

QUASI-MELTING OF SMALL PARTICLES

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We investigate the energetics of structural fluctuations in small particles, a phenomenon recently observed by high resolution electron microscopy. Using a continuum model with anisotropic surface energies and isotropic inhomogeneous elasticity, we estimate the activation energy for these transformations. The results indicate that the primary cause of the structural fluctuations is the reduction of the surface energy anisotropy as the temperature is raised, either the thermal or electronic temperature.

1. Introduction

An open question is the structure of small particles in the size range of 10 nm or less. Whereas the surface morphology of large particles (> 100 nm) is well established in terms of the Wulff construction [1,2], less is known about smaller particles. Many of the more complicated particle structures, particularly multiply-twinned particles [3–7], can be understood in terms of a modified-Wulff construction [6,8]. At smaller sizes and away from a simple static model of a small particle less is known. Reduction in the size emphasizes packing effects [9], as may the inclusion of more complicated phenomena such as three-body interactions [10]. Empirical quantum mechanical [11] or pair potential calculations [12,13] have provided some theoretical input, although these have yet to be tested in detail against experimental data.

One of the more interesting and earliest analyses of particles in the size range of a few atoms was that of Hoare and Pal [14]. These authors showed that it is necessary to calculate both the enthalpy and the entropy of a very small cluster. Indeed, a

free-floating cluster of a particle with a small number of atoms need not have a fixed structure (at room temperature) but instead can be dynamically fluctuating between different shapes. In effect the particle as a whole is almost a liquid, which we will call quasi-melting. Does the same phenomenon occur in larger particles?

It has become clear from recent results [15,16] obtained by high resolution electron microscopy that it does. Small particles in poor thermal contact with a support are heated by the electron beam and go into a state of continual fluctuation between different structures, quasi-melting. The exact nature of the heating is as yet unknown and may be either thermal, e.g. to 700°C or more, or electronic heating, i.e. an enhanced population of excited electronic states leading to enhanced diffusion. The full picture from these experimental results, namely the exact structures of the particle intermediary states and the detailed mechanism of the shape change, is not yet known. However, one fact seems to be clear, namely that the particles are transforming between different locally stable modified-Wulff construction [6,8] shapes.

Let us briefly recap what is known about these modified-Wulff shapes. Small particles of fcc materials, particularly gold and silver, often form in non-crystallographic shapes called multiply-twinned particles or MTP's [3–7]. Rather than being single crystals, these are composite structures built up from inhomogeneously strained [7] single crystal units, five such units twin-related yielding a decahedral MTP or Dh, twenty an icosahedral MTP or Ic. The twin units do not pack to a completely shape-filling structure, and particles are inhomogeneously strained to close the angular gaps. These strains correspond to a wedge disclination of $7\frac{1}{2}^\circ$ in the Dh's, six such disclinations in the Ic's.

Both the Dh and the Ic as described above are symmetrical, with all the segments having the same shape. There are also possible locally stable particle structures when the different segments have different shapes and volumes, and also for other particles containing twin boundaries [8]. The overview of small particle structure within this model is therefore one with many different possible particle morphologies, each of which is a local (not global) minimum of the energy (at constant volume). Quasi-melting will occur when the particle has sufficient thermal energy to surmount the energy barriers separating these different local minima.

The important question is the magnitude of this energy barrier, and we present preliminary results here. A full analysis of the (n -dimensional) particle potential energy surface including all the possible different facets on the particle surface is unrealistic. What we can solve is the energy barriers between a single crystal, the symmetrical Dh, two asymmetrical Dh's and a particle with one twin boundary (see fig. 1) for the case of only $\{100\}$ and $\{111\}$ surface facets. Motion from a

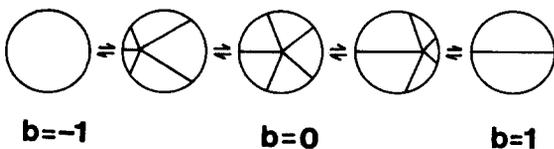


Fig. 1. Schematic diagram of the reaction path analysed herein between a single crystal ($b = -1$), a decahedral MTP ($b = 0$) and a particle containing one twin boundary ($b = 1$).

single crystal to a Dh corresponds to changes in the surface facets and motion of a $7\frac{1}{2}^\circ$ wedge disclination to the center of a particle, that from a Dh to a particle with one twin boundary motion of the disclination out of the opposing side. To calculate the energetics we need to know both the total surface energy and the internal strain energy as a function of the disclination position. In the following section we calculate these energy contributions in a continuum model with anisotropic surface energies and isotropic inhomogeneous elasticity.

