An Investigation of the Titanium–Antimony–Oxygen System by *X*-Ray Diffraction, Antimony-121 Mössbauer Spectroscopy, and Temperature-programmed Reduction

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Titanium–antimony oxides have been prepared by precipitation methods and investigated by a number of techniques. Powder *X*-ray diffraction has shown the initial precipitates to be amorphous materials which begin to form distinguishable crystalline phases when calcined in air at temperatures exceeding *ca.* 500 °C. The nature of the crystalline phases depends on the relative concentration of the titanium and antimony cations in the initial precipitates and the calcination temperatures. The oxidation states of antimony in the materials have been determined by antimony-121 Mössbauer spectroscopy. The materials formed at temperatures exceeding 1 000 °C may be described as solid solutions of < *ca.* 4% antimony(V) in titanium(IV) oxide. The reducibility of some amorphous hydroxides and crystalline oxides of titanium and antimony when treated in hydrogen and the nature of the reduction products has been studied by temperature-programmed reduction and antimony-121 Mössbauer spectroscopy. The results demonstrate the complementary nature of the two techniques and their capacity to examine the character of reduction processes in the amorphous and crystalline solid state. Similar investigations of the titanium–antimony oxides showed that the reduction properties of the materials in hydrogen are sensitive to the precalcination history and antimony concentration. Low concentrations of antimony in the mixed oxide phases dried in air at low temperatures suffered facile reduction in hydrogen at moderate temperatures, whereas similar concentrations of antimony(V) in titanium dioxide formed by high-temperature calcination were particularly stable to reduction in hydrogen.

Simple oxides such as titanium(IV) oxide or tin(IV) oxide which adopt rutile or rutile-related structures have for many years been known to be amenable to the accommodation of dopant cations. Although the fundamental properties of several of the mixed-metal oxide systems, especially those derived from tin(IV) oxide, have in recent years been investigated and related to known and potential catalytic and electronic properties,[1] the titanium–antimony–oxygen system has recently been identified[1] as having received a sparsity of attention.

We therefore initiated an investigation of this system but, during the formulation of this manuscript, other workers[2] described their investigations of the solid-state reaction between titanium(IV) oxide and antimony tetraoxide at 1 000 °C and, on the basis of *X*-ray diffraction and *X*-ray photoelectron data, reported the formation of a solid solution of up to 7 mol % of antimony(III) in rutile. These results are in distinct contrast to those obtained during our investigations of materials prepared by the calcination of precipitates containing antimony and titanium at elevated temperatures using a wider range of techniques. We have already replied in a preliminary communication[3] to the essence of the previous report[2] and now report in detail on our findings. In this paper we qualitatively describe the phases which may be formed by the calcination of precipitates containing both antimony and titanium in air and the changes which are induced in the materials under reducing conditions. In the following paper we describe in detail the results of our investigations of materials formed at high temperatures and which may be described as solid solutions of antimony in rutile titanium(IV) oxide.

Experimental

Titanium–antimony oxides were prepared by calcination of precipitates, with antimony concentrations ranging from 0 to 100 mol %, by a method similar to that described in the patent literature.[4] 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 titanium tetrachloride 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 sequentially calcined in air at temperatures between 380 and 1 200 °C for periods between 4 h and 10 d.

Powder *X*-ray diffraction patterns were recorded with a Philips PW 1 050/70 *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 and the chemical isomer shift data quoted relative to InSb.

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}.

Results and Discussion

Phases in Titanium–Antimony–Oxygen Systems.—The occurrence of the phases identified by powder *X*-ray diffraction in the titanium–antimony–oxygen system when the precipitates with antimony concentrations ranging in 10% increments from 0 to 100 mol % were calcined for 12-h periods at approximately 100 °C intervals between 100 and 1 200 °C were amenable to a similar interpretation to that recently proposed[5,6] to account for the thermally induced formation of phases from precipitates in the tin–antimony–oxygen and tin–molybdenum–oxygen systems. Materials calcined at low temperature, *i.e.* less than *ca.* 200—500 °C depending on the antimony concentration, were amorphous to *X*-rays. At low antimony concentrations, < *ca.* 30%, and temperatures exceeding *ca.* 200 °C the antimony was accommodated in poorly crystalline matrices resembling either the anatase or rutile modifications of titanium dioxide. The transformation of the anatase modifications to rutile occurred at temperatures between *ca.* 500 and 800 °C depending on the antimony content. These temperatures are significantly lower than the transition temperature of *ca.* 1 000 °C which has been reported.[7–9] The results suggest that antimony is able to induce the structural transformation at lower temperatures than expected and the observations are similar to those recorded during studies[10,11] of vanadium-doped titanium dioxide.

