CORRESPONDENCE

Direct lattice imaging of small metal particles

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ABSTRACT

Observations on small vapour-deposited particles of silver and gold with direct lattice imaging in the Cambridge University 600 kV high-resolution electron microscope have established unambiguously the presence of dislocations in particles as small as 15 nm in diameter. The detailed structure of more complicated 'polyparticles' can also be characterized directly.

Knowledge of the internal and surface structure of small metallic particles is basic to an understanding of the nucleation of thin metal films and any explanation of their important role in heterogeneous catalysis. Observations using electron diffraction and electron microscopy have proved invaluable in elucidating their crystallography, in particular in establishing the existence of multiple twinning within many particles (Ino 1966, Ino and Ogawa 1967, Allpress and Sanders 1967). These so-called multiple-twinned particles (MTPs) are known to be composed of either five or twenty tetrahedra which make up decahedra or icosahedra. (The icosahedral MTPs have a similar topological structure to spherical viruses (Caspar and Klug 1961) and geodesic domes (Fuller 1963).) However, such arrangements of tetrahedra are not completely space-filling, and some form of lattice distortion or imperfection is required.

Lattice imaging with axial illumination at 100 kV has been used previously to observe evaporated gold particles (Komoda 1968). Typically however, with an objective lens defocus, ΔZ, appropriate for best visibility of (111) lattice fringes of about 0.2–$0.4 \, \mu m$ (given by $\Delta Z = C_s \theta_{111}{}^2$, where C_s is the spherical aberration coefficient of the objective lens and θ_{111} is the diffraction angle), information about lattices of other periodicities cannot be seen unless the coherence of the incident illumination is adequate, and it is then considerably misplaced. At operating voltages of 500 kV or more the diffraction angles are much smaller than at 100 kV, substantially reducing the fringe displacements. Furthermore, the increased spatial coherence of the illumination afforded by the high-brightness lanthanum hexaboride electron gun

(Ahmed and Broers 1972) of the Cambridge HREM (Nixon, Ahmed, Catto, Cleaver, Smith, Timbs, Turner and Ross 1978, Cosslett 1980) results in a large depth of focus for fringe visibility. Moreover, the improved electron optical performance of this instrument (Cosslett, Camps, Saxton, Smith, Nixon, Ahmed, Catto, Cleaver, Smith, Timbs, Turner and Ross 1979) makes it possible to record details of the microstructure of MTPs over a wide range of lattice periodicities simultaneously (from as fine as 0·144 nm). Consequently, this particular microscope is well suited to direct lattice imaging of small metal particles.

The particles observed were prepared in a conventional manner by evaporation onto heated substrates of either NaCl (gold) or KCl (silver) which had been cleaved *in situ*. After coating with a thin film of amorphous carbon the samples were floated off in distilled water and mounted onto normal 3 mm specimen grids ready for electron microscopy. Operation was normally at magnifications of × 600 000 to × 700 000 for correction of any residual image astigmatism, but at magnifications of around × 300 000 to × 350 000 for the recording of micrographs (since there was no evidence that the emulsion grain size was limiting the fineness of the recorded detail, and the lower magnification afforded a larger field of view). A ± 30°, double-tilt specimen holder was normally used to ensure that the sample could be tilted to align the epitaxial normal parallel to the incident electron beam, as well as providing the means for tilting to other orientations where it was anticipated that further morphological features of interest might become apparent.

Typical of the decahedral MTPs observed is the particle of silver (measuring about 15 nm across) shown in fig. 1. This has been tilted to the ⟨100⟩ epitaxial orientation. The image typifies one of the major advantages of operating at

Fig. 1
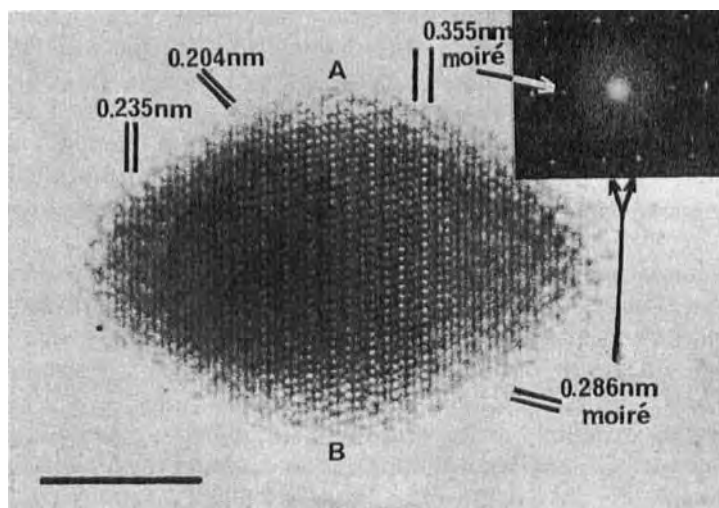
A decahedral MTP tilted to align the ⟨100⟩ epitaxial normal parallel to the incident beam direction. The optical diffractogram (inset) indicates the presence of lattice spacings of 0·204, 0·235, 0·286, 0·375 and 0·695 nm. Scale bar 5 nm.

