Antimony-doped Rutile Titanium(IV) Oxide†

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Titanium–antimony oxides formed by calcination of precipitates at elevated temperatures have been shown by powder *X*-ray diffraction, ^{121}Sb Mössbauer spectroscopy, energy-dispersive *X*-ray analysis, thermal analysis, and temperature-programmed reduction techniques to be materials in which small concentrations of antimony(V) are accommodated within the rutile titanium(IV) oxide lattice. The solids can be envisaged as being derived from the thermally induced dehydration and crystallisation of an initially amorphous titanium–antimony hydroxide precipitate such that the antimony which cannot be accommodated within the rutile lattice migrates to the surface to form a volatile antimony oxide phase. However, an examination of the monophasic antimony-doped titanium(IV) oxide by *X*-ray photoelectron spectroscopy showed no enrichment of the surfaces by antimony. An investigation of the titanium–antimony oxides by transmission electron microscopy identified planar defects which were shown by electron diffraction to be twin boundaries. The twin boundaries were found to be free of quinquevalent dopant. No evidence has been found for the occurrence of crystallographic shear planes.

Although the fundamental properties of antimony-doped rutile-related tin(IV) oxide have recently received substantial attention,[1–6] as indeed have several other mixed oxides with rutile-type structures,[7] the antimony-doped archetypal rutile titanium(IV) oxide has been identified in a recent review[7] as having received a sparsity of attention. We therefore initiated an investigation of the titanium–antimony–oxygen system but, as noted in the preceding paper,[8] other workers[9] reported investigations of antimony-doped rutile whilst our manuscripts were in preparation. In the preceding paper[8] we described how precipitates containing antimony and titanium give, when heated at high temperatures, antimony-containing titanium dioxide phases. Given the similarity in size of antimony(V) and titanium(IV) in octahedral oxygen co-ordination,[10] it is not unreasonable to expect that antimony could form a substitutional solid solution in rutile titanium dioxide. We have therefore investigated the bulk and surface properties of the titanium–antimony oxides formed by calcination of precipitates at high temperatures, using a range of techniques including *X*-ray diffraction, electron microscopy, ^{121}Sb Mössbauer spectroscopy, thermal analysis, temperature-programmed reduction methods, and *X*-ray photoelectron spectroscopy, and, in this paper, we report on the nature of these monophasic solids.

Experimental

Titanium–antimony oxides were prepared by calcination of precipitates nominally containing between 10 and 90% antimony. Titanium tetrachloride (10 g) in concentrated hydrochloric acid (37 cm^3) was mixed with water (51 g). Appropriate amounts of antimony(V) chloride were added to stirred aliquots of the titanium tetrachloride solution which had been diluted with water (500 cm^3). Ammonia was slowly added until the mixture attained a pH of *ca.* 8. The resulting precipitates were filtered off, washed with water, dried at 150 °C (12 h), and calcined in air at temperatures between 900 and 1 200 °C.

Powder *X*-ray diffraction patterns were recorded with a Philips PW 1050/70 *X*-ray diffractometer fitted with a vertical goniometer, using Cu-K_α radiation.

Antimony-121 Mössbauer spectra were recorded with a Cryophysics MS-121 microprocessor-controlled Mössbauer spectrometer using a 0.45-mCi Ca^{121m}SnO$_3$ source and samples containing *ca.* 30 mg ^{121}Sb per cm^2. The data were collected with both the source and absorber at 77 K. The drive velocity was calibrated with a cobalt-57/rhodium source and a natural iron-foil absorber. All the spectra were computer fitted.

Temperature-programmed reduction (t.p.r.) experiments using *ca.* 50 mg of sample and a flow rate of 10% hydrogen–90% nitrogen reducing gas of *ca.* 20 cm^3 min^{-1} were performed with either a Carbolite temperature programmer, a katharometer, and a Johnson Matthey hinged furnace, or a Pye Unicam series 104 gas chromatograph furnace and programmer. Preparative-scale experiments were performed with *ca.* 1 g samples and a flow rate of reducing gas of 120 cm^3 min^{-1}.