2. Model

The energetics in a continuum model can be split into two parts, the surface energy of the particle and the internal strain energy. We will handle these separately.

2.1. Surface energy

The problem here is the surface energy of the particle for a specified volume fraction for each of the five segments. A complete solution taking into account all the different faces that are possible is intractable, so we must simplify. Fortunately both earlier work [6] and the published results on the particle shape as it changes [15,16] imply that a good approximation is to consider only $\{111\}$ and $\{100\}$ faces. Furthermore we can also use some symmetry, a mirror plane common to all the five segments and a mirror plane for the different segments. Labelling the segments one to five, the latter indicates that segments two and five are identical, as are segments three and four.

The general shape for each segment (considering only $\{111\}$ and $\{100\}$ facets) is shown in fig. 2. It has a strong resemblance to the shape of a single crystal, except that it is missing one $\{100\}$ face which would appear along the common $\{110\}$ axis of the decahedral particle. All the lengths on this segment are variables. The procedure is then to evaluate the total surface and twin boundary energy of the segment as well as its volume, and then minimize the dimensionless parameter [6]

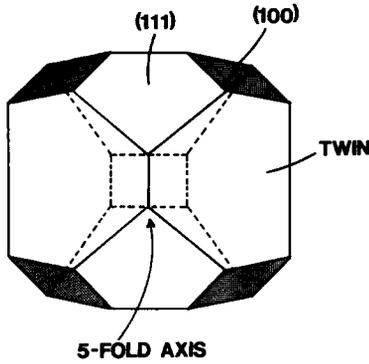


Fig. 2. General shape of each segment. All the dimensions were allowed to vary, with the constraint included that the twin boundaries between adjacent segments matched.

$$\epsilon_w = \int \gamma dS / \gamma_{111} V^{2/3},$$

where V is the volume and γ_{111} the (111) surface energy including, numerically, the constraints that the twin facets common to two segments have identical shapes. The latter ensures that the different segments “fit” into a complete structure. To adjust the relative volumes of the five segments we choose to fix the volume fraction of the third (equivalent to the fourth) segment, and investigate ϵ_w as a function of this parameter; when this fraction is 0.2 we have a symmetrical Dh and when it is 0.5 we have a bi-crystal with one twin boundary. This volume fraction can then be written in terms of the parameter b , the fractional distance of the disclination from the center (see fig. 4).

The results for ϵ_w plotted against b for three different values of $\alpha = \gamma_{100}/\gamma_{111}$ are shown in fig. 3. For all the curves the twin boundary energy γ_t has been set at $\gamma_t = 0.01\gamma_{111}$, a mean value for fcc metals. Note the strong minimum, as expected, for $b = 0$, a symmetrical Dh. As the ratio α is reduced, the variation in ϵ_w drops and very small minima or saddle points develop for $b \sim -0.6, 0.4$ for $\alpha = 1$. These correspond to asymmetrical Dh's. On the basis of the ϵ_w calculations alone, their stability is marginal, but as we will see later, this changes when the strain energy is added.

Extrapolating from these results, we can say that as the surface energy anisotropy drops, the

potential surface energy softens. This is to be expected as MTP's are unstable for an isotropic surface energy [7]. Note that one of the primary effects of raising the temperature is to reduce the anisotropy (which goes to zero at the melting point).

2.2. Elasticity

A full three-dimensional solution for the elastic strain energy is an intractable problem. We therefore simplify to a two-dimensional analysis as in previous work [7]. The problem now is to find the energy of an eccentric disclination in a circular cylinder as shown in fig. 4. The solution turns out to be surprisingly simple. The problem of a disclination in a circular cylinder with a free boundary is related to the problem of the vertical displacement of a circular plate clamped at the boundary and loaded by a transverse point load; the transverse deflection of the latter is identical except for a multiplier to the Airy stress function for the disclination problem [17,18]. In terms of the coordinate system shown in fig. 4, the Airy stress function is

$$U = \frac{\mu \epsilon_D}{2(1-\nu)} \left[r_1^2 \log\left(\frac{r_1}{br_2}\right) + \frac{1}{2}(b^2 r_2^2 - r_1^2) \right]. \quad (1)$$

Integrating over the disc, the strain energy per unit volume, W , is

$$W = W_{Dh}(1-b^2)^2, \quad (2)$$

where W_{Dh} is the strain energy per unit volume of a symmetrical Dh [7]:

$$W_{Dh} = \mu \epsilon_D^2 V / 4(1-\nu), \quad (3)$$

with μ = shear modulus, V = particle volume, $\epsilon_D = 0.0205$, and ν = Poisson's ratio.

