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Microstructural Investigations of Tin–Molybdenum Oxides by High-Resolution Electron Microscopy

DAVID J. SMITH* AND L. A. FREEMAN

High Resolution Electron Microscope, University of Cambridge, Free School Lane, Cambridge, CB2 3RQ, United Kingdom

AND FRANK J. BERRY AND C. HALLETT

Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham, B15 2TT, United Kingdom

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Tin–molybdenum oxides, formed by the calcination of precipitates in air, have been examined by high-resolution electron microscopy. Low-temperature calcination gives rise to the formation of small tin(IV) oxide-type crystals amidst an amorphous material whereas higher-temperature treatment results in the development of a highly crystalline rutile-related phase composed of larger particles. High concentrations of molybdenum in the initial precipitates inhibits the thermally induced crystal growth. The common occurrence of superficial disorder in the larger particles is associated with surface damage resulting from the volatilization of excess molybdenum as molybdenum(VI) oxide. Planar faults were frequently observed within the particles and, in some cases, these defects were identified as twin boundaries enriched with molybdenum. The formation of these planar faults is discussed in terms of the preparative procedure.

Introduction

The initial examinations of planar defects in pure and antimony-doped tin(IV) oxide by transmission electron microscopy (*1*, *2*) have recently been complemented (*3*–*5*) by investigations using a 500-kV high-resolution electron microscope (HREM). The availability of lattice resolutions on the scale of 2 Å or better in this instrument (*6*) has enabled detailed information about the structural morphology of these materials to be obtained, including the nature of planar defects (*4*), the coexistence of crystalline, disordered, and amorphous phases (*3*, *5*), and the presence of amorphous surface layers (*3*, *5*). We have recently prepared some tin–molybdenum oxides by the calcination of precipitates at high temperature and have found them to be amenable to description as crystalline, rutile-related tin(IV) oxide type structures in which molybdenum is incorporated (*7*). The examination of these materials by transmission electron microscopy (*8*) has shown that they also contain planar defects and that the molybdenum is located at the twin boundaries. In this paper we report on the examination by HREM of some tin–molybdenum oxides, formed by the calcination of precipitates, to elucidate their microstructural properties

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* Present address: Center for Solid State Science and Department of Physics, Arizona State University, Tempe, Ariz. 85287.

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including localized irregularities and surface phenomena.

Experimental

The tin–molybdenum oxides were prepared by precipitation techniques. Aqueous ammonia was added in 1-ml aliquots to aqueous solutions of hydrated tin(IV) chloride at 70°C until the white precipitates, which initially redissolved, persisted as cloudy suspensions. The addition of aqueous solutions of ammonium molybdate, containing the required proportions of molybdenum, gave white precipitates which were removed by centrifugation, washed thoroughly with water, dried at room temperature, and calcined in air according to the conditions described in Table I. Samples for electron microscopy were prepared by gently grinding the material with an agate pestle and mortar under ethanol and allowing a drop of the resulting suspension to dry on a holey carbon film. Specimens were examined with the Cambridge University 600-kV HREM (*6*) operated at an accelerating voltage of 500 kV, with micrographs being typically recorded at magnifications of ca. $2.5–4.0 \times 10^5$ times. Observations were restricted, when ever possible, to crystal areas projecting over holes in the support film to avoid overlap interference in the final image arising from the support. Calibration of diffraction pattern camera length and image magnifications enabled lattice spacings present in the tin–molybdenum oxide particules to be identified.

Results

A brief summary of the observations of the various tin–molybdenum oxides is given in Table I.

Tin–molybdenum oxide A. This material consisted of small crystalline particles coexisting with substantial amounts of amorphous material, as seen in the typical field of view shown in Fig. 1. These microcrystallites, which had diameters of ca. 30–50 Å, could, by calibration of lattice fringe spacings, be identified as being of tin(IV) oxide-type structure.