Simultaneous thermal analyses were performed in air with a Stanton Redcroft TG780 apparatus using platinum boats and an alumina reference. Samples (*ca.* 50 mg) were heated from 25 to 1 500 °C at a rate of 10 °C min^{-1}.

Transmission electron microscopy was performed with a Philips EM400T instrument operated at an accelerating voltage of 100 kV. Chemical analysis of the titanium–antimony 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 scanning-transmission and microprobe modes.

X-Ray photoelectron spectra were recorded with a Vacuum Generator ESCA III Mark 1 instrument using Al-K_α radiation. The samples were fine powders mounted on double-sided adhesive tape and examined at room temperature. The binding energies were measured relative to the carbon 1*s* signal at 284.6 eV arising from carbon impurity on the sample surfaces.

Results and Discussion

The four precipitates containing 5, 20, 30, and 80% antimony gave, following calcination at either 1 000 or 1 200 °C, powder *X*-ray diffraction patterns and ^{121}Sb Mössbauer spectra characteristic of antimony(V)-containing titanium(IV) oxide. The temperature-programmed reduction profiles were characteristic of the reduction of antimony in the mixed oxide[8] and, given the similarity between the data recorded from all the materials

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† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

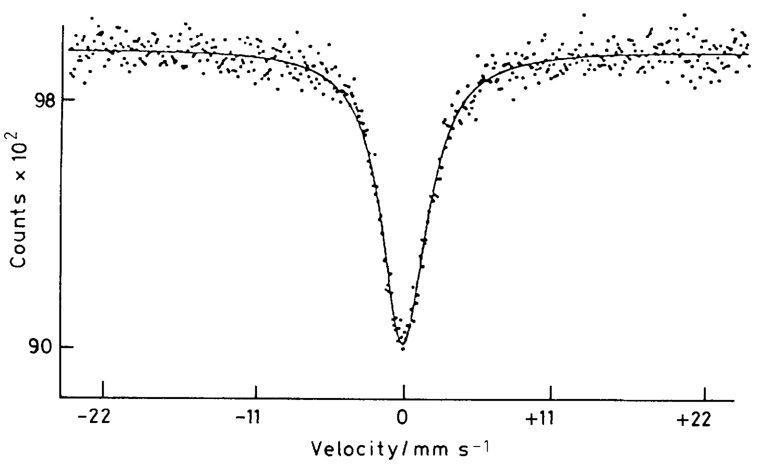

Figure 1. Antimony-121 Mössbauer spectrum recorded from a titanium–antimony oxide formed at 1 000 °C

and also the fingerprint character of t.p.r. profiles,[11,12] imply that the nature of the titanium–antimony oxides formed at high temperatures is independent of the antimony concentrations in the initial precipitates.

In this respect it is pertinent that the examination of the titanium–antimony oxides by energy-dispersive *X*-ray analysis showed the antimony concentrations in materials formed by calcination of precipitates nominally containing up to 90% antimony at 1 000 °C for 10 d to be less than *ca.* 4%. Calcination at 1 100 °C for 10 d gave mixed oxides in which the antimony concentrations were less than *ca.* 1.5%. Although the lattice parameters, as derived from powder *X*-ray diffraction data, of the mixed oxides calcined at any given temperature were essentially similar within the errors and independent of the antimony content in the initial precipitates, the lattice parameters of materials heated at 1 100 °C for 10 d, $a = b = 4.594 \pm 0.003$, $c = 2.962 \pm 0.003$ Å, were similar to those of pure titanium(IV) oxide, $a = b = 4.593 \pm 0.003$, $c = 2.959 \pm 0.003$ Å, and smaller than those recorded from the mixed oxides calcined at 1 000 °C for 1 d, $a = b = 4.598 \pm 0.003$, $c = 2.968 \pm 0.003$ Å. The results are consistent with the t.p.r. and energy-dispersive *X*-ray analysis data and are indicative of the thermally induced migration and volatilisation of antimony from the titanium(IV) oxide lattice at elevated temperatures. Indeed, simultaneous thermal analysis of the precipitates dried at 150 °C showed large weight losses from the materials of high antimony content at temperatures exceeding *ca.* 1 000 °C which can be associated with the volatilisation of large quantities of antimony oxide.