The poorly crystalline rutile-related phases formed in the temperature range *ca.* 500—1 000 °C when the antimony contents of the initial precipitates were between *ca.* 30 and 85% were found to coexist with another phase which was characterised by 29 peaks in the powder *X*-ray diffraction pattern. Twenty of these peaks corresponded to those recorded from a material described as[7] $4TiO_2 \cdot 3Sb_2O_4$ or $Sb_3Ti_2O_{10}$.[12] One other peak could be associated with that reported in the *X*-ray diffraction pattern of an uncharacterised titanium–antimony oxide.[13] Although the material is still the subject of investigation, our initial studies by electron diffraction, energy-dispersive *X*-ray analysis, ^{121}Sb Mössbauer spectroscopy, temperature-programmed reduction, and thermal analysis suggest that the material is likely to be a mixture of more than one phase, possibly similar to those reported earlier,[7,12,13] as opposed to a new monophasic titanium–antimony oxide.

The products formed when precipitates containing more than 85% antimony were heated at temperatures between *ca.* 500 and 1 000 °C were, in addition to the rutile and other material, also found to contain the antimony oxides Sb_6O_{13} or α-Sb_2O_4 depending on the calcination temperature.

All materials, when calcined at temperatures exceeding 1 000 °C, gave powder *X*-ray diffraction patterns characteristic of crystalline rutile titanium dioxide. It appears that under these conditions the rutile-related phase undergoes extensive crystallisation with a concomitant segregation and volatilisation of any antimony which cannot be accommodated within the rutile lattice. As will be shown in the following paper which reports on our investigations of antimony-doped rutile, all the titanium–antimony oxides calcined at temperatures above 1 000 °C gave powder *X*-ray diffraction patterns, energy-dispersive *X*-ray analysis data, and ^{121}Sb Mössbauer spectra characteristic of crystalline titanium(IV) oxide containing low concentrations of antimony(V). Indeed, despite previous reports[2,7,13] that up to *ca.* 15% antimony may be accommodated in the rutile structure, our results are more consistent with a significantly lower upper limit. For example, the antimony concentration in materials formed by calcination of precipitates nominally containing up to 90% antimony at 1 000 °C for 10 d was less than *ca.* 4%, whilst calcination at 1 100 °C for 10 d gave mixed oxides in which the antimony concentrations were less than *ca.* 1.5%. The results suggest that the tolerance of the bulk rutile lattice for the accommodation of antimony is critically dependent on the temperature and duration of thermal treatment. Given the similarity in size of antimony(V) and titanium(IV) in octahedral oxygen co-ordination[14] it would seem likely that antimony(V) would form a substitutional solid solution in rutile, but the results show that the mobility of antimony within the lattice is high and amenable to surface segregation and volatilisation at high temperature. The ^{121}Sb Mössbauer spectra gave no evidence for any species other than antimony(V) in these solids

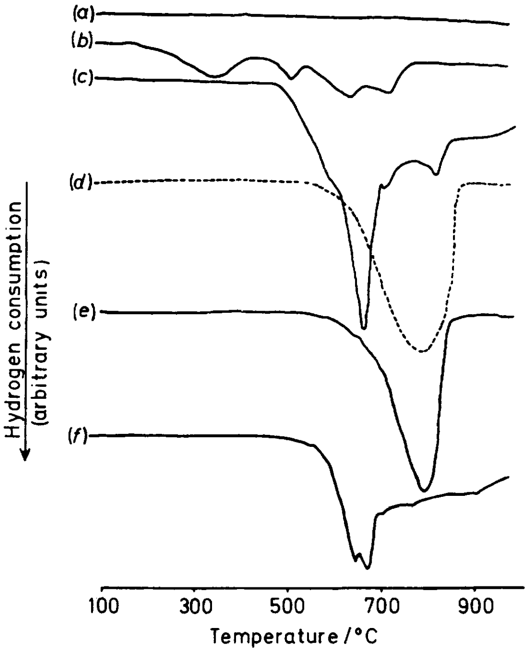

Figure 1. Temperature-programmed reduction (t.p.r.) profiles recorded for (*a*) rutile titanium(IV) oxide and antimony-containing precipitates heated at (*b*) 150, (*c*) 700, (*d*) 800, (*e*) 1 000 °C; (*f*) antimony(III) oxide

