THE SIGNIFICANCE OF THE STRUCTURE OF INTERNAL INTERFACES FOR THE PROPERTIES OF MATERIALS

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Abstract - The methods available to study the correlation between properties and atomic structure of interfaces are critically assessed by considering their specific limitations.

Studies of the behaviour of grain boundaries by means of the plate/sphere method are reported indicating that a few boundaries exhibit special properties which were observed for a particular interface independently of the property investigated (e.g. energy, corrosion, embrittlement). Most special boundaries were of high coincidence type. But not all high coincidence boundaries showed special properties. It seems the interatomic interaction which selects between special and "non-special" high coincidence boundaries. The properties of boundaries deviating from special misorientations were found to be controlled by the presence of (secondary) boundary dislocations.

Systematic studies of the properties of interphase boundaries between ionic crystals and noble metals showed that coincidence misorientations do not result in special behaviour which was observed only if close packed rows of atoms at the "surfaces" of the metal crystals "locked" into the "valleys" between close packed atomic rows at the "surfaces" of the ionic crystals ("lock-in" model of interphase boundaries).

The basic idea of nanocrystalline materials is to generate a new type of solids by exploiting the highly distorted atomic structure existing in the core of grain (interphase) boundaries. This is achieved by reducing the crystal size of a polycrystalline material to a few nanometers (nanocrystalline material) so that the volume fraction occupied by interfaces (interfacial component) and crystals are comparable. The interfacial component of such a material consists of many (typically 10^{19} cm^{-3}) boundaries. As the structures of these boundaries are all different, the interfacial component (i.e. the sum of all boundary structures) resembles a frozen gas. Experimental studies of nanocrystalline materials support this hypothesis and suggest that interfaces may be used as a structural component for generating a gas-like solid state structure.

INTRODUCTION

The object of this contribution is to assess some aspects of the correlation between the atomic structure and the properties of interfaces. For previous reviews we refer to the paper by Pumphrey (1) and Goodhew (2).

The main content of this presentation was set forth in papers which have appeared or will appear elsewhere. Here a summary will be given of the points which seem most pertinent to this symposium.

MICROSCOPIC STATISTICAL EXPERIMENTS VERSUS MACROSCOPIC BICRYSTAL MEASUREMENTS

Studies of the correlation between boundary structure and properties by means of bicrystals are carried out by growing from the melt a series of crystallographically well characterized bicrystals, the properties of which are measured (3) as a function of the crystallographic parameters. Although measurements of this type have made outstanding contributions to our present understanding of interfaces (c.f. for example in classical papers by Aust et al. (4), (5)), the method suffers primarily from three disadvantages. Growth from the melt is generally not applicable to inter-phase boundaries. As a consequence of the substructure present in the crystals, any boundary of macroscopic dimensions represents a mixture of different boundary structures. Hence, the properties measured by using macroscopic boundaries are in reality average values. The time consuming growth procedure of a bicrystal limits the number of measurements and, therefore, reduces the statistical confidence of the property-structure correlation derived. For the same reason, practically all measurements are biased in the sense that only specific (e.g. [110] tilt) boundaries have been investigated by the bicrystal method. As the selection of these boundaries is guided by a structural model, the danger of confirming pre-conceived ideas of the boundary structure is not unlikely. In order to remove these disadvantages, a statistical method has been proposed (6), (7). A large number ($10^4 \dots 10^7$) of grain boundaries is generated by sintering $10^4 \dots 10^7$ randomly oriented spheres of the same size ($0.5 \dots 100 \mu\text{m}$) onto a single crystal plate (Figs. 1 and 2a). During sintering, necks are formed between the spheres and the plate. Each neck contains a grain boundary the structure of which is determined by the orientation relationship between the plate and the sphere (Fig. 1). Hence, every specimen contains $10^4 \dots 10^7$ boundaries of different structures (Fig. 2a). As the small spheres are free of substructure, the structure of every boundary remains constant over the entire area of the neck*) and, hence, the two drawbacks of the bicrystal method mentioned above (poor statistics, varying boundary structure) are avoided.