higher accelerating voltages, namely the simultaneous imaging of many different spatial frequencies. Contributing to this particular image (as also shown by the optical diffractogram inset) are spacings of 0·204, 0·235, 0·286, 0·375 and 0·695 nm). On many occasions even finer fringes, of 0·102 and 0·118 nm, were observed in these decahedral MTPs. They are known to be caused by dynamical non-linear imaging effects, occurring only for certain crystal thicknesses, and so cannot be related directly to crystal planes of this spacing. It is appropriate to mention here that, unlike the structure images of atomic dimensions which can be obtained from many materials under optimum operating conditions with this microscope (Cosslett *et al.* 1979), the features observed in these MTP images do not necessarily correspond directly to atomic configurations. However, useful phase information can be obtained, as for example from the distinct kink in the 0·286 nm fringes across the line AB, which corresponds to a sharp change in the slope of the particle.
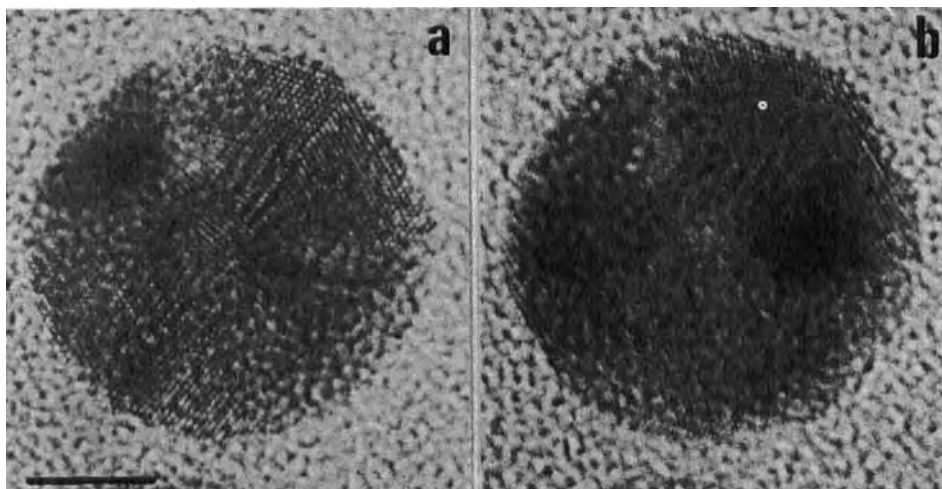
Fig. 2
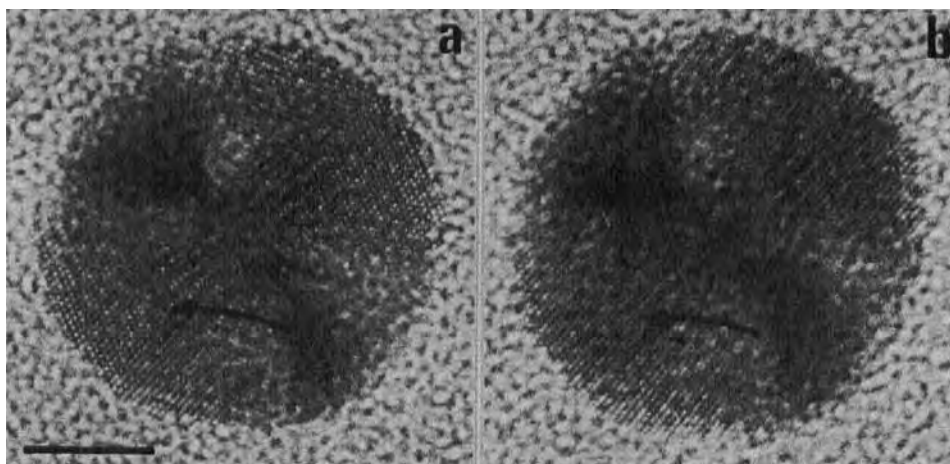
(*a*) An icosahedral MTP viewed down the ⟨112⟩ epitaxial normal, with partial dislocation arrowed. (*b*) The same particle, after tilting by 0·5°. Scale bar 5 nm.