Table. Antimony-121 Mössbauer parameters (mm s^{-1}) recorded from antimony-containing precipitates dried at 150 °C at different stages of reduction (Figure 1) and from some antimony oxides and antimony metal

	Sb^V		Sb^{III}			Sb^0		Peak area ratio
Sample	$\delta \pm 0.10$	$\Gamma \pm 0.10$	$\delta \pm 0.05$	$e^2qQ \pm 0.05$	$\Gamma \pm 0.05$	$\delta \pm 0.05$	$\Gamma \pm 0.05$	$Sb^{III}:Sb^V$
Before first reduction peak	8.61	4.90						
After first reduction peak	8.65	3.89	−5.61	16.13	5.57			0.75
After second reduction peak	8.59	3.50	−5.08	12.89	4.86	−1.38	2.75	2.14
After third reduction peak	8.53	3.50	−5.52	14.45	2.78	−1.66	3.72	2.52
After fourth reduction peak						−3.16	5.23	
Sb_6O_{13}	8.71	4.81	−6.21	17.01	4.30			0.55
α-Sb_2O_4	8.60	5.35	−6.05	17.11	4.30			0.98
Sb_2O_3			−3.19	18.92	4.50			
Antimony metal						−2.95	4.13	

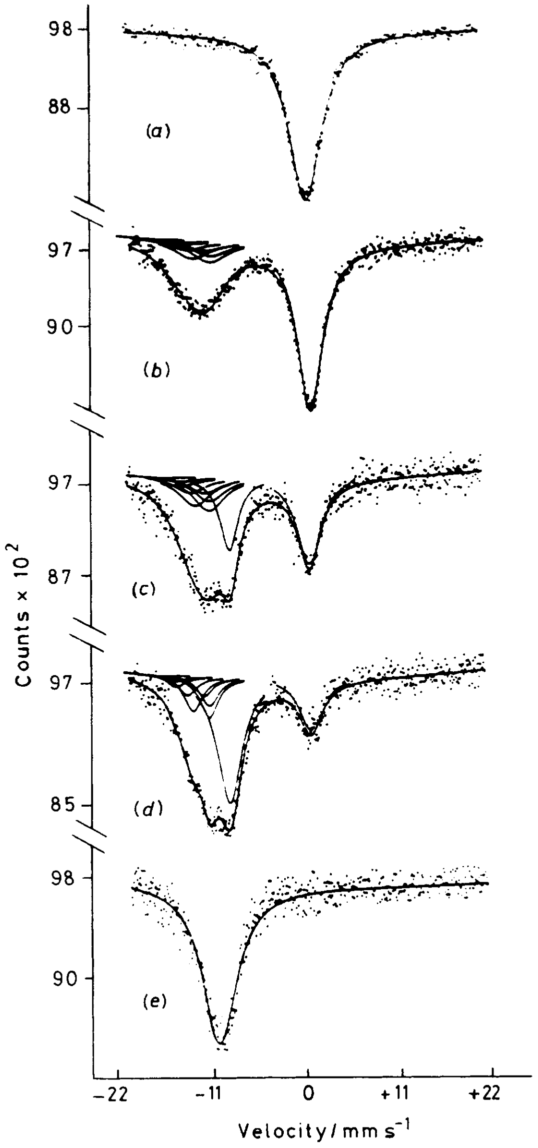

Figure 2. Antimony-121 Mössbauer spectra recorded for an antimony-containing precipitate dried at 150 °C at different stages of reduction (Figure 1): (*a*) before the first reduction peak; (*b*) after the first-, (*c*) after the second-, (*d*) after the third-, and (*e*) after the fourth-reduction peaks

formed at high temperature and it is possible that any charge compensation is achieved by reduction of titanium or by the creation of oxygen vacancies at the planar defects which were observed by electron microscopy and which are discussed in more detail in the following paper.