Two further advantages of the plate/sphere method are that grain boundaries as well as interphase boundaries may be generated (7) and that all boundaries are tested simultaneously under identical conditions. Clearly the plate/sphere method is limited to systems that can be sintered.

GRAIN BOUNDARY STUDIES

The plate/sphere method has been applied so far to study the correlations between boundary structure and boundary energy (6), (8) corrosivity (9), embrittlement (10), mobility (11), pressure (12) and temperature (13). The effect of the atomic structure on the energy of a boundary was investigated by annealing the specimens at elevated temperatures. In order to minimize the free energy of the system, the spheres rotate (by a diffusional and/or grain boundary sliding process) into such orientations which result in boundaries of minimum energy (14) (Fig. 1). Hence, in a single experiment all low energy boundaries can be identified by measuring (e.g. by means of a standard X-ray method) the orientations of the spheres after long sintering times. If the plate/sphere method is slightly modified, other properties, such as boundary embrittlement, mobility or corrosivity may be investigated and correlated with the boundary structure. For example, boundary corrosion was stud-

*) Structural variations due to different rigid body translations (31) in different areas of the boundary (32) cannot be ruled out. However, after long annealing times, the boundary probably approaches the translation corresponding the minimum free energy.

ied by immersing a sphere/plate specimen (Fig. 2b) with randomly oriented spheres into a chemical solution causing grain boundary corrosion.

Fig. 1

Fig. 2

Fig. 1: Formation of a grain boundary (AB) during sintering of a single crystal sphere (b) onto a single crystal plate (p). The crystal lattice of b is tilted θ^0 with respect to p. A rotation of b may be achieved for example by a diffusive flux of atoms removing a wedge shaped piece of material from the left part and inserting it at the right part of the boundary.

Fig. 2: Schematic diagram of the specimens used for the investigation of grain boundary properties by the plate/sphere method (a). b shows the process of removing individual spheres by boundary corrosion.

As the corrosion process occurs under identical conditions at all boundaries simultaneously, the boundaries with highest corrosion rates will be corroded through first and, hence, the corresponding spheres fall off first. Then, the spheres (boundaries) with the next higher corrosion rate follow and so on. In other words, if one measures the orientation of the spheres that fall off first (last), one knows the boundaries of maximum (minimum) corrosion rate. The entire boundary corrosion spectrum may be obtained in the same way if the orientation of the spheres falling off is monitored as a function of the corrosion time. In a similar fashion the boundary embrittlement (10) and boundary mobility (11) as a function of boundary structure was measured. In these studies (10), (11) the specimens were vibrated to break the spheres off or annealed to induce interface migration. The results obtained may be summarized as follows. (i) A correlation between boundary structure and properties exists. The orientation relationships for which boundaries with special properties (low energy, corrosivity and embrittlement) were observed, were the same and did not depend on the property studied. (ii) Most (but not all) special boundaries were of the high coincidence (or short periodicity) type. This result is consistent with the findings obtained from bicrystal experiments (18) - (21). However, the plate/sphere experiments showed that not all coincidence (short periodic) boundaries exhibited special properties. In fact, the selection between high coincidence boundaries with and without special properties seems to depend on the interatomic interaction (Table I) as compositional changes vary the orientation relationships for which special boundaries are observed. Parallelity of close packed directions (planes) apparently favours special properties (19); (c.f. poster A3 of this symposium and also the "lock-in" model of the subsequent section).

Table I: Comparison of some special boundaries in different materials (8)

Coinc. density Σ (15)	Plate surface {110}						Ni (16)
	Cu	Ag	Cu 1% Au	Cu 20% Au	Cu 0.2 Bi		
3	+	+	+	+	+		+
9	+	+	+	+	-		-
11	+	+	+	+	+		-
17b	-	-	+	+	-		-
33	+	+	-	+	-		-

+ /- special properties (low energy) observed /not observed/.

