3).

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