Tin–molybdenum oxide B. This sample was composed of medium-sized SnO_2 particles, ca. 500 Å diameter, containing large numbers of planar faults and substantial crystallographic order. For example, the particle D shown in Fig. 2 contains a well-

TABLE I

TIN–MOLYBDENUM OXIDES: DETAILS OF CALCINATION AND SUMMARY OF OBSERVATIONS

Sample	Nominal molybdenum content (%)	Calcination treatment	Observations
A	20	400°C/24 hr	Small particles, considerable disorder, some amorphous material
B	1	600°C/24 hr	Medium size particles, some twinned with varying degrees of order
C	20	600°C/24 hr	Small particles, substantial disorder
D	1	900°C/24 hr	Large particles, sometimes twinned, some polycrystalline material, substantial disorder and faulting, some superficial disorder
E	20	900°C/24 hr	Small particles, frequently twinned, some surface disorder
F	5	1000°C/14 days	Large particles, often twinned, surface disorder; rare occurrence of disordered material
G	50	1000°C/14 days	Medium size particles, often twinned, some regions of disorder and faulting, much surface disorder

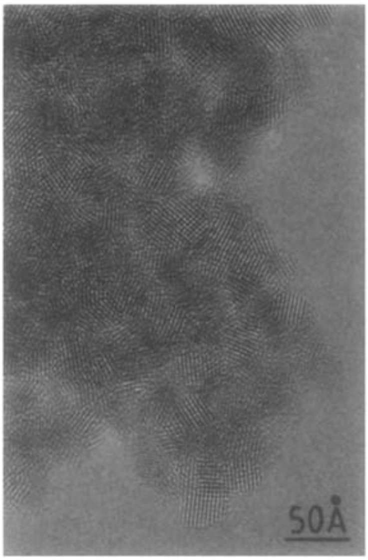

FIG. 1. High-resolution image of tin–molybdenum oxide A showing small crystalline particles coexisting with small fragments of amorphous material. The particles are identified as being Sn(IV) oxide by their lattice fringe spacings of 3.2 and 2.6 Å corresponding to the {001} and {011} lattice reflections, respectively.

ordered region separated from a highly disordered area by a planar boundary. Other particles were found to be heavily subdivided by planar defects which have the appearance of inclined twin boundaries. Many of the particles showed evidence of stepped surfaces, which possibly arise from the overlap of different-sized crystals. However, it is significant to note that, unlike the edges of particles calcined at higher temperatures, there was little indication of surface damage in this material.

Tin–molybdenum oxide C. In comparison with Sample B, also calcined at 600°C but only containing 1% Mo, this material consisted of much smaller tin dioxide-type particles of ca. 50 Å diameter. As shown in Fig. 3a, many of the particles were well-ordered with sharply defined edges, although others were considerably disordered. Some planar defects were visible, such as the twin boundary shown in Fig. 3b.

Tin–molybdenum oxide D. This sample was generally composed of larger, well-ordered, and sometimes twinned particles, ca. 500–700 Å diameter, between which small particles with highly disordered lattices were often found to coexist as shown by area D in Fig. 4a. It is also important to note the apparent misorientation of the lattice planes within ca. 5 Å of particle edges as shown in region S of Fig. 4b. Such narrow disordered regions at particle surfaces were a common feature of this and other materials calcined at high temperature. Some particles were heavily faulted.

Tin–molybdenum oxide E. The crystalline SnO_2 particles in Sample E were smaller, ca. 150–200 Å diameter, than those observed in Sample D calcined at the same temperature. The particles were frequently

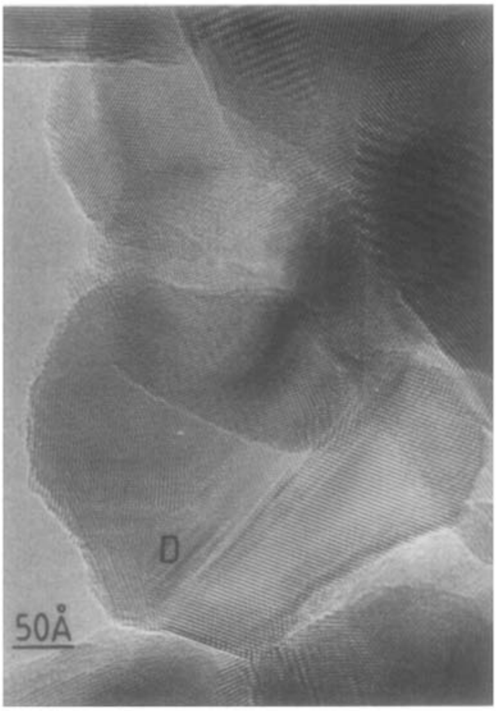

FIG. 2. Tin–molybdenum oxide B. High-resolution image showing typical particle morphology. The SnO_2 particle at D shows a well-ordered region separated from a highly distorted area by a twin boundary.

