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An Electron Microscopy Investigation of Tin–Molybdenum Oxides

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Tin–molybdenum oxides prepared by the calcination of precipitates at high temperatures have been investigated by electron microscopy. The solids, which adopt the rutile-related tin(IV) oxide-type structure, are composed of crystalline particles containing planar defects, some of which have been characterized as twin boundaries. Although molybdenum has been found to be concentrated at these planar faults the examination of pure tin(IV) oxide prepared by similar methods shows that their formation is not dependent on the presence of molybdenum. It is suggested that molybdenum segregates to the twin boundaries during the calcination process to accommodate itself in more favorable coordination.

Introduction

The presence of planar defects in crystalline rutile-related tin(IV) oxide has been identified during earlier investigations of tin dioxide by optical and electron microscopy (*1, 2*). Recent studies by electron microscopy of solid solutions of antimony in tin(IV) oxide (*2–6*), sometimes prepared by the calcination of precipitates at elevated temperatures, have also reported the occurrence of similar planar faults in the rutile-type structure. Although these defects have been tentatively associated with twin boundaries their origin has yet to be established.

We have recently shown that tin–molybdenum oxides prepared by the calcination of precipitates at 1000°C may be described as rutile-related solids containing very small amounts of molybdenum within the tin(IV) oxide lattice (*7*). Any excess molybdenum which cannot be accommodated within the structure is volatilized during the calcination process. We have continued our investigations of these materials by examining some tin–molybdenum oxides prepared at high temperatures by transmission electron microscopy to identify the nature of the defects and to elucidate their formation in rutile-related solids.

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) chlo-

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ride at 70°C until the white precipitates, which initially redissolved, persisted as cloudy suspensions. The addition of aqueous solutions of ammonium molybdate gave white precipitates which were removed by centrifugation, washed with water, dried at room temperature, and calcined in air at 1000°C for 14 days. Ground samples of the tin–molybdenum oxides were collected in a carbon film and supported on 3-mm copper grids.

Transmission electron microscopy was performed with a Philips EM400T instrument operated at an accelerating voltage of 100 kV. Chemical analysis of the tin–molybdenum oxides was achieved by use of a 9100/60 EDAX energy dispersive X-ray analysis system interfaced with the electron microscope which was operated in the STEM and in the microprobe mode. The concentration of molybdenum in the planar faults observed in the tin–molybdenum oxides was assessed by comparing the integrated count in the Mo$K\alpha$ peak with the integrated count in the background windows which were placed at energies slightly below and above the energy of the Mo$K\alpha$ peak. The window widths were adjusted to achieve identical background and Mo$K\alpha$ counts (within counting errors) when the probe was placed in the center of a crystal. Molybdenum enrichment of a planar fault was identified by a significant change in the Mo$K\alpha$ to background-count ratio when the probe was placed on a boundary.

Results and Discussion

The tin–molybdenum oxides formed at 1000°C gave X-ray diffraction patterns consistent with the formation of monophasic rutile-related solids. The particles, which were generally between 500 and 5000 Å in diameter, frequently contained planar boundaries (Fig. 1), similar to those which have been observed in antimony-doped tin(IV) oxides (*2–6*). In order to show that these boundaries are twin boundaries it is necessary to correlate diffraction information with image information so that the rotation between the regions on either side of the boundary may be defined. Evidence to show that the boundary is a coherent twin boundary which defines the composition plane of the twin may be obtained straightforwardly if the electron diffraction pattern be recorded after the sample has been tilted to bring the planar fault to vertical. Such a diffraction pattern (Fig. 2), obtained when the boundary plane was tilted to vertical, shows a mirror plane along the [101]* direction. The figure may, by comparison with the representations illustrated schematically in Fig. 3 which depict the relationship between electron diffraction patterns which would be expected from the matrix and a [101]* twin, be viewed as the superposition of two twin-related patterns. This was confirmed by recording individual diffraction patterns from either side of the vertical boundary and from the whole crystal (Fig. 4).