(iii) The properties of boundaries deviating from these special orientation relationships are determined by defects in the boundary structure. For example, boundary corrosion (9) was observed to initiate and proceed along (secondary) boundary dislocations. If these corrosion channels overlap, the boundary exhibited high corrosivity. A similar mechanism was found to control the embrittlement of grain boundaries (10). In the vicinity of the (secondary) boundary dislocations a cloud of solute atoms (17) is formed which embrittles the boundary locally. With increasing deviation from a special orientation relationship the spacing between these clouds (and, hence, the spacing between the embrittled areas) decreases so that the boundaries become more and more brittle. Observations of this kind would have been difficult by using the bicrystal method because an accuracy of the orientation relationship of less than 1° is required and the growth of preliminary unknown non-coincidence boundaries of low energy, corrosivity and embrittlement would have been necessary.

INTERPHASE BOUNDARY STUDIES

The understanding between atomic structure and properties of interphase boundaries is less developed than for grain boundaries (22). Probably, the various types of interphase boundaries will behave differently depending on the chemical bonding and physical properties of the crystals involved, such as polarizability, conductivity, molecular weight etc. This makes it difficult to compare the results obtained for different types of interphases. A first systematic study has been carried out (23) of the correlation between boundary energy and atomic structure of interphase boundaries formed by noble metals (Au, Ag, Cu) and a variety of ionic crystals (LiF, KCl, NaCl, MgO, Al_2O_3 , mica). The boundaries were generated by the plate/sphere method using about 10^7 spheres with diameters of 0.5 to 1 μm . The results obtained led to the following correlations between the boundary structure and properties ((23), poster A9 of this symposium). (i) Interphase boundary models based on the coincidence concept are not applicable to interfaces between noble metals and ionic crystals because the low energy boundaries observed were not of the coincidence type and conceivable coincidence relationships did not result in low energy boundaries. For example, Fig. 3 shows the schematic cross section through a $\Sigma = 11$ coincidence boundary (50.5° rotation about $[110]$) between Au and LiF which was not observed to be low energy, whereas the nearby non-coincidence boundary (54.7° $[110]$ rotation) exhibited low energy (Fig. 4).

Fig. 3

Fig. 4

Fig. 3: Schematic cross section through a $\Sigma = 11$ coincidence boundary between Au and LiF. The circles shown represent the atoms and scale with the Goldschmidt radii of the ions and atoms of both materials. The atoms (ions) at coincidence sites are indicated in black. This boundary was not observed to be of low energy.

Fig. 4: Schematic cross section through the low energy boundary between Au and LiF next to the $\Sigma = 11$ interface (Fig. 3). The orientation relationship observed (54.7° $[110]_{\text{Au}} \parallel [110]_{\text{LiF}}$) results in parallelism of close packed planes ($(111)_{\text{Au}} \parallel (001)_{\text{LiF}}$) and close packed directions $[110]_{\text{Au}} \parallel [110]_{\text{LiF}}$. However, this low energy boundary is not a high coincidence interface. For clarity, all boundary atoms between the "lock-in" rows of the Au crystal are removed.

(ii) All low energy boundaries observed experimentally may be described by means of the following atomic structure (lock-in model). A low energy interphase boundary results, if close packed rows of atoms at the "surface" of the metal crystal fit into the "valleys" between the close packed rows of atoms at the surface of the ionic crystal.

Examples of this type of boundary structure are shown in Figs. 4,5,6

Fig. 5

Fig. 6

Fig. 5: "Lock-in" structure of one of the low energy boundaries observed between Au and LiF. Adjacent close packed rows of gold atoms lock into adjacent "valleys" between close packed rows at the (001) "surface" of LiF. The boundary is not a coincidence boundary.

Fig. 6 "Lock-in" structure of a low energy Au/LiF interface.

This structural model not only explains (23) the experimentally observed orientation dependence of the boundary energy but also the variation of the boundary energy as a function of the boundary inclination, the lattice mismatch between the two phases which was varied in these experiments from about 1 % to 35 %. It may be of interest to point out a conceivable correlation between these results and the observations mentioned in the previous paragraph. The lock-in structure results in parallelism of close packed directions and planes in both crystals (cf. Figs. 3,4,5 and 6). A similar preference for parallelism of close packed directions and planes was also noticed in special grain boundaries (cf. Table I).

