

A MOLECULAR DYNAMICS STUDY OF GRAIN BOUNDARY BEHAVIOR AT ELEVATED
TEMPERATURES USING AN EMBEDDED ATOM POTENTIAL

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Introduction

The structural stability of grain boundaries (GBs) in metals at elevated temperatures has been a longstanding subject of debate in the interface community. Some molecular dynamics (MD) studies (1,2) have suggested that at approximately 50-70% of the bulk melting temperature, T_m , the solid-solid interface becomes structurally unstable and undergoes a structural transition into a solid-liquid-solid "premelted" state. Indeed, this transition has even been characterized as a first-order phase transition (3). Other studies (4,5) indicate that such a thermodynamic transition does not occur but that, instead, the solid (yet disordered) GB region becomes progressively wider as the temperature approaches T_m . In particular, in one such study (5) it was observed that GBs exhibiting such a continuous disordering process, melt at T_m while those which remain ordered even at high temperatures may be superheated above T_m . These results are in marked contrast to recent experiments on copper and silver (6,7) which indicate an absence of GB disordering up to 95.99% of T_m . Experiments on aluminum indicate no disordering up to 0.999 T_m (8).

In a recent MD investigation of the high-temperature stability of metal GBs a close connection between GB migration and the onset of thermal disordering near the interface was observed (9,10). It was pointed out that in all prior simulations from which the existence of a premelting or disordering transition was postulated, the center of mass of the bicrystal had been kept fixed, thus artificially constraining GB sliding, i.e., the relative motion of the two halves of the bicrystal parallel to the GB plane. When this constraint was removed, the disorder observed was found to be merely a transient intermediate state formed during the sliding and subsequent migration of the GB from one plane to the next.

The purpose of the present work is to extend these investigations in two ways. The first is to employ a recently developed Embedded Atom Method (EAM) potential (12) rather than the central-force or pseudopotentials which have been used in all previous studies of high-temperature GBs. EAM potentials are generally recognized as the best atomic level description of interatomic interactions in metals currently available. In particular, these are the only potentials which model the effect of local volume expansion on interatomic interactions. Since local volume expansion is characteristic of GBs in metals (12), the validity of the physical description of GBs obtained from potentials which do not include this effect is always in doubt.

The second point we wish to emphasize is the importance of the thermodynamic melting point. Because superheating of an ideal crystal is possible in computer simulations, the determination of T_m for a given potential is a highly nontrivial task (see, for example, Ref. (12)). For the Cu EAM potential used in this study, (see ref. (11) for details), a calculation of the temperature at which the liquid and solid free energies are equal has been performed (12) yielding a melting point of $T_m = 1171 \pm 50K$. However, superheating of the ideal crystal is possible up to about 1450 K. As has been previously discussed (5,14), and as will be shown below, simulations of GBs slightly above T_m are easily misinterpreted if T_m is not known.

Simulation Procedure

The GB simulations were performed using a recently developed model for the simulation of interfacial systems (12). The geometrical layout of our simulation cell combines 2-d periodic boundary conditions, (PBCs), in the plane of the interface with its embedding in bulk crystal regions. For that purpose the simulation cell is subdivided into two regions, a Region I in which the equations of motion are solved explicitly for all atoms and a Region II consisting of two rigid blocks, one on either side of the interface. Whereas the atoms in Region I are individually allowed to move in response to the forces acting on them, the atoms in Region II are held fixed at their ideal-crystal positions. However, each rigid block is permitted to move as a unit parallel to the interface plane in response to the total force exerted by Region I. Initially, the positions of the rigid blocks are fixed by taking the distance between the outermost plane of Region I and the first plane of Region II to be the perfect-crystal interplanar spacing appropriate for the simulation temperature. In addition, a restricted Parrinello-Rahman constant-pressure scheme (15), is used to allow the length of the simulation cell in the z-direction to fluctuate. The lengths in the x- and y-directions are fixed by the rigid blocks the interface is embedded in. Further details, including a demonstration of the quantitative accuracy of the model, are given elsewhere (10).