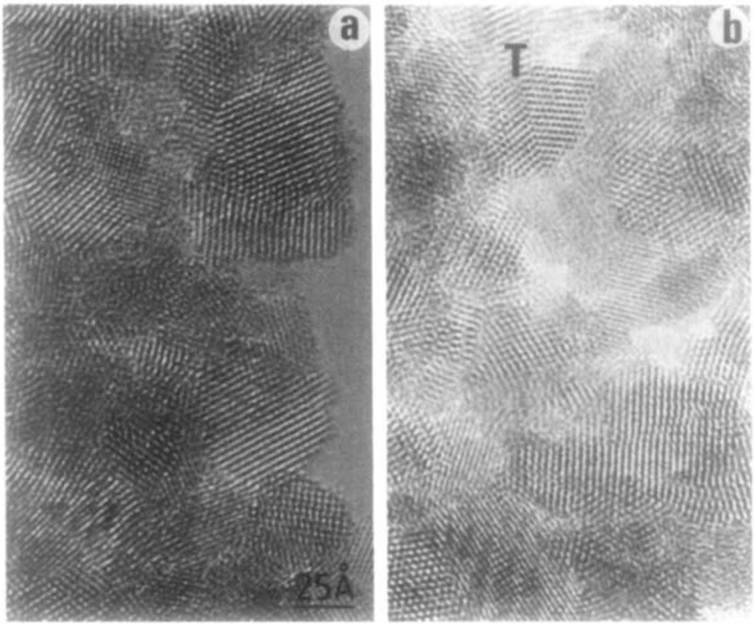

FIG. 3. Tin–molybdenum oxide C. (a) Small SnO_2 particles with well-defined edges. Lattice fringes visible have spacings of 3.2, 2.6, and 2.4 Å corresponding to {001}, {011}, and {020} reflections. (b) Similar region showing two small particles with short twin boundary (T) parallel to the beam direction.

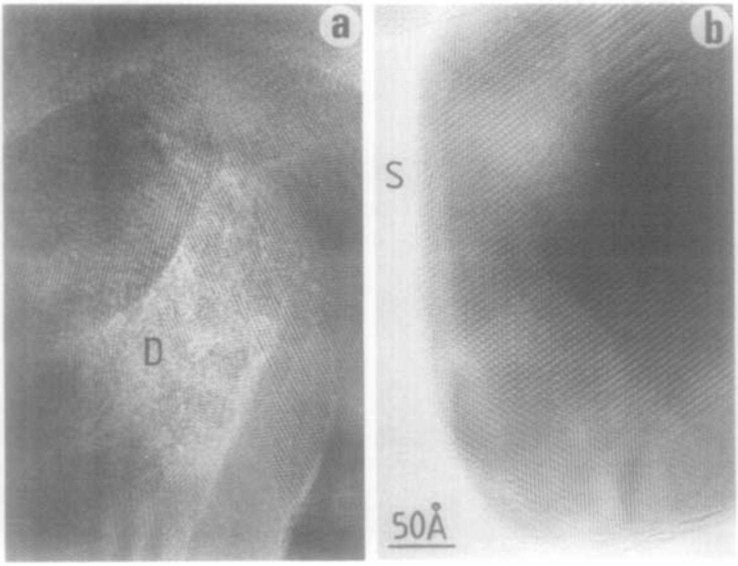

FIG. 4. Tin–molybdenum oxide D. (a) Small disordered particles (D), between larger crystalline particles, which were identified by lattice fringe spacings as being Sn(IV) oxide. (b) High-magnification image showing distorted lattice planes near the edge of a large SnO_2 crystal.

