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ON THE SEARCH FOR EXPERIMENTALLY OBSERVED GRAIN BOUNDARY PHASE TRANSITIONS

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Abstract - The phase space for a heterogeneous system containing a grain boundary involves a relatively large number of variables (i.e., at least six plus the number of components), and it is therefore conceptually possible to induce a large variety of grain boundary phase transitions by selectively varying these parameters. Despite this, a review of the literature reveals that there have been virtually no clear-cut experimental observations of transitions reported in which the boundary structure has been observed as a function of time under well defined conditions. In current work, we are searching for roughening/faceting transitions and melting transitions for boundaries in Al by hot stage transmission electron microscopy. A clear example of a reversible roughening/faceting transition has been found. No evidence for melting has been found for temperatures as high as $0.96 T_m$ (by monitoring GBD core delocalization in several special boundaries with $\Sigma \leq 13$) or $0.999 T_m$ (by observing the local diffraction contrast at general boundaries in polycrystalline specimens).

1. Introduction - Since grain boundaries may be regarded as phases, the local equilibrium of regions containing boundaries may be treated using the standard methods of the heterogeneous equilibrium of multi-phase systems. However, as discussed by Cahn (1), the phase space becomes relatively complicated since it is then necessary to introduce additional state variables in order to specify the boundary geometry. These variables include the three required to specify the crystal misorientation (R_1, R_2, R_3) and the two required to specify the inclination of the boundary plane (N_1, N_2). Under many conditions a boundary will automatically relax to its equilibrium translational state when the above five variables are fixed, and they are then sufficient to specify the boundary geometry. In the following, we shall assume, with Cahn (1), that this is the case. It therefore follows that the number of variables required for a heterogeneous system containing a boundary is $6+C$, where C is the number of components. A useful choice is $R_1, R_2, R_3, N_1, N_2, T, P, X_1, X_2, \dots, X_{C-1}$ where T = temperature, P = pressure, and the X_i are compositions. A patch of boundary corresponding to a given point in

Fig. 1. (a) Single phase flat boundary.
(b) Single phase curved boundary.
(c) Faceted two-phase boundary.
(d) Dissociated three-phase boundary.

phase space may consist of one boundary phase (if, for example, it belongs to a boundary which is flat or smoothly curved as in Fig. 1a or 1b) or more than one phase (if, for example, it is faceted as in Fig. 1c or dissociated as in Fig. 1d). Single phase and multiphase regions therefore exist, and appropriate phase diagrams may be constructed (1).

In view of the above, it seems likely that a rich variety of grain boundary phase transitions should occur over

different regions of phase space when the state variables are varied. Despite this expectation, there have been virtually no clear-cut experimental observations of such transitions reported in the literature where the structure has been observed at various stages of the transition under well defined conditions. In the following, we first give a brief review of some of the previous experimental work relevant to this point and then describe some current results from our laboratory in which we have searched for roughening, faceting and melting transitions under better defined conditions for boundaries in Al by hot stage transmission electron microscopy (TEM). The focus of the present paper is on experimental results, and little effort is made to discuss attempts to calculate boundary phase transitions.

2. Brief Review of Some Previous Experimental Results

- Numerous reports exist in which a discontinuity of some type has been found in some process associated with grain boundaries. It has often been suggested (e.g., citations in References 1-3 and also 4) that such discontinuities are due to boundary phase transitions. However, no direct evidence of this has been presented and they therefore remain unconvincing.

- Evidence for faceting transitions of the type [one-phase/flat boundary] $\rightarrow$ [two-phase/faceted boundary] driven by changes in composition has been found in (5, 6). Bishop, Hartt and Bruggeman (5) found that the faceting of tilt boundaries in zinc tended to fade out in regions of bicrystal specimens where relatively high concentrations of solute atoms were expected to be present. However, no actual concentrations were measured. Donald (6) found that the addition of small concentrations of Bi to polycrystalline Cu caused a high incidence of boundary faceting. Unfortunately, the behavior of specific boundaries, with and without Bi, could not be studied in this work.