We have not included a circular cut around the disclination (as in previous work [7]) since the strain energy density is integrable. It might be thought that the strain energy per unit volume for the three-dimensional case is between those for the long circular cylinder (plane strain) and a thin circular disc (plane stress). However, the ratio of the plane strain energy to the plane stress energy is $1/(1-\nu^2)$ which ranges only from 1 to 4/3.

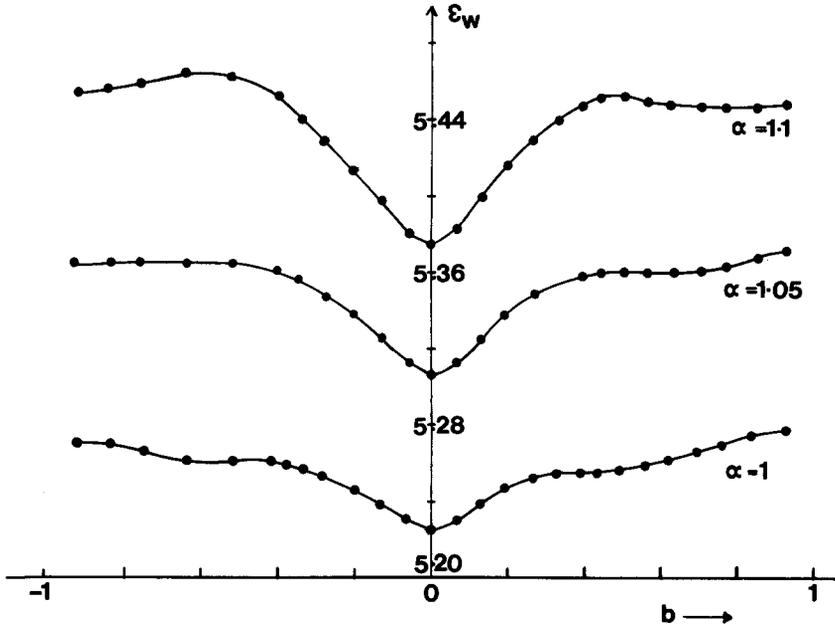


Fig. 3. Variation of ϵ_w versus b for three different values of α .

3. Total energy

The total energy, qualitatively, is

$$E = \gamma_{111}\epsilon_w V^{2/3} + VW \tag{4}$$

$$= \gamma_{111}V^{2/3}[\epsilon_w + C(1 - b^2)^2], \tag{5}$$

where

$$C = \mu\epsilon_D^2 V^{1/3} / 4(1 - \nu)\gamma_{111}. \tag{6}$$

This is plotted in fig. 5 as a function of b , for fixed values of C .

Some general features are of interest. Adding the strain energy softens the curves but does not destroy the local minimum for a Dh. Even when the total energy of a Dh is greater than that of a single crystal, the Dh remains locally stable. Secondly, note the effect of the strain on the local minima for the asymmetric Dh's, particularly for $b \sim 0.6, -0.7$ for $\alpha = 1$; minima develop depending upon the magnitude of C , which will vary with the particle size. This indicates that the metastability of these particles depends upon both the strain and surface energy terms, rather than just the surface energy as previously believed [8].

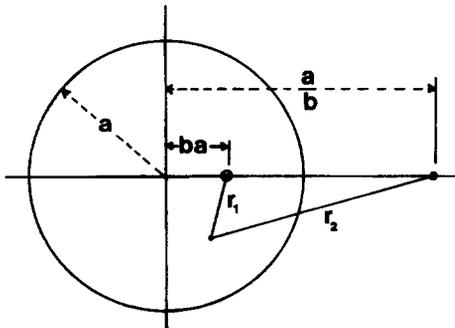


Fig. 4. Coordinate system for the off-axis disclination problem.