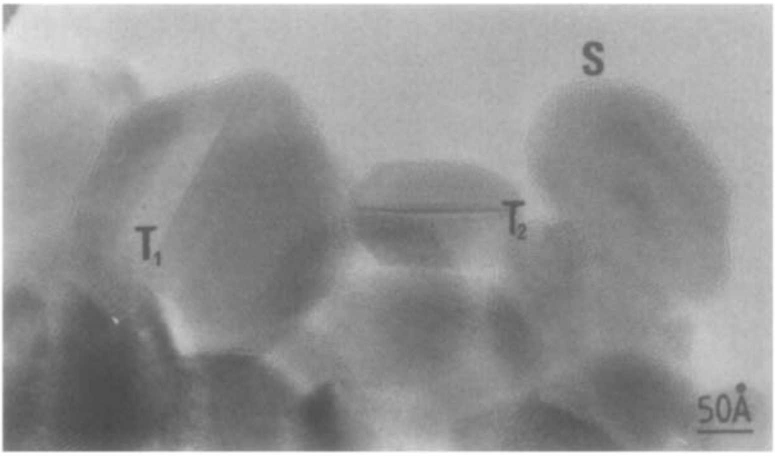

FIG. 5. Image of Sample E showing twinned SnO_2 crystals (T) and region of surface disorder (S).

twinned, as indicated by T_1 and T_2 in Fig. 5, and often contained disordered surfaces as is shown in region S.

Tin–molybdenum oxide F. This material was composed of large SnO_2 particles, ca. 2000 Å in diameter, which were frequently twinned. The typical twinned crystal shown in Fig. 6 exhibits the mirror symmetry relationship which is expected between the lattice plane across the boundary. Although the lattice fringes extend right to the edge of the particle, and the apparently well-formed surfaces exhibit no evidence of superficial disorder, other crystals in this sample displayed considerable surface disorder. The particle shown in Fig. 7, for example, has continuous lattice fringes characteristic of the bulk structure which extend to within ca. 5 Å of the surface, de-

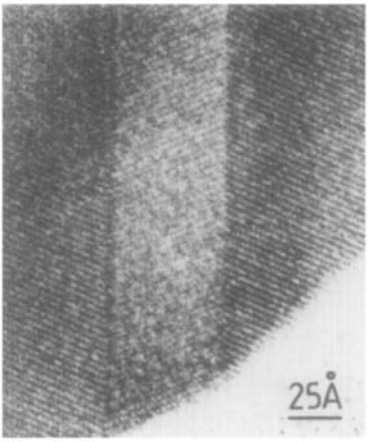

FIG. 6. Crystalline particle in tin–molybdenum oxide F showing mirror symmetry relationship of lattice planes across twin boundaries.

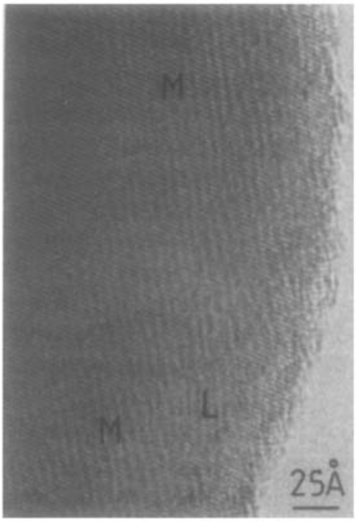

FIG. 7. Crystal in Sample F showing considerable surface disorder and Moire fringes (M) resulting from overlapping Sn(IV) oxide crystals.

spite the disordered area which exists within the region ca. 100 Å from the edge. The lattice planes in this region do not appear to be perfectly aligned and also contain Moire fringes (M) which are known to result from the overlap of misorientated lattice planes. The stepped appearance at L is also consistent with the crystal being constructed from the overlap of crystalline lamina of different sizes.

