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HIGH RESOLUTION STUDIES OF SMALL PARTICLES OF GOLD AND SILVER

II. Single crystals, lamellar twins and polyparticles

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Axial illumination lattice imaging with a high resolution electron microscope has been used to characterise directly the structures of complicated particles of silver and gold found in the early stages of particulate growth. Many of the particles are conveniently classified under a new, broad heading of "polyparticles", indicating their similarity to polycrystals. Whereas the latter are composed of single crystals, the former are constructed from smaller discrete particles (e.g. icosahedral multiply-twinned particles).

1. Introduction

Our initial studies of the internal and surface structure of small metal particles with the Cambridge University 600 kV high resolution electron microscope (HREM) [1,2] have established, unequivocably, the presence of dislocations in small multiply-twinned particles (MTPs) [3,4]: detailed observations of both decahedral and icosahedral MTPs (hereafter abbreviated to Dh and Ic respectively) of silver and gold are presented in a companion paper [5], hereafter labelled I.

We have also shown that, with axial illumination lattice imaging, it is relatively straightforward to characterise directly the structure of more complicated particles. Indeed, a variety of particles with different internal structures have been observed – the purpose of the present paper is to describe these in detail. It is convenient to classify many of these particles under the broad heading "polyparticles", as they are similar to polycrystals but with definite particles (e.g. Ics) replacing single crystals as the basic units.

2. Results

Details of specimen preparation and microscope operating conditions are given in I, and are not repeated here.

2.1. Single crystals

The shapes of the single crystals were in agreement with previous work on similar epitaxially-deposited particles (e.g. ref. [6]): nearly square shapes with a ⟨100⟩ epitaxy (fig. 1), and triangles for the ⟨111⟩ epitaxy (fig. 2). A few rectangular ⟨100⟩ particles were also observed, almost certainly as a result of particle coalescence. Supporting evidence is shown in fig. 3 and 4. The (200) lattice fringes in fig. 3 display a definite orientation change along a line between the two arrows, indicating either a low angle grain boundary or a sharp change in the thickness gradient. Both of these possibilities are associated with late stages in coalescence. Fig. 4 shows two particles "frozen", probably by the cooling of the sub-

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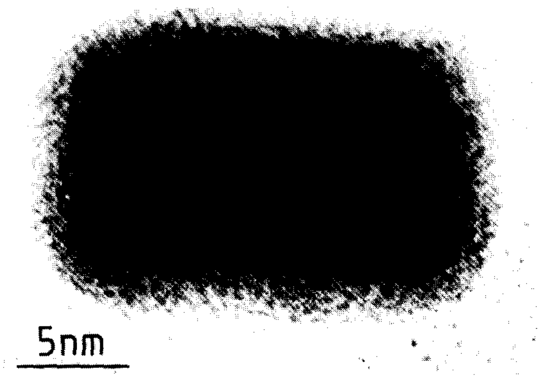

Fig. 1. Typical, slightly rectangular, ⟨100⟩ epitaxed single crystal of silver. Crossed (020) and (002) lattice fringes of 0.203 nm spacing are evident.

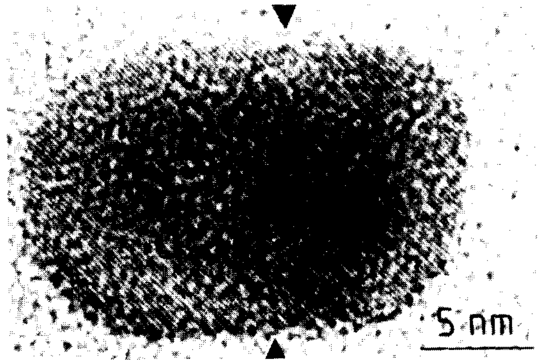

Fig. 3. A rectangular particle of silver in ⟨100⟩ epitaxy with evidence for particle coalescence. There is a distinct change in the lattice fringe orientation on a line between the arrows, indicating either the presence of a low angle grain boundary or a sharp change in the thickness gradient

strate, in the necking stage of coalescence. Similar, though lower resolution, images have been previously published [7].