The formation of the phases identified in the titanium–antimony–oxygen system appears to resemble results previously reported in detail[5,6] for other antimony- and molybdenum-doped rutile-related systems. It seems that calcination induces dehydration of the precipitates and crystallisation of the rutile phase with a simultaneous migration of antimony to form a discrete antimony oxide which is volatilised at high temperatures. The materials formed at temperatures exceeding 1 000 °C contain antimony within the rutile structure but it is clear that, as found in other doped-rutile-related systems,[5,6] the dopant is amenable to further thermally induced migration and the conditions under which bulk equilibrium is achieved are difficult to define.

Studies of the Hydroxides and Oxides of Titanium and Antimony by ^{121}Sb *Mössbauer Spectroscopy and Temperature-programmed Reduction.*—The t.p.r. profiles recorded from rutile titanium(IV) oxide and antimony(III) oxide together with some hydroxides and oxides of antimony prepared by identical methods to those used for the synthesis of the titanium–antimony oxides are depicted in Figure 1.

The absence of peaks in the t.p.r. profile recorded from titanium dioxide [Figure 1(*a*)] illustrates the resistance of the rutile structure to hydrogen reduction under the conditions used here.

The antimony-containing precipitate dried at 150 °C which was amorphous to powder *X*-ray diffraction and which may be described as partially dehydrated antimonic acid gave a t.p.r. profile [Figure 1(*b*)] showing four reduction peaks at *ca.* 350, 550, 670, and 750 °C. The corresponding reduction processes can be identified from the ^{121}Sb Mössbauer spectra recorded for the sample at different stages of reduction (Figure 2 and Table). The results show that the material dried in air at 150 °C and pretreated in hydrogen at 250 °C, *i.e.* before the first reduction peak, contains only antimony(V) [Figure 2(*a*)]. The Mössbauer spectrum therefore demonstrates that such low-temperature treatment in a potentially reducing atmosphere is insufficient to induce the reduction of antimony(V). However, further treatment at *ca.* 450 °C, *i.e.* after the first reduction peak, caused *ca.* 47% of the antimony(V) to be reduced to antimony(III) [Figure 2(*b*)]. The Mössbauer spectrum recorded for the sample following treatment in hydrogen at 600 °C, *i.e.* after the second reduction peak, showed that some antimony(V) and antimony(III) had been reduced to antimony metal [Figure 2(*c*)] and demonstrates that all three oxidation states of antimony may coexist in materials which have been heated in hydrogen at moderate temperatures. A comparison of the t.p.r. profile [Figure 1(*b*)] with that recorded for antimony(III) oxide [Figure 1(*f*)] suggests that the remaining material contained antimony(III) oxide which melts at 656 °C. Further treatment in hydrogen at *ca.* 730 °C, *i.e.* after the third reduction peak, gave a solid for which the Mössbauer spectrum [Figure 2(*d*)] showed significant reduction of antimony(V) and antimony(III) to antimony metal, indeed the peak-area ratios indicate that approximately 42% of the total spectrum may be associated with the formation of elemental antimony. Following treatment in hydrogen at 900 °C, *i.e.* after the final reduction peak, all the remaining antimony(V) and antimony(III) was shown by Mössbauer spectroscopy to be reduced to elemental antimony [Figure 2(*e*)]. The reduction processes observed in these hydrogen-treated materials may be associated with thermally induced structural changes[15] which are accompanied by partial reduction of antimony(V) to antimony(III) and, following subsequent treatment in hydrogen at higher temperatures, with further reduction of the antimony(V) and antimony(III) to metallic antimony.

The t.p.r. profile recorded for the precipitate calcined at 700 °C, and which was shown by *X*-ray diffraction to be the mixed-valence antimony oxide Sb_6O_{13}, is shown in Figure 1(*c*). It is pertinent to note the stability of this phase, formed by calcination at high temperature, to reduction in hydrogen. The examination by ^{121}Sb Mössbauer spectroscopy of the solid remaining after the first reduction peak showed that treatment in hydrogen at temperatures between 600 and 700 °C induces the nearly complete reduction of antimony(V) in Sb_6O_{13} to antimony(III). Although the peak positions in the remaining portion of the t.p.r. profile depicted in Figure 1(*c*) show some resemblance to those recorded from antimony(III) oxide [Figure 1(*f*)] it is important to note that both profiles are complicated by the melting of Sb_2O_3 at 656 °C.