Tin–molybdenum oxide G. Sample G was composed of smaller particles, ca. 500–1000 Å in diameter, than those observed in Sample F which was calcined under the same conditions. This material contained numerous particles with planar defects and regions of disorder as can be seen in Fig. 8a. Moreover, the surfaces of many particles were highly disordered. Figure 8b, for example, shows an area S_1 where the surface is heavily stepped with irregular lattice planes while S_2 shows well-formed crystal planes which diffuse into a narrow, disordered surface region. It is possible that some of these differences in appearance of the particle edges may result from the different orientations of the crystals in the electron beam.

Discussion

The development of small crystalline regions in the initially amorphous precipitates heated at low temperatures may be envisaged as the first stage in the growth of the rutile-type phase with the aggregation of these small crystalline regions being the origin of formation of the planar defects, including the occurrence of twin boundaries. Hence the particle morphology, the extent of surface disorder, and the development of planar defects in these tin–molybdenum oxides requires consideration in terms of the calcination treatment and the molybdenum concentration of the initial precipitates.

Effect of calcination temperature. The changes which are induced at higher calcination temperatures are well illustrated by the HREM observations recorded from the

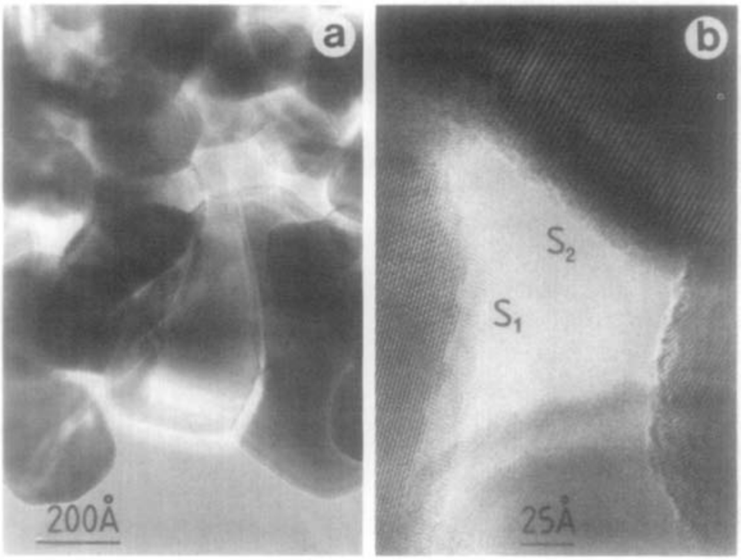

FIG. 8. Tin–molybdenum oxide G. (a) Low-magnification image showing numerous planar faults and regions of disorder in medium-sized particles. (b) High-magnification image showing particles, respectively, with heavily stepped surface (S_1) and narrow, disordered surface (S_2).

precipitates which initially contained 20% molybdenum. The coexistence of small, considerably disordered, tin dioxide-type crystals, and substantial quantities of amorphous material when the initial precipitate was heated to 400°C (Sample A), is consistent with the X-ray diffraction data which indicated that crystallization was initiated in the precipitates heated to low temperatures by the aggregation of SnO_2 units within the partially dehydrated matrix (*7*). Heating to 600°C (Sample C) resulted in the limited sintering of these small particles, although it is relevant to note that the amorphous phase observed at 400°C had apparently crystallized at this slightly higher temperature. Calcination at 900°C (Sample E) resulted in larger tin(IV) oxide-type crystals although it is significant that the particles were generally smaller than those obtained by the calcination of precipitates containing 1% molybdenum at temperatures as low as 600°C (Sample B). The pronounced surface disorder seen in the solids heated at elevated temperatures is discussed separately below.

Effects of molybdenum concentration. An inspection of the HREM images recorded from tin–molybdenum oxides which had received identical calcination treatments, namely Samples B and C heated at 600°C, Samples D and E heated at 900°C, and Samples F and G heated at 1000°C, shows that the materials with the low concentrations of molybdenum are composed, in all cases, of larger and generally better-ordered particles. These observations would appear to reflect the inhibition to crystal growth and crystallographic order which arises from the presence of large concentrations of molybdenum in the initial precipitate, although the differences in the particle size of samples F and G which were heated at 1000°C for 14 days is somewhat surprising.