4. Discussion

We have presented here preliminary results for the variations of the total energy as a function of the particle shape. The physical sense of the results is apparent, despite the limitations of the model. The important effect is that the energy

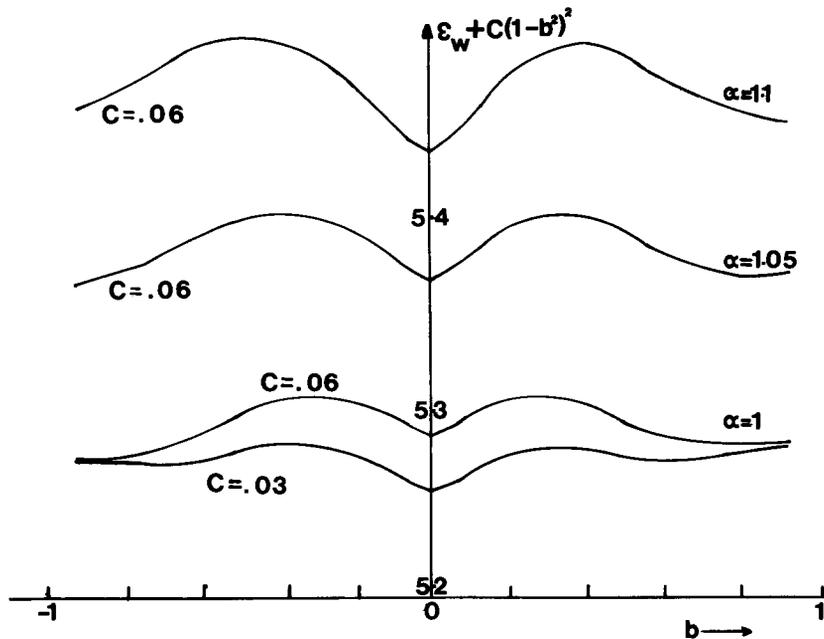


Fig. 5. Plot of the combined surface and bulk strain energies for the values of C and α shown.

variation softens as the anisotropy of the surface energy drops. This indicates that the cause of the quasi-melting of small particles is probably the increased temperature. At the melting point the surface energy is completely isotropic, so any surface energy favouring of MTP's will vanish. As mentioned earlier, this temperature may be simply beam heating, or enhanced atomic diffusivity due to electronic excitations which could mimic an increase in temperature. As yet we do not have sufficient experimental data to pin down the exact source.

There are a number of phenomena which are also part of this problem and which we have not covered here. The energy contribution of the surface stress is important [7], as will be the thermal stresses in the particles. These will be discussed in detail elsewhere [19]. Both effects will tend to reduce the energy variations, being larger for the more strained symmetrical Dh's. In addition, the thermal stresses and the stress concentration around features such as the re-entrant surfaces may be important in nucleating dislocations as a means of changing the particle morphology.

5. Conclusions

Calculations of the potential energy surface for the transformations of small particles indicates that the activation energy barrier will soften as the temperature is raised due to primarily the reduction in the surface energy anisotropy. The temperature increase may be either thermal or electronic in nature.

References

- [1] C. Herring, *Phys. Rev.* 82 (1951) 87.
- [2] R.G. Linford, *Solid State Surface Science II* (Dekker, New York, 1973) p. 1.
- [3] S. Ino, *J. Phys. Soc. Japan* 21 (1966) 346.
- [4] S. Ino and T. Ogawa, *J. Phys. Soc. Japan* 22 (1967) 1369.
- [5] L.D. Marks and D.J. Smith, *J. Microscopy* 130 (1982) 249.
- [6] L.D. Marks, *Phil. Mag.* 49 (1984) 81.
- [7] A. Howie and L.D. Marks, *Phil. Mag.* 49 (1984) 95.
- [8] L.D. Marks, *J. Crystal Growth* 61 (1983) 556.
- [9] L.D. Marks, *Surface Sci.* 150 (1985) 302.
- [10] S. Wang, L.M. Falcon and A.W. Searcy, *Surface Sci.* 143 (1984) 609.
- [11] M.B. Gordon, F. Cyrot-Lackmann and M.C. Desjonquères, *Surface Sci.* 80 (1979) 159.

- [12] J.G. Allpress and J.V. Sanders, *Australian J. Phys.* 23 (1970) 23.
- [13] J. Farges, M.F. de Feraudy, B. Raoult and J. Torchet, *Surface Sci.* 106 (1981) 95.
- [14] M.R. Hoare and P. Pal, *J. Crystal Growth* 17 (1972) 77.
- [15] S. Iijima and T. Ichihashi, *Phys. Rev. Letters* 56 (1986) 616.
- [16] L.R. Wallenberg, J.-O. Bovin, A.K. Petford and D.J. Smith, *Ultramicroscopy* 20 (1986) 1.
- [17] R.D. Mindlin and M.G. Salvador, in: *Handbook of Experimental Stress Analysis*, Ed. M. Hetenyi (Wiley, New York, 1950) ch. 16, p. 775.
- [18] J.H. Michell, *Proc. London Math. Soc.* 34 (1902) 223.
- [19] P.M. Ajayan, L.D. Marks and J. Dundurs, to be submitted.