2.2. Lamellar-twinned particles

Lamellar-twinned particles (or LTPs) are characterised by two or more parallel twin boundaries, though the simplest example, shown in fig. 5, has only one twin boundary. These can be classified as a simple type of polycrsystal, although we feel they

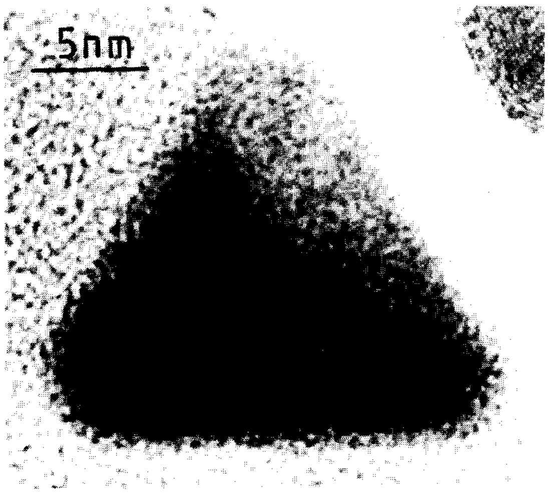

Fig. 2. Triangular particle of silver with ⟨111⟩ epitaxy.

Fig. 4. Two ⟨100⟩ oriented particles of silver "frozen" in the necking stage of coalescence. Crossed (020) and (002) lattice fringes of 0.203 nm spacing are visible in one particle and (020)- half spacing fringes of 0.102 nm, as well as faint 0.144 nm fringes, are visible in the other.

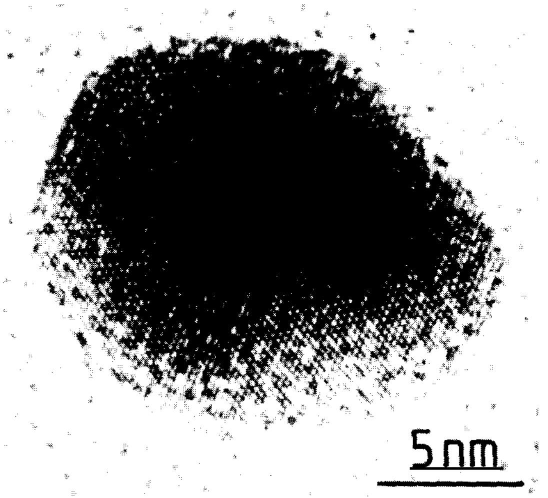

Fig. 5. A lamellar-twinned particle of silver imaged down the shared ⟨110⟩ axis. The actual position of the twin boundary is ill-defined.

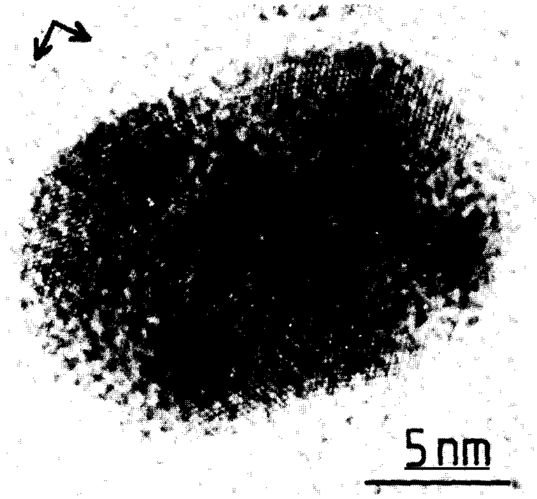

Fig. 6. Bi-icosahedral MTP of silver probably a result of interparticular coalescence. The two epitaxial directions of the Ics on the substrate are indicated: possible dislocations are also arrowed.

should be considered as a distinct particle type, given their frequent observation (e.g. ref. [8]).

2.3. Polyparticles

A very common observation was of particles which appeared to contain MTPs or LTPs either "embedded" among other crystals or recognisably coalesced with them. These were readily identified by the characteristic pattern of lattice fringes inside the particles.

2.3.1. Poly-icosahedral MTPs

These particles consist of Ics sharing decahedra. The simplest example is the bi-icosahedral MTP of silver shown in fig. 6. The epitaxial directions for the two Ics are also marked. It is clear that neither of the constituent particles is adopting the epitaxial alignment, suggesting that this particle results from the coalescence of two Ics, rather than from the nucleation of one Ic upon another. (A nucleation process would be expected to occur with one of the MTPs epitaxially oriented.) Particles resembling coalesced MTPs were tentatively suggested by Ino [6] and Komoda [9], although neither were able to provide clear structural identifications.