NANOCRYSTALLINE MATERIALS

If the crystal size of a polycrystal is reduced to a few nanometers, the volume fraction occupied by the interfaces becomes comparable to the volume fraction of the crystals. In other words, in materials of this type (called nanocrystalline materials), the interfaces may no longer be regarded as perturbations of the crystalline structure. The sum of all interfaces (called the "interfacial component") represents a part of the microstructure just like the other more conventional structural components, such as precipitates, grains of a second phase etc. (24). One of the attractive features of such nanocrystalline materials may be that they provide a means of generating solids having an atomic structure with negligible short and long range order, i.e. the structure of a frozen gas (25), (26). If this were so, nanocrystalline materials would represent a solid state structure different from the two known solid states (crystalline and glassy state) to one of which all materials presently available belong. The reason for the formation of a frozen-gas-like structure in nanocrystalline substances may be rationalized as follows. In metals, and presumably also in many ionic and covalently bonded materials, grain boundaries are probably two-dimensional periodic structures the periodicity of which and, hence, the positional correlation function of the interfacial atoms depends on the orientation relationship between adjacent crystals. Hence, if a polycrystal contains many boundaries, and if the orientation relationship for every boundary is different, it comprises many different boundary structures. For example, if we consider a nanocrystalline material of crystallographically

Fig. 7 : Schematic structure of a nanocrystalline material. For simplicity, the boundary (crystal) regions are indicated by broken lines. The boundary atoms are marked in black for clarity. This does not imply that they are chemically different from the atoms in the crystals.

randomly oriented crystallites (the diameter is assumed to be 5 nm, the interfacial thickness 1 nm), it contains about 10^{19} interfaces per cm^3 which occupy a volume fraction of roughly 40 % (Fig. 7). As the orientation relationship (and, therefore, the boundary structure) are different (and uncorrelated) for every interface due to the random texture, the interfacial component of the nanocrystalline material considered is the sum of many (roughly 10^{19}) different and uncorrelated boundary structures. The average over so many uncorrelated structures is unlikely to exhibit any significant short or long range order, i.e. the atomic arrangement may be comparable to that of a frozen gas. In the case of a gas, it is the entropy which forces the systems to form a large number of atomic configurations; in the case of a nanocrystalline material, it is the boundary conditions (varying from interface to interface) which force the atoms in any interface to form different atomic arrangements. The results of structural studies by X-ray diffraction, transmission electron microscopy and Mössbauer spectroscopy seem to support the idea that the interfacial component of a nanocrystalline material has a structure with little short or long range order.

Fig. 8

Fig. 9

Fig. 8: X-ray diffraction curve (line C) of the interfacial component of nanocrystalline iron with a crystal size of about 6 nm. The line D represents the elastic X-ray diffraction of a gas of iron atoms with the same density as the material of curve C. E is the measured diffraction intensity of the iron glass $\text{Fe}_{80}\text{P}_{13}\text{C}_7$ (27) which is similar to that of molten iron (28).

Fig. 9: Mössbauer spectrum of the interfacial (A) and crystalline component (B) of the same nanocrystalline iron as in Fig. 8.

For example, Figs. 8 and 9 show the Mössbauer spectrum and the X-ray scattering curve of the interfacial component of 6 nm nanocrystalline iron. It may be seen (Fig. 8) that practically no interference effects due to short range order are present so that a frozen gas-like structure is suggested. Measurements of properties that are sensitive to short range order (e.g. saturation magnetization of 3d ferromagnets, specific heat and positron annihilation) suggest the atomic arrangement in nanocrystalline materials to be different from glasses and crystals. This result agrees with the structural investigations (Figs. 8 and 9) mentioned. For example, the saturation magnetization of α -iron which differs by only a few percent between the crystalline and the glassy state (29) but it changes by a factor ≈ 2 if one goes from the crystalline to the nanocrystalline state (25). The proposed interpretation of the effects reported in terms of the numerous atomic structures present in the interfaces is supported by the following two observations. Annealing of nanocrystalline materials at elevated temperatures converts them back into conventional iron as soon as

the boundaries are removed by grain growth. Measurements on isolated 6 nm iron crystals out of which the nanocrystalline materials were produced (cf. next paragraph) did not reveal any of these effects. In fact, all effects were only seen when a high density of grain boundaries was present.