The antimony-containing precipitates which had been calcined at 800 and 1 000 °C, and which were identified by powder

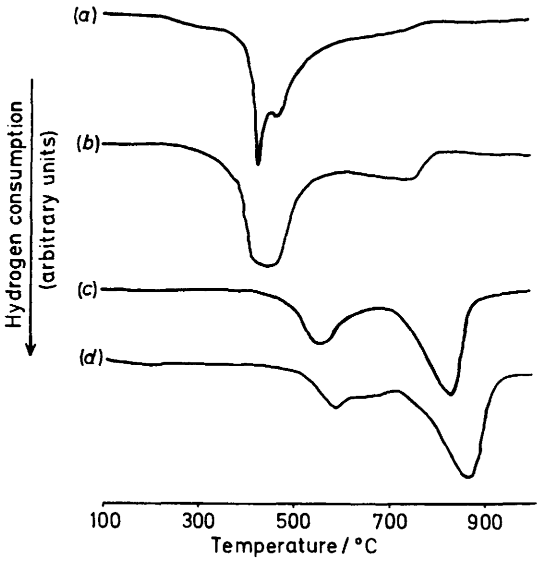

Figure 3. T.p.r. profiles recorded for precipitates containing 5% antimony–95% titanium and calcined in air at (*a*) 150, (*b*) 550, (*c*) 800, and (*d*) 1 000 °C

X-ray diffraction as α-Sb_2O_4 which contains both antimony(V) and antimony(III), gave t.p.r. profiles showing the enhanced stability of antimony(V) in materials heated at elevated temperatures and the presence of only one major reduction peak [Figure 1(*d*) and (*e*)]. Indeed, the ^{121}Sb Mössbauer spectrum recorded for the material following treatment in hydrogen at 500 °C, *i.e.* before the reduction peak, showed the presence of both antimony(V) and antimony(III). The Mössbauer spectra recorded for products isolated after the reduction peak showed that hydrogen treatment between 600 and 900 °C gives rise to the simultaneous reduction of antimony(V) and antimony(III) to metallic antimony. Hydrogen reduction of antimony tetraoxide therefore appears to proceed to completion without the formation of Sb_2O_3.

The results of the experiments summarised in Figures 1 and 2 demonstrate that the stability to reduction in hydrogen of materials containing both antimony-(V) and -(III) increases when the solids are calcined at increasingly higher temperatures. It also appears that the formation of Sb_2O_3 is a feature only of the hydrogen reduction of antimony oxides prepared by calcination in air at relatively low temperatures, *e.g.* below *ca.* 800 °C. The results also show the capacity of Mössbauer spectroscopy to complement the *X*-ray diffraction and temperature-programmed reduction data and demonstrate the power of the combined application of these techniques for the investigation of reduction processes in the solid state.

Studies of Titanium–Antimony Oxides by Antimony-121 *Mössbauer Spectroscopy and Temperature-programmed Reduction.*—The t.p.r. profiles recorded for precipitates containing 5% antimony and calcined over a range of temperatures are depicted in Figure 3. Given that rutile titanium dioxide fails to give a t.p.r. profile showing reduction peaks [Figure 1(*a*)], the results shown in Figure 3 may be associated with the reduction of antimony. However these profiles are quite different from those recorded for samples containing only antimony which were calcined in air at comparable temperatures [Figure 1(*b*)—(*e*)]. The differences are particularly well illustrated by a comparison of the samples calcined above 550 °C where the pure antimony oxide undergoes a single-step reduction [Figure 1(*d*) and (*e*)] whilst the mixed oxide containing 5% antimony is reduced in two stages [Figure 3(*c*) and (*d*)]. The ^{121}Sb Mössbauer spectra showed (Figure 4) that the first t.p.r. peak recorded for the mixed oxide corresponds to the partial reduction of antimony(V) to antimony(III) and that the higher-temperature peak is associated with the simultaneous reduction of both antimony(V) and antimony(III) to antimony metal. Given that the *X*-ray diffraction patterns recorded for the mixed oxides calcined above 550 °C were characteristic of a monophasic rutile titanium(IV) oxide-type solid it seems reasonable to envisage that the antimony detected during the t.p.r. experiments is incorporated within the titanium dioxide lattice. The results are therefore a notable demonstration of the thermal stability of antimony(V) when accommodated in the rutile structure.