Further evidence for coalescence as the mechanism for the formation of these particles in shown in figs. 7 and 8. The composite particle in fig. 7 suggests two Ics with the same epitaxy in the process of coalescing into a single Ic. Fig. 8 shows an Ic necking with another which is itself part of a com-

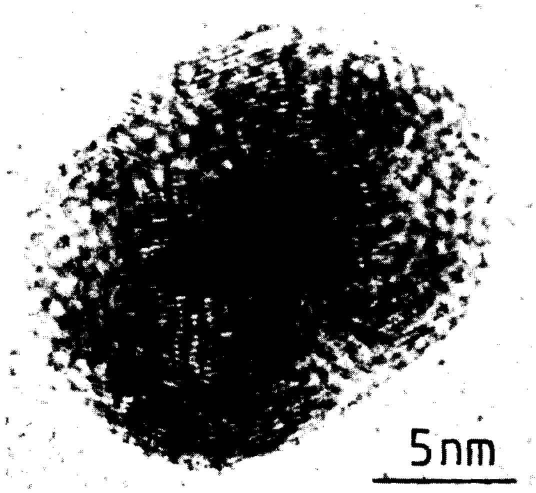

Fig. 7. A composite particle of silver suggesting coalescence as the origin of polyicosahedral MTPs. Two ⟨112⟩ epitaxed Ics can be identified, frozen in the process of coalescing into a single Ic.

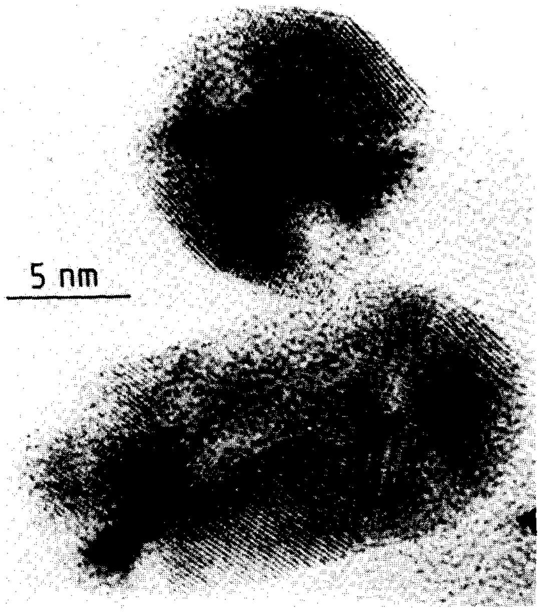

Fig. 8. Coalescence between an Ic and an elongated bi-icosahedral MTP. The continuity of the lattice fringes across the "neck" should be noted.

posite particle. The continuity of the directions of the lattice fringes between the two Ics should be noted. Finally note that, in common with the discrete icosahedral MTP, these poly-icosahedral par-

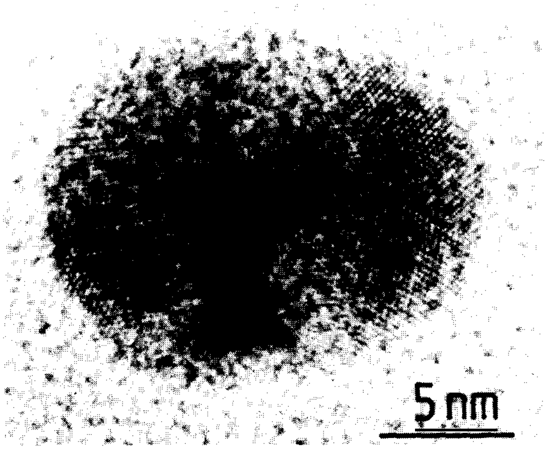

Fig. 9. Icosahedral-decahedral MTP. The Ic on the left and the Dh on the right are sharing two tetrahedral segments.

Fig. 10. Example of a decahedral MTP forming a bridge between two icosahedral MTPs.

ticles may contain strain-relieving dislocations; possible examples can be seen in fig. 6.