This model has been used to study the stability of a $\Sigma 29$ twist grain boundary on the (001) plane in Cu using an EAM potential described previously (11,13). Region I of our system consists of 32 (001) planes of atoms parallel to the interface plane with 29 atoms per plane for a total of 928 atoms. At zero temperature, the dimensions of the simulation cell in the x- y- and z- directions were 3.808, 3.808, and 16.08 lattice parameters, respectively. The twist angle for this boundary is $\theta = 43.60^\circ$. The two factors motivating the choice of this geometry were the relatively large interplanar spacing of the (001) planes and the relatively large primitive planar unit cell of the $\Sigma 29$ grain boundary. Because of the large interplanar spacing, the lattice planes are easily distinguished thus making clear the onset of disorder should the boundary prove unstable at elevated temperatures. The large planar unit cell allows us to consider this a "generic" high-angle boundary as opposed to boundaries with small planar unit cells for which the energy is known to be especially sensitive to translations (16) and for which multiple primitive planar unit cells must be combined in a non-primitive simulation cell to satisfy the condition that no particle interacts with its own image. Similarly, we chose a twist rather than a tilt boundary (as has been used in all the previous studies of high-temperature stability of GBs) for the reason that the symmetrical tilt boundary on a given lattice plane has the smallest planar unit cell of all GBs on that plane and, hence, is also highly sensitive to translations (16).

To investigate the breakdown of crystalline order upon melting we define the square of the magnitude of the static structure factor, $S(\underline{k})$ (which, for brevity, we simply denote by $S^2(\underline{k})$):

$$S^2(\underline{k}) \equiv |S(\underline{k})|^2 = \left[\frac{1}{N} \sum_{i=1}^n \cos(\underline{k} \cdot \underline{q}_i) \right]^2 + \left[\frac{1}{N} \sum_{i=1}^n \sin(\underline{k} \cdot \underline{q}_i) \right]^2, \quad (1)$$

where \underline{q}_i is the position of atom i . For the overall $S^2(\underline{k})$, all atoms in the simulation cell are included in the sums in Eq. (1) whereas for a planar structure factor, $S_p^2(\underline{k})$, only the atoms in a given lattice plane are considered. For an ideal-crystal lattice plane at zero temperature $S_p^2(\underline{k})$ then is unity for any wave vector, \underline{k} , which is a reciprocal lattice vector in that plane. By contrast, in the liquid state (without long-range order in the plane), $S_p^2(\underline{k})$ fluctuates near zero. As the two halves of the bicrystal are rotated with respect to each other about the GB-plane normal (in this case by $\theta = 43.60^\circ$), two different wave vectors, \underline{k}_1 and \underline{k}_2 , are required, each corresponding to a principal direction in the related half. For a well-defined crystalline lattice plane, say, in semi-crystal 1, $S_p^2(\underline{k}_1)$ then fluctuates near a finite value (\leq) appropriate for that temperature whereas $S_p^2(\underline{k}_2) \approx 0$. In the GB region, due to the local disorder, one expects somewhat smaller values for $S_p^2(\underline{k}_1)$. By monitoring $S_p^2(\underline{k}_1)$ and $S_p^2(\underline{k}_2)$, every lattice plane may thus be identified as (a) belonging to semi-crystal 1 ($S_p^2(\underline{k}_1)$ finite, $S_p^2(\underline{k}_2) \approx 0$), (b) belonging to semi-crystal 2 ($S_p^2(\underline{k}_1) \approx 0$, $S_p^2(\underline{k}_2)$ finite) or (c) disordered or liquid-like ($S_p^2(\underline{k}_1) \approx S_p^2(\underline{k}_2) \approx 0$).

As another measure of the disorder in the system, the number of "defected atoms", N_{def} , was monitored. An atom is considered defected if its nearest neighbor (nn) coordination, is different from that in an ideal-crystal environment. As merely a semi-quantitative measure we have defined the nn shell to end halfway between the ideal-crystal first and second nn distances. Any disordering or melting of the system, and subsequent density change, will be indicated by an increase in N_{def} . (Even though the nn coordination is the same in the liquid and the solid, the nn shell is considerably larger in the liquid than it is in the solid thus causing a liquid atom to be classified as defected by our criteria.)

Results

The GB was initially relaxed at zero temperature and zero pressure to its minimum-energy configuration. The temperature was then raised, instantaneously, to 600K which was maintained for 1,000 timesteps. (Throughout the simulations, the temperature was held constant by rescaling the velocities of the atoms in every time step.) The temperature was subsequently raised by 100K every 200 time steps until it reached 1000K which was again maintained for 1000 time steps. The temperature was then raised to 1100K.

Figure 1(a) shows the instantaneous plane-by-plane profile of the planar structure factor after 1,000 timesteps at 1100K. At the edges of the simulation cell, away from the GB, the structure factors assume values typical of an ideal crystal at this temperature. The GB is sharply defined and lies between the 16th and 17th planes. Planar profiles of the energy and mean-squared displacement show similar behavior.