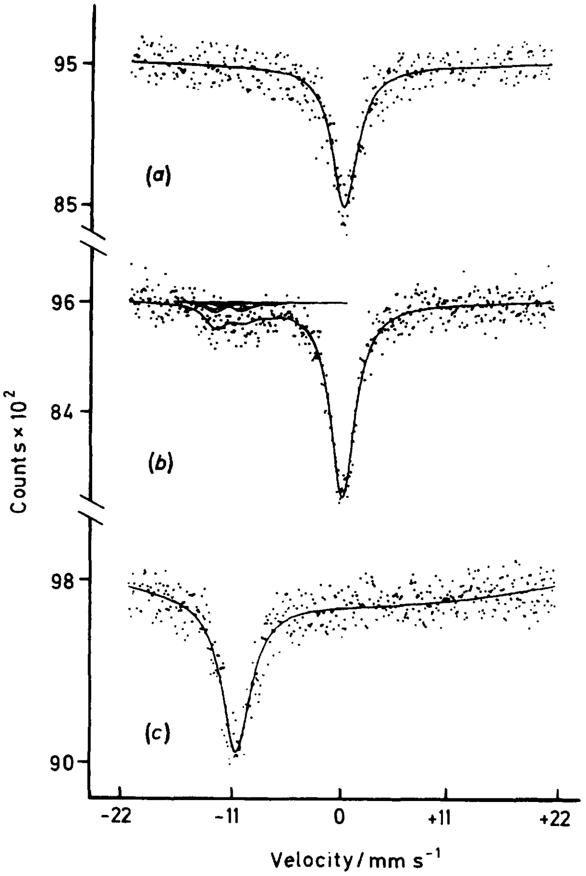

Figure 4. Antimony-121 Mössbauer spectra recorded for a precipitate containing 5% antimony–95% titanium and calcined in air at 800 °C at different stages of reduction [Figure 3(*c*)]: (*a*) before the first reduction peak, (*b*) after the first reduction peak, and (*c*) after the second reduction peak

The t.p.r. profiles recorded from titanium- and antimony-containing precipitates of various compositions and dried in air at 150 °C are shown in Figure 5. The results show that the major reduction process is completed at lower temperatures in materials with higher titanium concentrations, as might be expected if titanium promoted the reduction of the dopant antimony species. The results endorse previous observations[16] of the capacity of one cation to induce the reduction of another and contrast with the stabilising influence of titania on the reduction of antimony in materials precalcined at high temperatures (see above).

It is interesting that the reduction peaks at *ca.* 350, 500, and 600 °C in the t.p.r. profiles recorded for precipitates containing

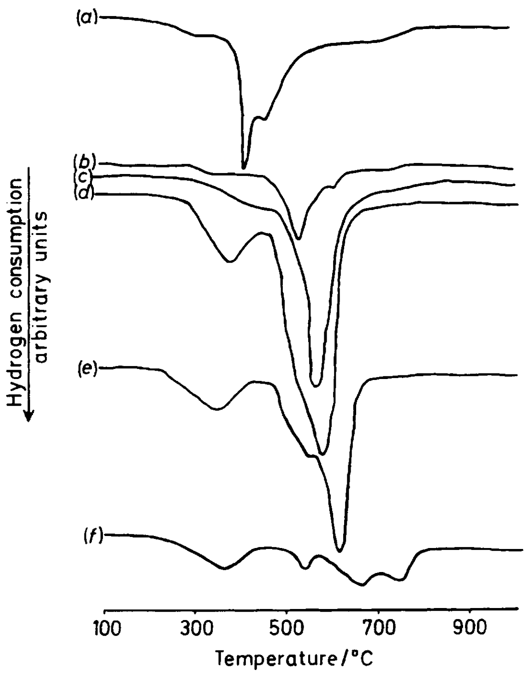

Figure 5. T.p.r. profiles recorded from titanium- and antimony-containing precipitates of various compositions and calcined in air at 150 °C: (*a*) 5, (*b*) 20, (*c*) 30, (*d*) 50, (*e*) 80, and (*f*) 100% Sb