- Dissociated grain boundary structures of the type illustrated in Fig. 1d have been observed, e.g. (7, 8), but actual transitions from, say, a [one-phase/flat boundary] to such a [three-phase/dissociated boundary] have not.

- Sickafus and Sass (9) reported that patches of two different boundary structures (phases) coexisted in flat areas of small angle [001] twist boundaries in Fe containing certain Au solute atom concentrations. Furthermore, the ratio of the amounts of the two phases changed as the apparent solute concentration changed, and they took this as evidence of a boundary phase transition of the type [one-phase/flat boundary] $\rightarrow$ [two-phase/flat boundary] driven by a change in composition. However, it was known that the distribution of Au atoms was not equilibrated throughout the specimens and, furthermore, the actual concentrations were not measured locally. Also, the relative amounts of the two phases did not always vary systematically with the apparent Au concentration as expected in a two-phase mixture. Further work seems called for.

● Glicksman and Vold (10) reported an apparent discontinuity in the dihedral angle produced by the surface tension of symmetric tilt boundaries in Bi at the liquid/solid interface as the tilt angle, θ , was increased as shown in Fig. 4 of (10). This was interpreted as a first order congruent phase transition of the type [solid phase/flat boundary] $\rightarrow$ [liquid phase/flat boundary] driven by the change in θ at a temperature very close to the bulk melting temperature, T_m . However, as discussed by Rottmann (11), such a discontinuity does not seem plausible thermodynamically, and further work is therefore called for.

● Many efforts, summarized in (12), have been made to determine whether grain boundaries (including both general boundaries and particular grain boundaries) undergo congruent melting [1]* before bulk lattice melting upon raising the temperature to T_m . Most of those experiments using bulk specimens have yielded ambiguous results (12), but Glicksman and Vold (13,14) used hot stage TEM to observe directly the structure of the grain boundaries present in nominally 99.999% pure polycrystalline Bi films which were directly adjacent to regions which were completely melted. Under these conditions, a temperature gradient existed in a direction normal to the liquid/solid interface, and grain boundaries adjacent to the interface could be observed at temperatures only very slightly below T_m . Narrow melted regions along many of these grain boundaries (particularly at triple junctions) were observed indicating grain boundary melting at temperatures only very slightly below T_m . However, no information was provided regarding: (a) the magnitudes of the temperature differences which existed; (b) the possible presence of impurities which may have affected the observations; and (c) the degree to which the specimens were equilibrated.

● Chan, Liu and Balluffi (3) used hot stage TEM to study the behavior of grain boundary dislocations (GBDs) in near-Σ5 [001] twist and [001] symmetric tilt boundaries in Al during heating to near T_m . The GBDs were still clearly visible via dislocation-type diffraction contrast at temperatures as high as $0.89 T_m$ (for the twists) and $0.92 T_m$ (for the tilts). This result indicates that the boundaries retained significant order to these temperatures and had not melted, since melting would have caused a delocalization of the GBDs.

[1]* We take a "melted" boundary to be a boundary which consists of a layer of material having a structure similar to that of a liquid. We do not consider as "melted" a boundary which is undergoing the low temperature structural transitions which may precede complete melting in the manner described by Kikuchi and Cahn (23). (See our further discussion of this point in Section 4.)

Fig. 2. Structure of $\Sigma 3\langle 111 \rangle$ tilt boundary in Al as a function of heating, (a)→(d), and subsequent cooling, (d)→(g). (Unrelaxed atomistic structure shown in Fig. 3) Dark field diffraction contrast with lower crystal excited. Time at each temperature ≈ 40 min.

● Erb and Gleiter (15) sintered a random distribution of single crystal Cu balls to a single crystal Cu plate and observed the rotations of the balls into misorientations which produced boundaries of relatively low energy in the neck regions between the balls and the plate. It was found that many of the low energy misorientations which were observed persisted to temperatures as high as $0.98 T_m$. This indicates that the boundaries corresponding to at least these low energy misorientations must have retained significant order and were not melted at this relatively high temperature. Unfortunately, these boundaries were not identified geometrically.

