The Segregation of Molybdenum to Twin Boundaries in Molybdenum-doped Tin(IV) Oxide

Frank J. Berry,*[a] Christopher Hallett,[a] Michael H. Loretto,[b] and David J. Smith[c]

[a] *Department of Chemistry, and* [b] *Department of Metallurgy and Materials, University of Birmingham, Birmingham B15 2TT, U.K.*
[c] *Department of Metallurgy and Material Science, University of Cambridge, Cambridge CB2 3RQ, U.K.*

Molybdenum-doped tin(IV) oxide has been shown by electron microscopy to contain many planar defects including twin boundaries; the segregation of molybdenum to these twin boundaries has been unequivocally established by *X*-ray microanalysis and associated with the thermally induced migration of molybdenum to more favourable sites within the rutile-type lattice.

Although some recent investigations of antimony-doped tin(IV) oxide have reported the formation of twin boundaries within the crystalline particles,[1—5] there is much uncertainty as to whether the dopant induces the formation of these planar faults by segregating to the twin boundaries. Indeed, recent computer simulations of antimony-free twin boundaries in tin(IV) oxide have given excellent agreement with the high-resolution electron microscope images recorded from antimony-doped tin(IV) oxide.[4] The experimental determination of whether or not molybdenum segregates to planar defects is therefore of intrinsic interest, and, possibly of greater significance, may also contribute towards an understanding of the causes and mechanisms of planar fault formation in rutile-related structures.

Several molybdenum-doped tin(IV) 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 gave white precipitates

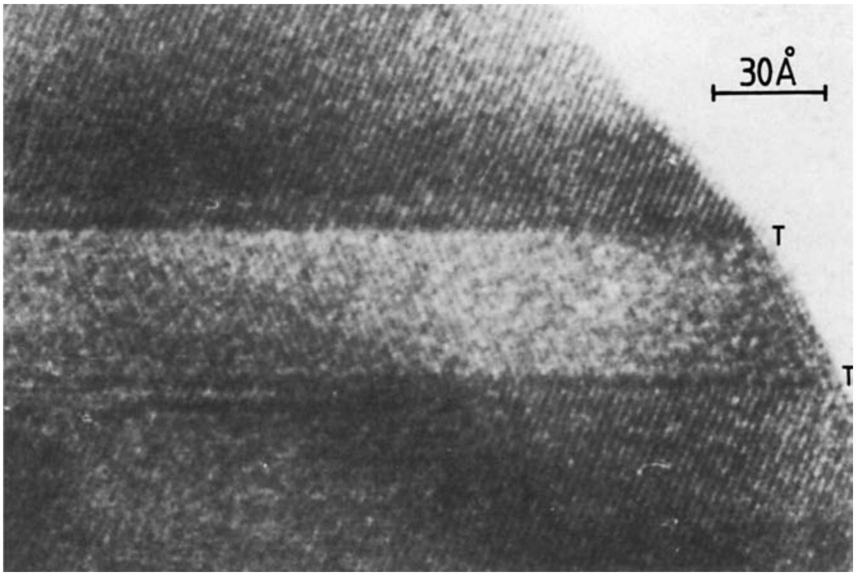

Figure 1. High-resolution electron microscope image of a crystalline particle of molybdenum-doped tin(IV) oxide formed at 1000 °C showing the mirror symmetry relationship of lattice planes across the twin boundaries (T).