higher concentrations of antimony [Figure 5(*d*) and (*e*)] can also be identified in the t.p.r. profile recorded for the precipitate containing only antimony [Figure 5(*f*)] and the results are therefore indicative of the presence of similar partially dehydrated antimonic acid phases in all three materials. However, the high-temperature reduction peak at *ca.* 750 °C in Figure 5(*f*) is absent in the t.p.r. profiles recorded for the mixed cation-containing precipitates [Figure 5(*d*) and (*e*)]. The results may reflect the capacity of titanium to induce the reduction of antimony in the poorly crystalline partially dehydrated antimonic acid at lower temperatures. These results are consistent with the *X*-ray diffraction data recorded from the more crystalline samples and indicate that antimony, even in the amorphous precursors containing high concentrations of antimony, can exist in at least two poorly defined phases one of which contains antimony and titanium whilst the other contains only antimony.

The dried precipitates containing lower concentrations of antimony gave t.p.r. profiles [Figure 5(*a*)—(*c*)] showing little similarity to the reduction profile of the pure antimony-containing material [Figure 5(*f*)]. The antimony in such materials heated at very mild temperatures may be imagined to be in intimate association with the high concentration of titanium and that this close association is reflected in the t.p.r. results shown in Figure 5(*a*)—(*c*).

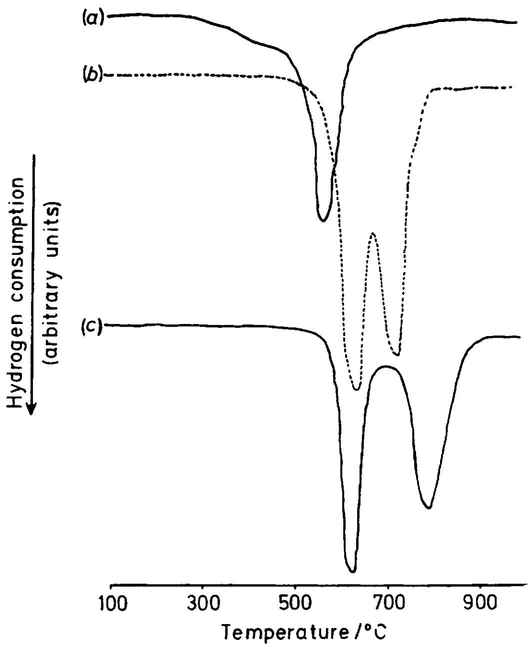

Figure 6. T.p.r. profiles recorded from precipitates containing 30% antimony–70% titanium and calcined in air at (*a*) 150, (*b*) 800, and (*c*) 1 000 °C

The dried precipitate containing 30% antimony gave the single-peak t.p.r. profile shown in Figure 5(*c*) which was shown by ^{121}Sb Mössbauer spectroscopy to correspond to the complete reduction of antimony(V) to antimony metal. Powder *X*-ray diffraction confirmed the result and also showed the rutile titanium dioxide to remain unchanged. In contrast, the dried precipitate containing 50% antimony gave a two-peak t.p.r. profile [Figure 5(*d*)] which was shown by Mössbauer spectroscopy to correspond to the initial conversion of some antimony(V) into antimony(III) followed, at the higher temperature, by the simultaneous reduction of antimony(V) and antimony(III) to antimony metal. It would seem likely that the precipitates containing more than 30% antimony undergo a phase segregation process during the thermal treatment in hydrogen which does not occur in the precipitates containing the lower concentrations of antimony.

Temperature-programmed reduction profiles recorded for the precipitates containing 30% antimony and calcined at the higher temperatures of 800 and 1 000 °C are compared with that obtained for the sample dried at 150 °C in Figure 6. The essentially single-peaked t.p.r. profile recorded for the dried sample splits progressively into two distinct reduction peaks when the precipitate is heated to higher temperatures. The two reduction peaks in Figure 6(*b*) were shown by Mössbauer spectroscopy to correspond to the initial partial reduction of antimony(V) to antimony(III) followed by the simultaneous reduction of antimony(V) and antimony(III) to antimony metal. The material formed by calcination at 1 000 °C gave a similar t.p.r. profile [Figure 6(*c*)] although the second reduction peak was shifted to a higher temperature illustrating the stability of antimony(III) to reduction. The influence on the reduction properties of the yet uncharacterised phase which was identified by *X*-ray diffraction is currently unknown.

Taken together, the results illustrate the influence of pre-calcination and dopant-ion concentration on the reducibility of the titanium- and antimony-containing materials prepared during this work.

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