The reasons for the occurrence of such planar defects in these tin–molybdenum oxides now requires consideration. In this respect it is pertinent to note that an electron microscopy study of single crystals of pure and antimony-doped tin(IV) oxide prepared by deposition from the vapor phase at high temperature (*2*) reported planar defects only in the doped material. In contrast a previous optical microscopy study of tin(IV) oxide prepared by vapor phase deposition has described (*1*) the widespread occurrence of planar defects in the pure single crystals. It is also relevant to record that computer simulations of antimony-free {001} twin boundaries have recently been reported to give excellent agreement with the high-resolution electron microscope images recorded from antimony-doped tin(IV) oxide (*5*). Hence the tendency of pure tin(IV) oxide to form twinned crystals and the extent to which dopant cations segre-

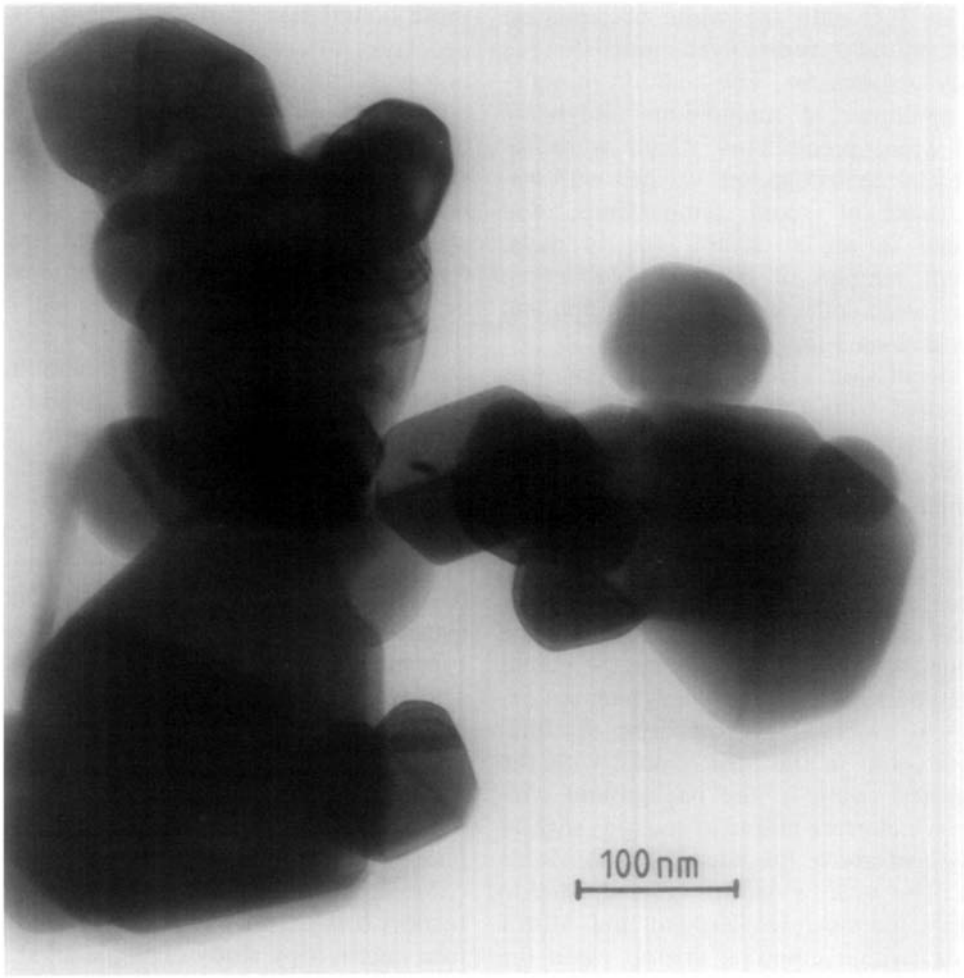

FIG. 1. Image of tin–molybdenum oxide calcined at 1000°C showing planar boundaries.

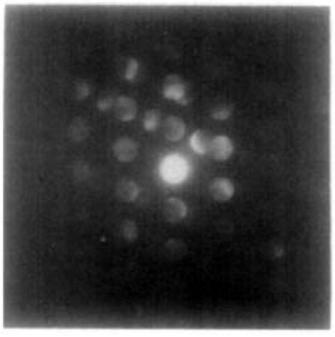

FIG. 2. Electron diffraction pattern recorded from a tin–molybdenum oxide calcined at 1000°C tilted to bring the boundary to vertical.

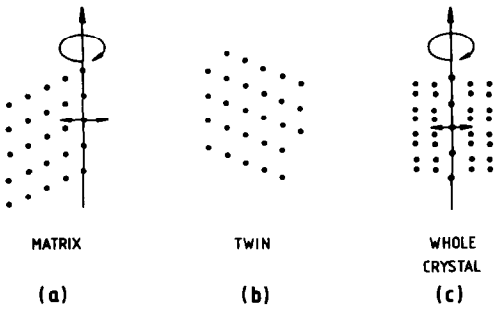

FIG. 3. Schematic representation of the relationship between electron diffraction patterns characterizing a matrix and its twin.