Typical of the icosahedral MTPs imaged is the particle of silver (measuring about 12 nm across) shown in fig. 2 (*a*), with its ⟨112⟩ epitaxial normal parallel to the beam direction. The presence of a dislocation, which is suggested by the fringe behaviour within this particle (as arrowed), is established unequivocally by the image of the same particle, shown in fig. 2 (*b*), which was recorded after tilting the specimen by 0·5° with respect to the conditions used for fig. 2 (*a*). The position of this lattice defect clearly remains unaltered after tilting, which would not be the case should such an apparent defect be caused solely by some sort of imaging artefact arising from dynamical electron interactions within the particle. For example, it is well known that the appearance of moiré

fringes (which arise here from overlapping tetrahedra), and in particular their interaction with thickness extinction fringes, varies greatly with crystal orientation (Hashimoto, Mannami and Naiki 1961) and objective lens defocus. The presence and significance of such effects is clearly seen both in this particle, and in the images of many others such as that shown in fig. 3, which was recorded under identical conditions to those used in recording fig. 2. Our earlier preliminary work (Marks, Howie and Smith 1979) did not differentiate between these various possibilities so that our tentative identification of dislocations therein could have been incorrect.

Fig. 3

(a) An icosahedral MTP viewed down the $\langle 112 \rangle$ epitaxial normal. (b) The same particle, after tilting by 0·5°. Scale bar 5 nm.

It should be noted that partial dislocations and stacking faults were relatively common in both gold and silver MTPs. These often appeared to be quite diffuse, suggesting either the possibility of some screw component to the dislocation, or that the particles might be slightly tilted away from the orientation for best visibility. Complete characterization of the dislocations observed is thus far from straightforward, particularly given that it is not possible at present to observe them directly on the fluorescent screen of the HREM. However, it should at least be feasible to enumerate their occurrence as a function both of particle size and method of preparation. Eventually, we hope also to establish whether the presence and type of dislocations in these MTPs has any substantial influence on catalytic rates.

Many of the particles commonly observed in both the gold and silver samples could be shown, by means of their characteristic lattice fringe patterns, to contain one or more MTPs, both icosahedral and decahedral. In turn, this enabled the overall structures to be clarified. We have termed these ' poly-particles ' since they appear to be constructed in a similar manner to the more standard polycrystals, but with discrete particles such as (MTPs) being the

basic units rather than single crystals. For example, the polyparticle in fig. 4, is clearly an icosahedral–decahedral MTP sharing two tetrahedral segments. We hope eventually to use such images to study the nucleation and growth of MTPs and polyparticles into continuous thin films.

Fig. 4
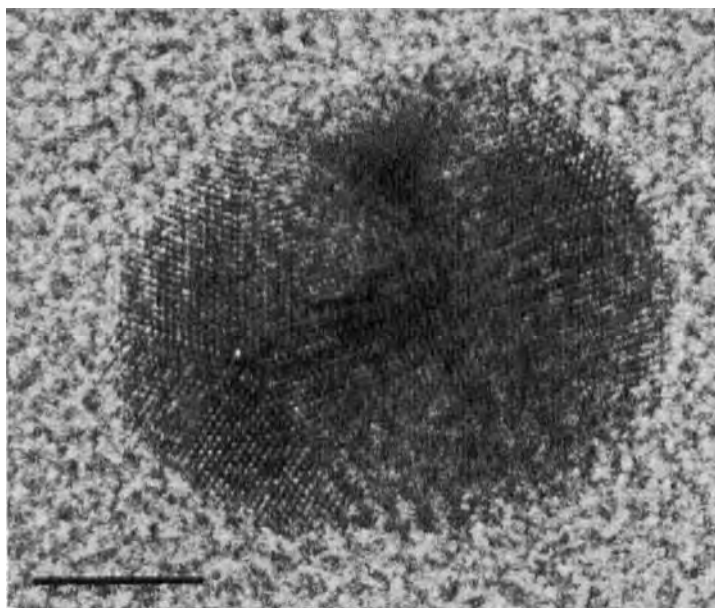
A multiply-twinned 'polyparticle' which can be identified directly as consisting of an icosahedron and a decahedron sharing two tetrahedral segments. Scale bar 5 nm.

Finally, it is to be expected that direct imaging of small metal particles, especially after their use as catalysts, will provide considerable insight into the catalytic process. Indeed, the ability to characterize directly the detailed structure of these particles, rather than simply noting their size and distribution, should permit extensive advances in this important area. The suggestion that MTPs may behave as unusual catalysts (Marks and Howie 1979) must now be reinforced by our observations of dislocations inside these particles, even when their sizes are so small.

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