Surface disorder. The thermally induced segregation of molybdenum away from the crystallizing rutile-related tin(IV) oxide-type matrix has been shown (*7*) to result in the formation of a macroscopically distinguishable molybdenum(VI) oxide phase which subsequently evaporates at sufficiently high temperatures. This process, which appears to be associated with the inability of molybdenum to find suitable accommodation within the rutile-type matrix (*7, 8*), appears to continue when the materials are calcined at higher temperatures but the nucleation at the surface of a discrete molybdenum(VI) oxide is precluded by the volatility of MoO_3 at these elevated conditions. Hence, the surface disorder which is observed in the tin–molybdenum oxides heated at the higher temperatures appears to be a reflection of superficial damage resulting from the segregation of molybdenum to the surface and its partial rapid volatilization as molybdenum(VI) oxide. In this respect it is also significant to note that the surfaces of these tin–molybdenum oxides have been shown by X-ray photoelectron spectroscopy (XPS) (*9*) to be enriched in molybdenum some of which is in a reduced state as a result of the loss of oxygen from the lattice at high temperatures. However, the surface disorder observed here, together with the XPS results (*9*), give no evidence for the existence of a discrete phase consisting of a reduced oxide at the surface.

Twin boundary formation. Planar defects, including twin boundaries, are not features of the solids when prepared at low temperature, especially those in which only limited crystal growth occurs. However, following higher temperature calcination, when extensive particle coalescence takes place, many crystals may be identified that contain twin boundaries which have been shown (*8*) by *X*-ray microanalysis to be enriched in molybdenum. Indeed, any molybdenum remaining in the lattice has been found to be below the level of detection by X-ray microanalysis (*8*). It is also pertinent to note that our studies of pure tin(IV) oxide made by precipitation methods (*8*) show that the presence of a dopant in the initial precipitate is not the sole cause of twin boundary formation. The HREM observations reported here may be interpreted in terms of the likely mechanism of twin boundary formation in these types of solids. The HREM images of the tin–molybdenum oxide prepared by the calcination of a precipitate containing 20% molybdenum at 600°C showed little evidence for planar faults but had surfaces which were shown by X-ray photoelectron spectroscopy to be enriched in molybdenum (*9*). Hence it is possible that some of the molybdenum detected at the twin boundaries by X-ray microanalysis (*8*) in samples heated to high temperatures may be trapped when the faults are formed by the sintering of small crystals. Further molybdenum may also segregate to the twin boundaries as a part of the general migration of molybdenum at elevated temperatures and remain isolated while the other molybdenum in the crystallizing rutile-type lattice is expelled to the surface where it subsequently volatilizes. The migration and segregation of molybdenum to twin boundaries implies that molybdenum located at these sites is accommodated in more favorable coordination than is available within the bulk matrix and is consistent with theoretical models with have been proposed for twin boundary formation (*4, 10*).

Comparison with tin–antimony oxides. Some of the structural features of the tin–molybdenum oxides revealed by the present HREM study are similar to those observed previously (*3, 5*) in tin–antimony oxides which were also formed by precipitation techniques. For example, both the thermal treatment and the cation concentration have marked effects on the size of the rutile-related tin(IV) oxide particles which develop from the calcination of the precipitates, with larger crystals resulting from the higher-temperature treatment of precipitates with initially lower cation concentrations. Planar defects, including twin boundaries, are relatively common features of both systems but, in the case of the tin–molybdenum oxides, microanalysis has also established (*8*) local enrichment of the twin boundaries with molybdenum, thus suggesting that similar enrichment with antimony might also occur for the tin–antimony oxides, as previously proposed (*3*) but not assessed. Finally, in both cases, the limited dopant solubility in tin(IV) oxide at higher temperatures results in the evolution of a separate oxide to the surface of the SnO_2 particles. Although thin amorphous surface layers were seen in the tin–antimony oxide materials (*3, 5*) it is interesting that, in the tin–molybdenum oxides, the crystalline surfaces were found to be highly disordered as a result of the segregation and subsequent volatilization of molybdenum from the surface as molybdenum(VI) oxide.

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