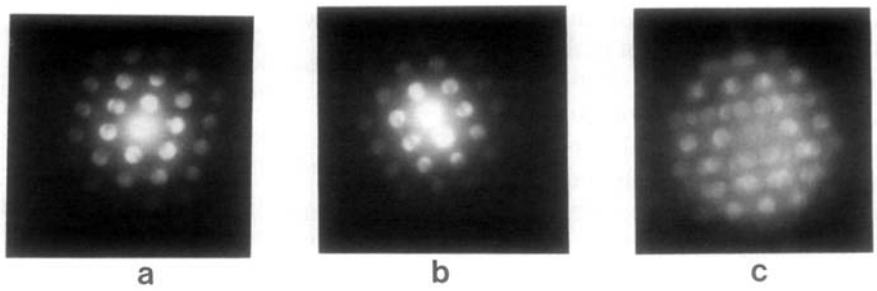

FIG. 4. Electron diffraction patterns recorded from a twinned crystal of tin–molybdenum oxide calcined at 1000°C: (a) diffraction pattern from the matrix; (b) diffraction pattern from the twin; (c) diffraction pattern from whole crystal.

gate to occupy sites at the twin boundaries in doped tin(IV) oxide is currently unclear.

Transmission electron micrographs recorded from a sample of pure white tin(IV) oxide prepared by the calcination at 1000°C of a thoroughly washed precipitate formed by the addition of base to an aqueous solution of tin(IV) chloride were similar to those recorded from the tin–molybdenum oxides. The examination of separate crystals by electron microscopy showed the presence of twin boundaries. It therefore appears that the formation of twin boundaries in antimony or molybdenum-doped tin(IV) oxides formed by precipitation technique is not necessarily related to the influence of the dopant on the rutile-type structure of tin(IV) oxide. However, analysis of the twin boundaries observed in the molybdenum-containing samples using an electron probe of ca. 50 Å diameter gave results in which the integrated Mo$K\alpha$ signal was found to be significantly greater than the background intensity at a 95% confidence level (Fig. 5). In a few cases no significant difference was observed and, although it is possible that such isolated observations were indicative of no detectable molybdenum segregation, it is more likely that slight specimen drift (ca. 10–20 Å) which is not easy to observe was responsible for the reduction of the molybdenum signal to background level.

The probe size and unknown sample thickness precluded an unequivocal evaluation of whether the molybdenum concentration corresponded to a single atomic plane at the twin boundary. However, the total molybdenum signal which corresponded to ca. 0.2 at.% Mo may, given the probe size and assuming a contribution from beam spreading caused by high-angle elastic scattering of the incident electrons, be associated with about 50 atomic planes of SnO_2 and suggests that less than the equivalent of one monolayer of molybdenum segregates to a twin boundary.

The origin of the high concentrations of molybdenum at the twin boundaries may be associated with the migration of molybdenum away from the crystallizing rutile-type phase under the influence of high tempera-

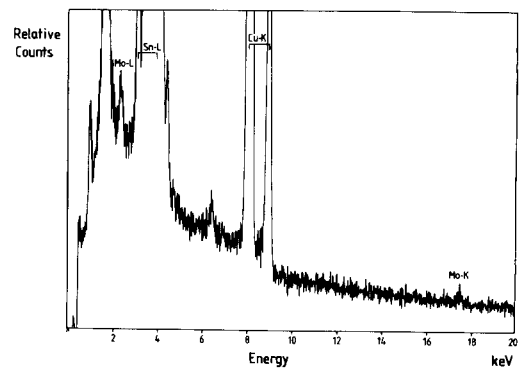

FIG. 5. X-Ray spectrum recorded from twin boundary in a tin–molybdenum oxide calcined at 1000°C.

ture calcination (7). Although this process may involve the movement of molybdenum to the surface of the tin–molybdenum oxides and its subsequent volatilization as molybdenum(VI) oxide is also reasonable that some molybdenum should migrate through the matrix to the twin boundaries from where volatilization is difficult. Such a process would imply that the molybdenum located at the twin boundaries and in the surface is accommodated in more favorable coordination than is available within the bulk matrix.

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