The antimony-121 Mössbauer spectra recorded from all the titanium–antimony oxides calcined at 1 000 °C showed single absorptions characteristic of antimony(V) (Figure 1). No evidence was observed for the presence of antimony in any other oxidation state in these solid solutions formed at high temperatures.

Hence the results, taken together, suggest that the titanium–antimony oxides formed at high temperatures are best described as materials in which small concentrations of antimony(V) are accommodated within the titanium(IV) oxide lattice. The results are distinctly different from those recently reported[9] from an *X*-ray diffraction and *X*-ray photoelectron study of the product of the solid-state reaction of TiO_2 and Sb_2O_4 at 1 000 °C which was described as a solid solution of up to 7 mol % of antimony(III) in rutile. It seems that the solids investigated here derive from the thermally induced dehydration and crystallisation of an initially amorphous titanium–antimony hydroxide precipitate such that the antimony which cannot be accommodated within the octahedral sites in the rutile lattice, such as antimony(III) which was identified by ^{121}Sb Mössbauer spectroscopy in materials heated at moderate temperatures and which is formed[13] by partial thermal reduction of antimony(V), migrates to the surface of the rutile-type phase to form α-antimony tetraoxide which volatilises at elevated temperatures. This model is similar to that previously proposed[1] for the formation of solid solutions of low concentrations of antimony in rutile-related tin(IV) oxides which were subsequently shown[5,6] to have surfaces enriched in antimony as a result of the migration of antimony through the rutile-type lattice to the solid surface.

Hence three of the titanium–antimony oxides prepared here by calcination of precipitates containing 20, 50, and 80% antimony at 1 100 °C for 10 d, together with samples of rutile titanium dioxide and α-antimony tetraoxide, were examined by *X*-ray photoelectron spectroscopy. Although the data recorded here were not amenable to interpretation in terms of the oxidation state of antimony, as has been experienced by other workers,[6,14,15] a comparison of the Ti $2p_{\frac{3}{2}}$ and Sb $3p_{\frac{3}{2}}$ peak intensity ratios indicated that the surface antimony concentrations were not significantly different from the antimony contents of the bulk which were determined by energy-dispersive *X*-ray analysis. Hence the results are strikingly different from those determined[5,6] by *X*-ray photoelectron spectroscopy of the rutile-related tin–antimony oxides where, despite low concentrations of antimony in the bulk, the surfaces were significantly enriched by antimony.

The examination by transmission electron microscopy of a titanium–antimony oxide prepared by calcination of a precipitate nominally containing 5% antimony at 1 000 °C for 24 h showed the material to be composed of particles, *ca.* 3 500 Å in diameter, some of which appeared to be divided by dark lines. Although the introduction of trivalent cations into the titanium dioxide rutile lattice has been shown to induce crystallographic shear,[16–21] the diffraction contrast observed in the particles examined here did not correspond to the occurrence of crystallographic shear planes. In these respects it is relevant that recent studies of antimony- and molybdenum-doped rutile-related tin(IV) oxide prepared by calcination of precipitates have also identified planar defects in the rutile-related tin dioxide lattice which are similar to those observed here and which have been identified as twin boundaries.[3,4,22–24]

The planar defects observed here in the antimony(V)-doped rutile titanium(IV) oxide were shown to be coherent twin boundaries by recording micro diffraction patterns from either side of a vertical boundary. The results (Figure 2) demonstrate