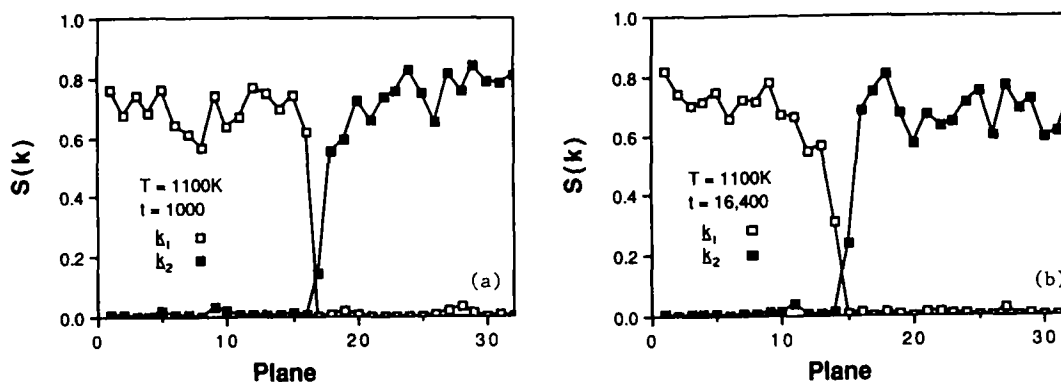


Fig. 1. Instantaneous values of $S_P^2(k_1)$ and $S_P^2(k_2)$ for the 32 planes parallel to the (001) Σ 29 GB after 1000 time steps (Fig. 1a) and 16,400 time steps (Fig. 1b) at 1100K.

Shown in Fig. 1(b) shows the instantaneous profile of the planar structure factor after 16,400 time steps. It is apparent that the GB is still sharply defined although it has migrated and now lies between the 14th and 15th plane. As discussed previously (9,10), this thermally-activated migration is typical of GBs at elevated temperatures when sliding of the two halves of the bicrystal is allowed. During migration, a single plane adjacent to the GB enters a metastable disordered state and eventually recrystallizes into a plane with the symmetry of the opposite half of the bicrystal. This metastable disordered state can be stabilized when the unconstrained sliding of the two halves of the bicrystal relative to one another is not allowed (9). The present results indicate that this GB, chosen to be a "typical" high-angle GB, migrates but does not enter into any stable disordered or "premelting" state at temperatures as high as 94% of T_m . (This is the highest temperature below T_m that we studied.)

In contrast, Figs. 2(a) and 2(b) show the structure-factor profiles of the GB after 5,000 and 10,000 timesteps, respectively, at 1300K. This temperature is above T_m although still below the ideal-crystal superheating limit. As the figures illustrate, a disordered region forms at the boundary and propagates outward. The diffusion constant in the disordered region is $1.1 \times 10^{-5} \text{ cm}^2/\text{s}$, which is typical of a liquid. From the mobility, the loss of structure and the overall volume expansion when the entire system becomes disordered, the disordered state can be identified as the liquid state. As the disorder spreads, the number of defected atoms increases linearly with time. Because there are 29 atoms per plane, and two liquid-solid interfaces, the

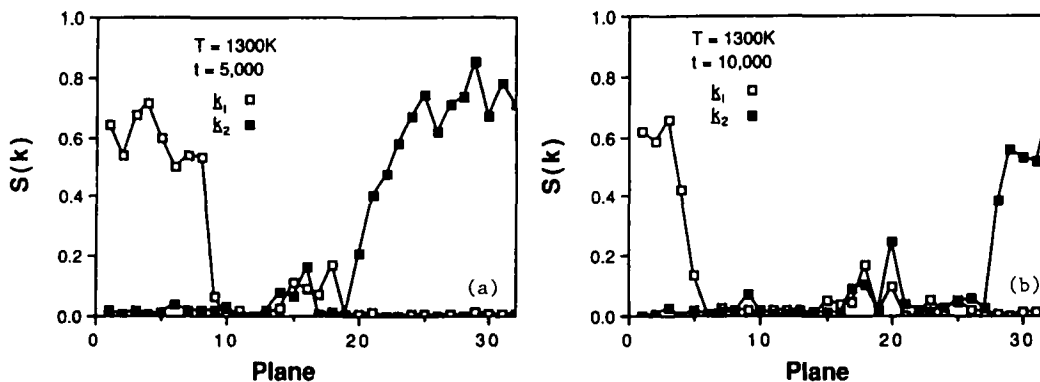


Fig. 2. Instantaneous values of $S_P^2(k_1)$ and $S_P^2(k_2)$ for the 32 planes parallel to the (001) Σ 29 GB after 5000 time steps (Fig. 2a) and 10,000 time steps (Fig. 2b) at 1300K.

velocity of spreading, v , can be simply obtained from

$$v = \frac{1}{58} \frac{dN_{\text{def}}}{dt} \quad (2)$$

Figure 3 shows the velocity of spreading as a function of temperature as well as a quadratic fit to the data. The intercept of the curve indicates that the liquid state does not spread below a temperature of $1179 \pm 20\text{K}$ which is in striking agreement with the thermodynamic melting point of $T_m = 1171 \pm 50\text{K}$ (12).