2.3.2. Icosahedral-decahedral MTPs

In a similar manner to that described above for the poly-icosahedral MTPs, these particles are the result of combining an Ic with a Dh by sharing two tetrahedral segments. An example is shown in fig. 9. Furthermore, not only does this poly-particle structure occur separately, it also appears as part of a more complicated particle. Fig. 10, for example, shows a Dh bridging two Ics in perfect register with the left-hand Ic.

2.3.3. Decahedral-lamellar MTPs

This particular structure (see fig. 11) is again similar to those described above in that it corresponds to a low energy matching between two particles. An alternative interpretation of this particle would be as

Fig. 11. A decahedral-lamellar MTP of silver.

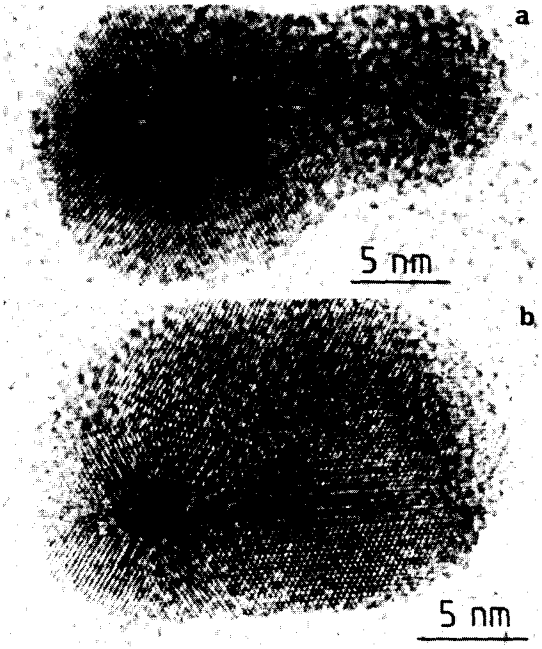

Fig. 12. (a) Polyparticle of gold. Left-hand particle is a ⟨111⟩ oriented Ic coalesced with another which may be an Ic. A possible partial dislocation is arrowed. (b) Polyparticle of gold showing a ⟨111⟩ oriented Ic embedded in the lower left and a possible lamellar twin in the lower right.

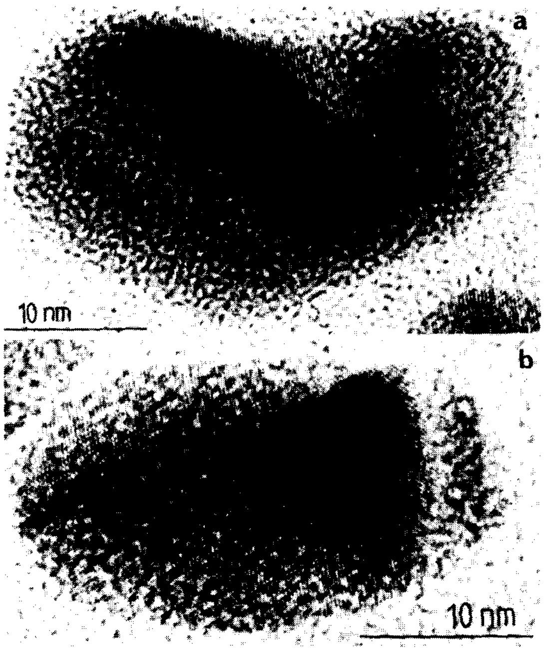

Fig. 13. (a) Polycrystal of gold with suggestions of lamellar twinning along the left lower edge. (b) Polycrystal of gold with some evidence for lamellar twinning.

a Dh with two rather extended segments and an additional twinned segment. However, the former classification seems more appropriate to the manner in which we believe these particles are formed, i.e. by coalescence.

2.3.4. More complicated polyparticles

Particles with an identifiable segment embedded within a large undecodable region were frequently observed. Two typical examples are shown in fig. 12, as explained in the figure caption. The present method of identification is not always capable of completely decoding such particles. However, these observations provide further evidence that particles retain their integrity as units even when coalesced.

2.4. Polycrystals

A number of particles were observed which could not be readily classified; two examples are shown in fig. 13. It is possible to group these particles under the rather loose title of polycrystals but this may be misleading. It is suspected that they are polyparticles which are not being observed in an orientation suitable for decoding their structures via lattice imaging.