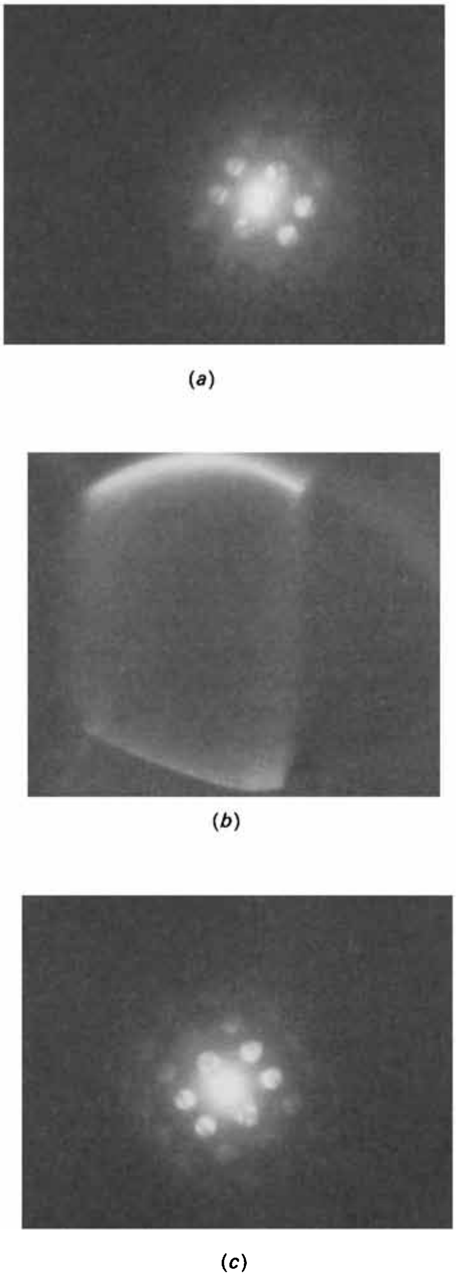

Figure 2. Dark field image and electron diffraction patterns recorded from antimony(V)-doped rutile titanium(IV) oxide: (*a*) diffraction pattern recorded from one side of the boundary indicated in the dark field image (*b*) where 2 cm = 0.1 μm; (*c*) diffraction pattern recorded from the other side of the boundary

that the diffraction patterns [Figure 2(*a*) and (*c*)] are related by a reflection and C_2 symmetry operation as expected for a twinned crystal in which the boundary is parallel to the vertical $\{011\}$ twin plane [Figure 2(*b*)]. Thus the twin plane in antimony(V)-doped rutile titanium(IV) oxide is crystallographically similar to the $\{101\}$-type twin planes previously observed in antimony(V)-doped rutile-related tin(IV) oxide.[3,4,22] Selected area diffraction recorded from an area covering the vertical twin boundary in the antimony(V)-doped rutile titanium(IV) oxide showed the expected doubling of spots and dark field images [Figure 2(*b*)] showed intensity on only one side of the boundary. Both results are consistent with the planar defect being a twin boundary. All the observations were confirmed by repeating the experiments on other particles and, taken together, demonstrate the occurrence of twin boundaries in antimony(V)-doped rutile titanium(IV) oxide.

Pure rutile titanium(IV) oxide investigated during this study did not show any evidence of planar defects and this only appears to have been induced in the past by mechanical grinding.[25] Given that trivalent cations induce crystallographic shear in rutile titanium dioxide,[16–21] it seems possible that the occurrence of twin planes in antimony(V)-doped rutile titanium(IV) oxide, which are similar to those previously identified in antimony(V)-doped rutile tin(IV) oxide[3,4,22] and molybdenum(V)-doped rutile tin(IV) oxide,[23,24] may be associated with the quinquevalent dopant. However, the examination of the antimony(V)-doped rutile titanium dioxide by energy-dispersive *X*-ray analysis with the microprobe positioned at, and subsequently on either side of, the twin boundary failed to detect any segregation of antimony to the planar fault. Although electron beam broadening degrades the spatial resolution according to $t^{\frac{3}{2}}$, where t is the particle thickness, such that segregation to the planar defects in the larger particles examined here might be difficult to detect and similar experiments performed on small particles with a more intense electron source are desirable, it remains relevant that the energy-dispersive *X*-ray data reported here showed the antimony content to be consistent over the crystal with a 98% confidence limit. The result therefore contrasts with that recorded[23,24] from molybdenum(V)-doped rutile-related tin(IV) oxide where the dopant was found to segregate to the twin boundary. Given the similarity in size of antimony(V) and titanium(IV) in octahedral oxygen co-ordination,[10] it seems likely that low concentrations of antimony(V) form a substitutional solid solution in rutile titanium(IV) oxide. The influence of such substitution on the ensuing defect structure must await further more detailed investigation.

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