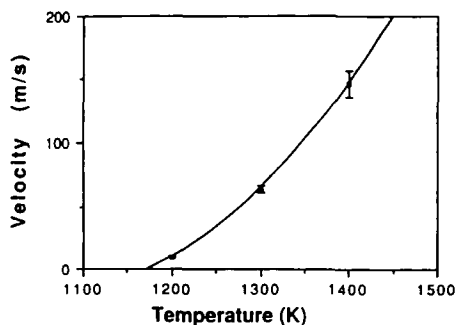


Fig. 3. Velocity of melting vs. temperature and extrapolation to zero velocity. The error bars are taken to be $\pm 2\sigma$, where σ is the standard deviation of the fit of N_{def} to a linear function of time.

Discussion

The results discussed here show that no disordering or "premelting" behavior occur in the Σ 29 (001) GB at temperatures as high as 94% of T_m . We believe this result to be more general since the GB studied was chosen as a high-angle twist GB. Since this class of GBs includes a vast number of GBs, it seems that GB disordering, if it occurs at all, is not a common phenomenon. As has been discussed previously (8,9), no prior simulation study showing GB disordering allowed for the unconstrained sliding of the two halves of the bicrystal and the disorder associated with migration may, therefore, have been artificially stabilized.

In one particularly significant study (5), it was argued that GB disordering occurs because above a certain temperature, T_0 , but below T_m , the free energy of some GBs becomes higher than that of a system consisting of a liquid region bounded by bulk solid (i.e., a solid-liquid-solid interface). It was concluded that GBs with this property melt at T_m while those remaining stable with respect to the liquid below T_m may be superheated above T_m . However, the GB studied here clearly melts at T_m but does not "premelting" below T_m . We speculate that this discrepancy may be understood if T_0 is identified not as the premelting temperature but the activation temperature

for GB migration. This seems likely since a solid-liquid-solid system would itself be unstable towards recrystallization below T_m . Thermally-activated migration would then occur if a given plane, say in the top half of the bicrystal, recrystallized into the bottom half of the bicrystal. Sliding would be necessary so that the reconstituted GB is not in an energetically unfavorable atomistic configuration.

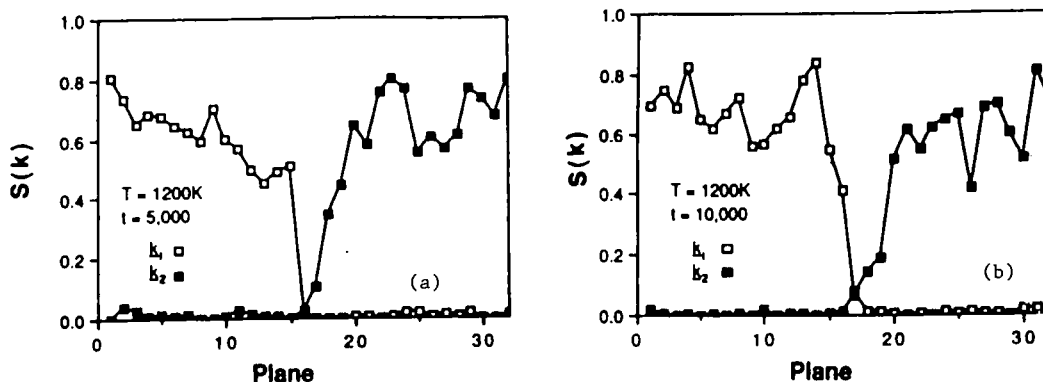


Fig. 4. Instantaneous values of $S_P^2(k_1)$ and $S_P^2(k_2)$ for the 32 planes parallel to the (001) Σ 29 GB after 5,000 time steps (Fig. 4a) and 10,000 time steps (Fig. 4b) at 1200K.

Finally, the importance, in the study of GB stability, of a careful determination of T_m has been previously noted (5,14). This is illustrated in the present study by our results at 1200K. Figures 4(a) and (b) show the 1200K GB after 5,000 and 10,000 time steps, respectively. From the structure-factor profile, as from profiles of other properties, it appears that a single plane has completely disordered but that this disordering has not spread. However, the number of defected atoms rises linearly. The velocity of spreading at this temperature is, in fact, quite consistent with the results at higher temperatures (see Fig. 4). Indeed, the velocity of about 10 m/s translates into a disordering of 1/2 plane on either side of the GB after 10,000 timesteps. Without knowledge of T_m and the behavior above T_m , such melting behavior could easily be misinterpreted as stabilized premelting.

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