3. Discussion

The results presented here demonstrate the usefulness of lattice imaging as a method of directly identifying and characterising small particles, as well as showing its potential for in-situ studies as a means of following the initial stages of particle nucleation. The technique is somewhat analogous to the selected zone dark field (SZDF) method employed by Heinemann and Poppa [10] whereby the (111) and (200) dark field images are recorded, along with the direction of translations with defocus, to give the origins of the various diffracted beams. The major advantage of direct lattice imaging is that it enables all (111) and (200) dark field images to be recorded simultaneously on a single micrograph with full directional information and very high spatial resolution. This is of substantial convenience for decoding complicated particles.

The predominant feature of the present observations is the manner in which various particles, such as MTPs and LTPs, appear to retain their integrity as units when involved in a larger particle. The general name polyparticles has been adopted to distinguish these from polycrystals and in many ways the analogy between polycrystals and polyparticles is useful: both are constructed from unit particles (single crystals or twinned particles respectively) with "grain boundaries" at the interfaces. This approach does not change qualitatively with more complicated units, although the rules for producing low energy grain boundaries do. In common with polycrystals, polyparticles appear to have certain low energy boundaries, as for example represented by the shared decahedra present in poly-icosahedral MTPs.

From the present results, the stability of these particles remains unclear. Their configurations may correspond to local energy minima stable to small perturbations, or they may be unstable intermediaries "frozen" in place during cooling of the substrate, and left with insufficient energy for a re-arrangement to a more favourable structure. The former is suspected to be true for many of the polyparticles. Indeed, as evidenced by many of the micrographs displayed here which were obtained months after the initial specimen preparation, this must be the case unless the current theoretical estimates for surface diffusion rates in small metal particles (e.g. ref. [11]) are several orders of magnitude too high. It is possible that the faceting of the particles plays an important role. For example, a recent theoretical analysis has shown that MTPs will be stable only when they have many large surface facets [12–14]. This type of behaviour might also be applicable to the polyparticles. However, the situation will only be properly resolved by high resolution in-situ studies of the annealing of polyparticles and further theoretical analysis.

Finally, it is interesting to note the similarity between the structures observed here and some models for amorphous films. Various authors (e.g. refs. [15–17]) have suggested the possibility of polytetrahedral structures (which are polyicosahedral MTPs in a 3D network) in amorphous materials. Our observations of polyicosahedral MTPs appear to provide some circumstantial evidence for these models.

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References

[1] V.E. Cosslett, Proc. Roy. Soc. (London) A370 (1980) 1.
[2] W.C. Nixon, H. Ahmed, C.J.D. Catto, J.R.A. Cleaver, K. C.A. Smith, A.E. Timbs, P.W. Turner and P.M. Ross, in: *Developments in Electron Microscopy and Analysis 1977.*, Ed. D.L. Misell (Institute of Physics, Bristol, 1977) p. 13.
[3] L.D. Marks, A. Howie and D.J. Smith, in: *Electron Microscopy and Analysis, 1979,* Ed. T. Mulvey (Institute of Physics, Bristol, 1980) p. 397.
[4] D.J. Smith and L.D. Marks, Phil. Mag., in press.
[5] L.D. Marks and D.J. Smith, J. Crystal Growth 54 (1981) 425.
[6] S. Ino, J. Phys. Soc. Japan 21 (1966) 346.
[7] D.W. Pashley, M.J. Stowell, M.H. Jacobs and T.J. Law, Phil. Mag. 10 (1964) 103, 127.
[8] Y. Saito, S. Yatsuya, K. Mihama and R. Uyeda, Japan J. Appl. Phys. 17 (1978) 1149.
[9] T. Komoda, Japan, J. Appl. Phys. 7 (1968) 27.
[10] K. Heinemann and H. Poppa, Appl. Phys. Letters 16 (1970) 515.
[11] A.D. Brailsford and N.A. Gjostein, J. Appl. Phys. 46 (1975) 2390.
[12] L.D. Marks, PhD Thesis, University of Cambridge (1980).
[13] L.D. Marks, in preparation.
[14] L.D. Marks, A. Howie and E. Yoffe, in preparation.
[15] M.R. Hoare and P. Pal, J. Crystal Growth 17 (1972) 77.
[16] P.H. Gaskell, Phil. Mag. 32 (1975) 211.
[17] P.H. Gaskell and A.B. Mistry, Phil. Mag. A39 (1979) 245.