3. Current Experimental Results

3.1. Experimental procedure - Two main types of Al TEM specimens containing grain boundaries were prepared using material of initial 99.999 purity. Polycrystalline thin films (~ 400 nm thick) of grain size $\sim 1 \mu m$ were prepared by vapor deposition on (100) cleaved NaCl single crystal surfaces at $\sim 250^\circ C$ in a standard 10^{-7} torr bell jar system. In addition, bicrystal thin film specimens (~ 400 nm thick), each containing a single straight grain boundary of controlled geometry running perpendicular to its surface, as illustrated.

in Fig. 1 of (3), were prepared by epitaxial vapor deposition on specially prepared NaCl bicrystal substrates at 340°C . Further details are given in (3). The polycrystalline specimens were then oxidized in air at 500°C for 10h in order to increase the grain size and grow a moderately thick oxide layer on each surface. These specimens were then clamped between folding Au grids and mounted in the double-tilt hot stage of a JEOL 200 CX microscope for observation during heating and cooling experiments up to the melting point. These specimens had the advantage that they possessed transverse boundary structures which were quite stable against migration, and a stable encapsulating oxide film which: (a) maintained specimen integrity even after patches of the metal were locally melted; and (b) protected the Al films from outside impurity contamination by acting as an effective diffusion barrier (see below). The hot stage and its temperature calibration are described in (3).

Fig. 3. Unrelaxed structure of faceted $\Sigma 3\langle 111 \rangle$ tilt boundary in Al viewed along $\langle 111 \rangle$. Different symbols indicate different planes in the ABCABC...stacking sequence.

Fig. 4. Average amplitude, l/l_0 , of facets on $\Sigma 3\langle 111 \rangle$ tilt boundary in Al (shown in Fig. 2) as a function of temperature during heating and cooling. Total heating time ≈ 300 min. Total cooling time ≈ 150 min.

3.2. Observation of boundary roughening/faceting during heating and cooling - A search of a polycrystalline specimen revealed the boundary shown in Fig. 2a which was identified as a $\Sigma 3\langle 111 \rangle$ tilt boundary having an average inclination along the common $\{101\}$ planes of Crystals 1 and 2 in the $\Sigma 3$ CSL and two sets of facets each inclined along common $\{112\}$ planes of Crystals 1 and 2, as shown in Fig. 3. Upon heating, the faceted structure became progressively rounded as roughening occurred (Fig. 2b) and eventually became essentially flat (Fig. 2d). Upon cooling, the boundary structure reversed its history and eventually became sharply faceted again (Fig. 2g). The time-temperature dependence of the transition was studied by heating in a step-wise fashion. The degree of roughening (as measured by the average amplitude of the facets) increased rapidly during each incremental temperature increase and then quickly became constant during each subsequent isothermal holding period. This result demonstrated that the degree of roughening was a unique function of

temperature and was reinforced by the results in Fig. 4 which show the degree of roughening as a function of temperature during both slow heating and cooling. No hysteresis is apparent.

3.3. Observation of melting at grain boundaries during heating and cooling - Polycrystalline specimens were slowly heated to a point where they were partially melted and contained relatively large discrete patches of encapsulated liquid. The temperature was then stabilized, and the boundaries adjacent to the liquid/solid interface were examined under steady state conditions in the manner of Glicksman and Vold (13,14). A typical structure is shown in Fig. 5, and it is seen that many boundaries were wet by the liquid and replaced by narrow layers of liquid. The melted regions were clearly distinguished from the crystalline regions by differences in the local diffraction contrast. The liquid regions generally appeared dark and

Fig. 5. Structure of polycrystalline Al specimen adjacent to periphery of relatively large melted region (indicated by large arrows). Boundaries near the periphery are wet by the liquid, particularly evident at triple junctions (indicated by small arrows). Structure shown was held ~5 min under steady state conditions before being photographed.

