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ON SURFACE ENERGY MEASUREMENT FROM THE SHAPE OF SMALL CRYSTALS

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Introduction

The equilibrium shape of a crystal is determined by the anisotropy of its surface energy, as represented conventionally by the gamma-plot. A simple geometrical procedure, the Wulff construction, enables the equilibrium shape to be determined graphically from the gamma-plot (1,2). A similar criterion applies to the shape of holes in crystals (3). It is quite straightforward to reverse the procedure and to deduce some features of the gamma-plot from the observed shape of small single crystals (4,5,6) or pores (3). Two sets of superficially similar experiments have been reported using small single crystals of gold and it is interesting to consider why they give dramatically different results. Sundquist (4) found substantial faceting on {111}, {100} and {110} and deduced in particular that $\gamma_{f(\equiv\gamma_{111})} \sim 0.83\gamma_m$, where γ_m is the maximum surface energy. In contrast Heyraud and Metois (5) found relatively small facets on {111} and {100} and deduced that $\gamma_f \sim 0.97\ \gamma_m$. Both sets of experiments involved the annealing of small crystals (diameters 1-5μm) at 1000°C; the major difference in technique was the exposure of the gold to air by Sundquist immediately prior to the formation of the particles. This may have resulted in the modification of surface energies by the adsorption of oxygen and is discussed below. However it is not clear that a small sphere can readily develop facets of the size predicted by the Wulff construction because of the difficulty of nucleating a step on, in particular, the atomically flat (111) plane. The nucleation of such steps is a problem which is known to restrict the mobility of faceted gas bubbles in metals (7,8) in conditions when the driving force is low. It is the purpose of this paper to demonstrate that the driving force which causes small spherical particles to facet is also small and that the development of equilibrium faceting may take an extremely long time even at temperatures where surface diffusion is rapid. The implications of this conclusion on the use of particle faceting to determine the shape of the gamma-plot are also discussed.

Analysis of the Problem

The production of faceted crystal spheres can be considered to take place in two stages, illustrated in Figure 1. A thin film (typically a few 100 nm thick) is annealed on a support film until it breaks up into flat discs (Figure 1d). This process has been observed by Heyraud and Metois (4). Under the conditions used in the experiments quoted above we can assume that surface diffusion is the dominant mechanism responsible for the change in shape; indeed it is known (9) that under conditions of evaporation or deposition different crystal shapes result. The changes of shape illustrated in Figure 1 (disc to sphere and sphere to faceted sphere) both require that atoms be transported to or from a flat facet. This must involve the creation of a step, probably a single atom high, and since there is an energy per unit length, ε, associated with such a step a critical nucleus must be formed before a single layer of atoms can be added to or removed from each facet. The critical nucleus size and hence the necessary activation energy can be calculated using the following assumptions:

Let the nucleus be a semi-circular pillbox of radius r_n, height h and step energy ε. Such a semi-circular nucleus, growing from the edge of a facet, is of a lower energy than a circular pillbox nucleated in the middle of the facet. If the free energy change for the mass transport

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