For convenience, the nanocrystalline materials were generated by a modified method of powder metallurgy. The substance, (e.g. Fe) was evaporated in an inert (He) atmosphere (pressure 1 - 2 kPa). The evaporated material loses its thermal energy to the He and condenses in the form of small (1 - 10 nm) crystals (30). These crystals were accumulated and, subsequently, compacted mechanically (~ 70 MPa pressure) into nanocrystalline solids. This method was selected among other conceivable procedures for the following reasons. The size of the crystals can easily be manipulated by means of the evaporation rate and/or the He pressure, the resulting texture is random, and the concentration of the impurities picked-up during preparation is in the order of 10^{-3} . Clearly, nanocrystalline solids are not restricted to pure elements. Simultaneous or consecutive evaporation of several components lead to multiphase materials. One of the attractive features of multiphase nanocrystalline materials (nanocrystalline "alloys") is that one is not limited by miscibility of the components in the liquid state as in the case of melt spinning, for example. According to preliminary tests, nanocrystalline alloys can be generated irrespective of the type of chemical bonding, crystal structure, molecular weight, etc.

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DISCUSSION

K.L. Merkle: Would you care to speculate about the physics behind the great reduction in saturation magnetization of the sintered Fe polycrystals? What is the reduction in bulk density?

H. Gleiter: The reduction in the macroscopic density of the nanocrystalline material is about 50%. At present we do not know how much of this density deficit is due to small voids and how much results from the presence of the high density of interfaces. The observed reduction in saturation magnetization is assumed to be due to the deviation of nearest neighbour distances of the iron atoms in the boundary regions as compared to the perfect lattice. It has been shown theoretically that a change of a few percent in the spacing between neighbouring iron atoms results in a strong reduction of the magnetic moment. Perhaps the most well known experimental evidence for this effect is the change of the magnetic properties of iron when grown as a thin film epitaxially on suitable substrates so that the spacing between neighbouring iron atoms deviates from the equilibrium value in the bulk (cf. also the comments Prof. Andersen).

O.K. Andersen: I would like to remark that the magnetization of iron is highly sensitive to the local atomic coordination. For instance, at a pressure of 100

kbars, which merely decreases the lattice constant and the magnetization by a few percent, bcc Fe undergoes a first order phase transition and becomes hcp and non-magnetic, just like Ru and Os. This fact, that a few percent decrease of the magnetization causes the hcp rather than the bcc structure to be stable was explained by us several years ago as the basis of the electronic structure. If Fe is constrained to remain in the hcp (or fcc) structure (for instance, as an epitaxial layer grown on a noble-metal substrate) and the lattice constant is now increasing a few percent (by changing the composition of the substrate alloy) the magnetization rises abruptly from $0\mu_B/\text{atom}$ (or $0.6\mu_B/\text{atom}$ in the fcc structure) to about $3\mu_B/\text{atom}$.

H. Gleiter: We are aware of these observations. In fact, they have been used to interpret the low saturation magnetization observed (cf. ref. 25 of the manuscript).

G. Kalonji: I would like to comment on the orientation relationship observed in your interphase boundary experiments. If you were to consider the entire intersection group (and not only its translational subgroup, the so-called CSL) you would find that all of your orientation relations are by symmetry dictated to yield extreme in interfacial properties. Since you have seen them, we know they are minimas. This is a fine example where symmetry arguments, when used in a generalized and unrestricted way may yield useful information about properties.

H. Gleiter: I fully agree with Prof. Kalonji's comment. Of course, the prime motivation for our experiments was to find the physical principle which selects the low energy boundaries from the entire set of boundaries which can be expected on the basis of symmetry operations to yield extrema in the interfacial properties. In fact, the problem of physically understanding the atomistic structure of interfaces is analogous to the determination of the stable crystal structure of a particular material. Crystallography provides the framework of the conceivable atom arrangements. However, in order to select the stable structure among all conceivable structures, we have to understand the physical effects controlling structural stability.