Fig. 6. Disappearance of melted regions at grain boundaries in polycrystalline Al during cooling ((a)→(c)) from very near T_m .

exhibited no diffraction contrast, whereas the crystalline regions exhibited the expected strong diffraction contrast. This melting at the grain boundaries was especially evident at triple junctions (see also Fig. 6) and became less extensive as the distance from the liquid/solid interface increased, i.e., as the temperature dropped progressively below T_m because of the temperature gradient which existed perpendicular to the interface. Also, no sign of melting was observed at low angle boundaries, i.e., relatively low energy boundaries with structures composed of arrays of discrete lattice dislocations. (No detailed information has yet been obtained which allows us to distinguish structurally between the remaining boundaries which appeared structureless under the microscope and were either associated, or not associated, with a melted layer.) Upon subsequent cooling, the liquid/solid interface moved toward the liquid as expected, and the liquid layers at the melted boundaries progressively disappeared (i.e., crystallized) in an apparently reversible fashion as the local temperature decreased, as seen in Fig. 6.

Careful examination of micrographs such as Fig. 5 showed that no detectable melting at any grain boundaries (including triple junctions) could be detected at distances from the liquid/solid interface $\geq 15 \mu\text{m}$. A conservative estimate of the minimum width of the melted region at a boundary which could be deduced from work with the present specimens using the diffraction contrast method is about 1 nm. This is based on the observation that the melted material was most readily detected at the triple junctions where the width of the pools was measured to be several times as wide as the corresponding melted width at a straight section of boundary (e.g., Fig. 6). The narrowest triple junction images which could be observed were about 2 nm wide, and, hence, the corresponding narrowest melted width at a straight section is $\sim 2/3 = 0.7 \text{ nm}$.

It is of primary importance to estimate an upper limit for the temperature drop, ΔT , which existed between the temperature at the liquid/solid interface and the temperature at which no melting at the boundaries could be detected. The disc-shaped specimen was clamped around its periphery in the heating stage and heated by inward conduction. On the other hand, the surface lost heat everywhere by radiation causing a cooling of the central region of the specimen. The steady state heat equation for this situation is then

$$\frac{d^2T}{dr^2} + \frac{1}{r} \frac{dT}{dr} = \frac{2\epsilon(5.679 \times 10^{-12})T^4}{Kt}$$

where ϵ = hemispherical emissivity, K = thermal conductivity, and t = specimen thickness. This non-linear equation was integrated numerically, and the results indicated a maximum temperature gradient in the specimen ≈ 450 K/cm. However, the focused electron microscope beam delivered energy to the specimen locally which tended to heat the specimen interior in a reverse fashion. This effect was estimated using methods similar to those described in (16), and the results indicated a gradient ≤ 240 K/cm in the region under observation. Since these gradients would tend to oppose each other over most of the specimen, and since the gradient due to radiation losses is a generous upper limit, we may conclude that ΔT was certainly $< 1^\circ$. We therefore conclude that no grain boundary melting was detectable by local diffraction contrast at temperatures $< 0.999 T_m$.

It is important to point out that impurities may have played at least some role in the very limited amount of boundary melting observed since it is conceivable that low concentrations of impurities were picked up in a manner which could not be detected. For example, we note that concentrations of typical solutes at the 10^{-4} level can depress the bulk liquidus temperature by several tenths of a degree. Typical diffusion lengths for substitutional solutes in Al at T_m after the relatively short time of 10^2 s are 10-20 μm , and since the grain size was $\sim 3\mu\text{m}$, impurity atoms should easily have been able to equilibrate throughout the specimens in the present experiments. In any event, our conclusion that no boundary melting was detected at any boundaries below $0.999 T_m$ still stands.