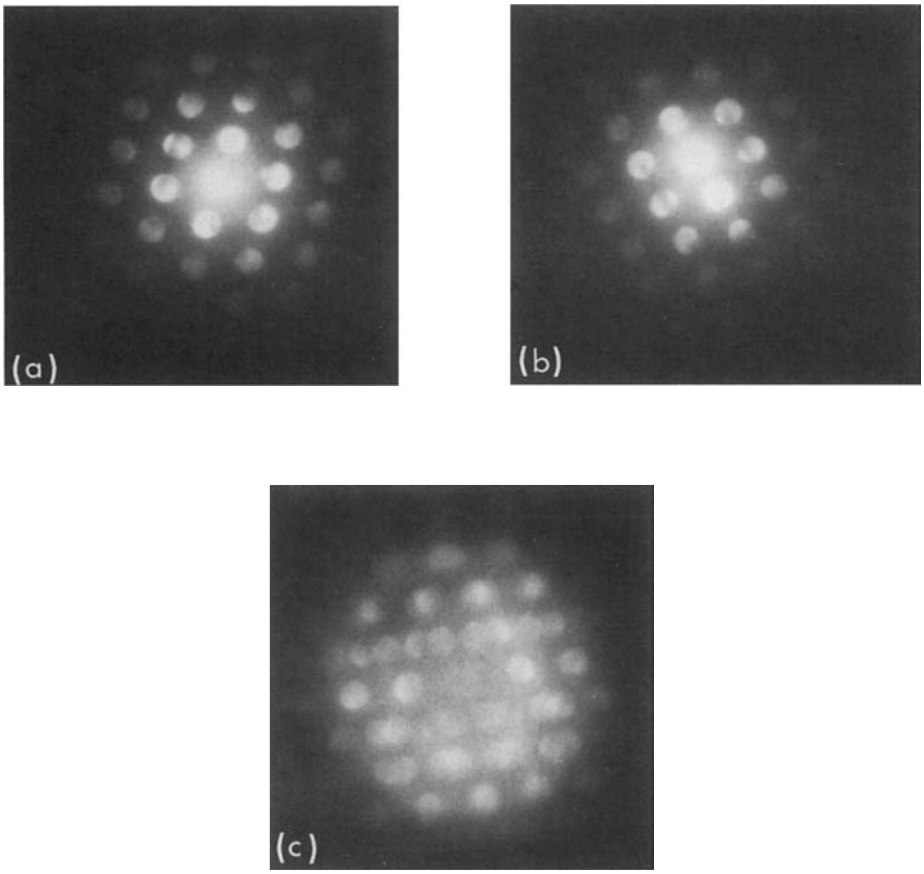

Figure 2. Electron diffraction patterns recorded from a twinned crystal of molybdenum-doped tin(IV) oxide calcined at 1000 °C: (a) from one side of the boundary, (b) from the other side, (c) from the whole crystal.

which were removed by centrifugation, washed with water, dried at room temperature, and calcined in air at 1000 °C for 14 days. Transmission electron microscopy was performed with a Philips EM400T instrument and *X*-ray microanalysis recorded by use of a 9100/60 EDAX energy-dispersive *X*-ray analysis system interfaced with the electron microscope. High-resolution electron microscopy was performed with the Cambridge University 600 kV instrument.[6]

The tin–molybdenum oxides prepared at 1000 °C gave *X*-ray diffraction patterns consistent with the formation of monophasic rutile-related solids. Electron microscopy established that the materials consisted of tin(IV) oxide-type crystals, generally between 500 and 5000 Å in diameter, which frequently contained planar defects, many of which could be identified as twin boundaries. The image of the large SnO_2-type particle recorded with the high-resolution electron microscope (Figure 1) shows the expected mirror symmetry relationship of the lattice planes across the twin boundary.

Electron diffraction patterns recorded from either side of the vertical planar boundary and from the whole crystal using a small probe confirmed the description of the planar defects as twin boundaries (Figure 2). The electron diffraction pattern recorded from the matrix on one side of the boundary (Figure 2a) is identical to that from the other side (Figure 2b), except for a rotation about the beam direction, and the two patterns are clearly related by both the reflection and C_2 symmetry operations as expected for a twinned crystal. Furthermore, the diffraction pattern recorded from the whole crystal (Figure 2c) is characterised by pairs of spots which originate from each side of the twin boundary.

The occurrence of such planar defects in these molybdenum-doped tin(IV) oxides requires a consideration of the tendency of pure tin(IV) oxide to form twinned crystals and the extent to which dopant cations segregate to sites at the twin boundaries. Micrographs recorded from pure 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, with many of the crystals containing twin boundaries. The result demonstrates that the formation of twin boundaries in the molybdenum-doped tin(IV) oxides formed by precipitation techniques is not necessarily related to the influence of the dopant on the rutile-type structure of tin(IV) oxide.

However, it is significant that *X*-ray microanalysis at the twin boundaries in the molybdenum-doped tin(IV) oxide particles, using an electron probe of *ca.* 50 Å diameter, showed that the integrated Mo-K_α signal was significantly greater than the background intensity at 95% confidence level (Figure 3). Moreover, analysis of regions away from the twin boundaries showed no detectable concentrations of molybdenum.

The presence of molybdenum at the twin boundaries can be associated with the migration of molybdenum away from the crystallising rutile-type phase under the influence of high-temperature calcination. Although this process may involve the movement of molybdenum to the surface of the tin–molybdenum oxide and its subsequent volatilisation as molybdenum(VI) oxide, it is also reasonable that some molybdenum should migrate through the matrix to the twin boundaries from where volatilisation is difficult. Such a process would imply that the molybdenum located at the twin boundaries is accommodated in more favourable co-ordination than is available within the bulk matrix and is consistent with theoretical models[7] for twin boundary formation.

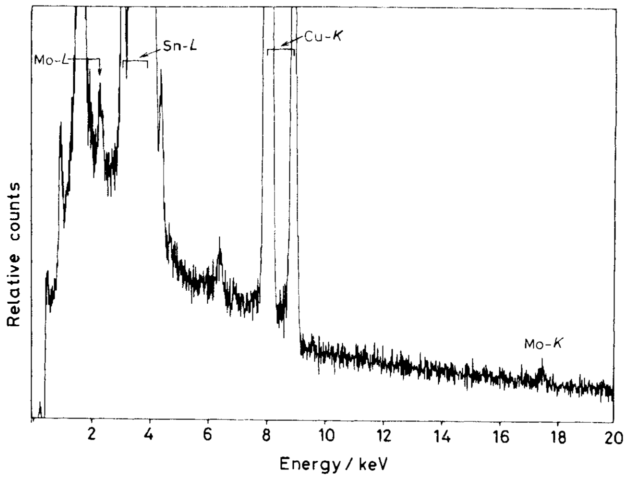

Figure 3. *X*-Ray spectrum recorded at a twin boundary in molybdenum-doped tin(IV) oxide formed at 1000 °C showing a small, but significant, Mo-K_α peak.

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