D. Ast: (i) Could you comment on the density deficit of the sintered phase? How is this volume distributed? Mostly as "large" (say nm) voids or as atomic size or subatomic size "free volume"? (ii) Is the sintered phase stabilized by gas? During recrystallization, is gas desorbing?

H. Gleiter: (i) Small angle x-ray scattering experiments indicate the presence of voids the average size of which was about 7 nm in nanocrystalline iron with an average crystal size of 6 nm. The scattering experiments showed little evidence

for voids smaller than about 2 nm. On the basis of these results and TEM observations on the density of voids (defocus contrast observations), one is led to conclude that a considerable fraction of the observed density deficit between bulk iron and nanocrystalline iron results from the presence of the grain boundaries. (ii) There is little evidence that the nanocrystalline structure is stabilized by gas. Iron specimens were heated up to 1400 K in a mass-spectrometer, so that the desorption process could be followed. These experiments showed no measurable desorption of He.

R. Raj: Could you please comment on the stability of your nanometer grain size polycrystal?

H. Gleiter: On the basis of stability studies involving several nanocrystalline metals as well as nanocrystalline solids with ionic and covalent bonding, it appears that the thermal stability of the nanocrystalline microstructure scales approximately with the melting temperature. Roughly speaking, metals with melting points higher than about 500°C are found to be stable at ambient temperature or below.

J.M. Gibson: What is the impurity content of the nanocrystalline iron? Have you done, for example, x-ray fluorescence looking for oxygen? It seems that the massive surface area of the powder used to prepare this material might absorb considerable amounts of impurities.

H. Gleiter: The impurity content was 0.5% or less (cf. written version of the manuscript). We have analyzed the chemical composition of our specimens by mass spectroscopy and atomic absorption spectroscopy (cf. ref. 25 in the written version). The oxygen content was determined by a special method capable of revealing an oxygen concentration of 1 ppm. Furthermore oxide formation in annealed specimens was checked by Mossbauer spectroscopy. None of the methods revealed measurable amounts of gases. It is correct that the material might adsorb considerable amounts of impurities at the large free surface. In order to avoid this adsorption, the material was produced by a "self-cleaning" method (similar to a Wilson chamber) in a He atmosphere the reactive impurities of which were removed by gettering them with evaporated iron. The getter material resulting from this procedure was accumulated on a separate cold trap so that it could not interfere with the iron evaporated subsequently into the "cleaned" He in order to obtain the nanocrystalline material. This precautions turned out to be crucial for obtaining nanocrystalline iron with an impurity content of < 0.5%.

Y. Ishida: Comment: Mössbauer experiment on ^{119m}Sn in the grain boundary of Fe showed ferromagnetism is largely changed by IVB to VIB elements (including P). It

appears that your spectrum should take into account this effect. The argument of specimen structure upon sintering the fine particles may be clarified either by HREM or by examining similar fine grained structures such as Ar^+ bombarded Fe thin foil.

H. Gleiter: The point concerning the IVB and VIB impurities is well taken. However, as we know from chemical analysis that our specimens contain no measurable amount of impurities of this kind, we neglected these effects so far. HREM studies as well as EXAFS (e.g. NMR, low temperature specific heat, XPS) are applied to characterize the new structure.

H.T. Sawhill: We also frequently see alignment of low index directions in Ni/NiO interfaces. In this case the geometry would not follow such a "lock-in structure". Would you expect that such a model would apply also to transition metal/ionic interfaces or can you make conclusions only about noble metal/ionic interfaces?

H. Gleiter: On the basis of the data presently available we can draw conclusions only about noble metal/ionic interfaces. An attempt to extend the work to other metals will be made.

G. Elssner: Would you agree that your locked-in type of interface may be restricted to combinations of metal and ionic crystals or sapphire, respectively, with low interface energy or low chemical affinity?

H. Gleiter: It is difficult to comment without having measurements on systems with high interface energy and/or high chemical affinity. However, my guess is that such systems may well show different behaviour. Additional research is planned to check the validity of the "lock-in" model proposed for systems other than noble metals and ionic crystals.