3.4. Observation of localized GBDs at elevated temperatures - In this work, the appearance of localized GBDs in bicrystal specimens was monitored during quasi-equilibrium heating to T_m in hot stage TEM experiments similar to those conducted by Chan, Liu and Balluffi (3) described in Section 2. Of central interest was the extent to which the GBDs remained localized during the heating. In the previous work, near- $\Sigma 5$ boundaries were studied, and no evidence for boundary melting was found at temperatures $\leq 0.92 T_m$. The question of whether longer period boundaries of higher Σ melt at lower temperatures remains, however, and we therefore tested near- $\Sigma 13$ [001] symmetric tilt boundaries running parallel to {510} planes. These boundaries possessed arrays of edge GBDs with Burgers vector $\vec{b} = a/\sqrt{26} \langle 510 \rangle$ accommodating a small tilt misorientation as seen in Fig. 7a. No detectable delocalization of the GBD cores was found upon heating to $0.96 T_m$ as seen in Fig. 7b. We therefore conclude that $\Sigma 13$ boundaries do not melt at temperatures $\leq 0.96 T_m$.

Fig. 7. Localized GBDs observed in near- $\Sigma 13$ [001] symmetric tilt boundary running parallel to {510} planes in Al. (a) at 25°C . (b) at $0.96 T_m$.

4. Concluding Remarks

The roughening/faceting boundary transition which we have observed proceeded just as would be expected on the basis of analogous roughening/faceting transitions on free surfaces where sharply faceted structures are stable at low temperatures and where rounding of the edges occurs and more isotropic shapes become stable as the temperature is raised (17). As Cahn has pointed out (1), faceting boundary transitions may generally be expected to be relatively common types of transitions.

Our results that no evidence for melting could be detected at temperatures as high as $0.96 T_m$ for several boundaries with $\Sigma \leq 13$ (by the GBD core delocalization technique) or as high as $0.999 T_m$ for general boundaries in polycrystals (by observing the local diffraction contrast) seem mutually consistent. We also remark that these results seem to be consistent with the single crystal ball rotation experiments of Erb and Gleiter (15) discussed in Section 2.

With respect to calculations, we note that the experimental results described here appear to be inconsistent with calculations reported in (18-20) and apparently consistent with those reported in (21-23). In (18-20) boundaries were found to melt suddenly by first order transitions at temperatures well below T_m . In (21-23) boundaries were found to undergo a continuous transition which first became perceptible at relatively low temperatures. This disordering progressed steadily as the temperature was raised, and, at least in (23), culminated finally with complete boundary melting which occurred rather abruptly at T_m . (For example, in (23) the boundary entropy diverged as $-\ln(T_m - T)$ near T_m .) Kikuchi and Cahn (23) pointed out that the low and high temperature phenomena are parts of the same overall process and elected to term the entire process a "melting transition". In our opinion, it might be appropriate to consider the low temperature phenomena as "premelting". Needless to say, the present experiments could not have detected any such premelting.

More effort is required at this point to extend this work over a wider range of specific boundary types, to approach T_m more closely and to evaluate the role of very small impurity concentrations. It would also be useful to employ a more powerful method to study grain boundary disordering on a local atomistic scale such as grain boundary x-ray diffraction. For example, this technique might be capable of detecting the disordering associated with the predicted boundary premelting discussed above.

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N.W. Ashcroft: Can the encapsulation geometry encompass the possibility of significant voids in the Al film, so that the question of surface melting might be examined? On a free surface of lead, surface melting has been reported (Franck & Van der Veem) to begin at a temperature very substantially below the bulk temperature. If a surface melting signature was available in your technique, the difference between grain boundary and surface melting (if it exists) might be demonstratable.

R.W. Balluffi: The encapsulation of a specimen containing suitable voids with clean surfaces would probably not be feasible because they would be unstable at temperatures near T_m and quickly disappear or be modified in detrimental ways. Unfortunately, mass transport over distances of several microns becomes very rapid near T_m .

V. Pontikis: Comment on N. Ashcroft question. The photon beam channeling experiments by Freuken and Van der Veem were able to show that disorder appears on surfaces above $T=0.8 T_m$, but more evidence exists for a long range order loss. Then the question of surface melting is still controversial.