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# An Investigation of the Surface Properties of Tin–Molybdenum Oxides by X-ray Photoelectron Spectroscopy

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## Abstract

Tin–molybdenum oxides formed by moderate temperature calcination of precipitates adopt poorly crystalline rutile-related structures. X-ray photoelectron spectroscopy shows that the molybdenum in these highy disordered solids undergoes thermally induced migration to surface sites to form, in some cases, macroscopically distinguishable molybdenum(VI) oxide phases. Further calcination at elevated temperatures leads to the volatilization of any molybdenum(VI) oxide and gives highly crystalline rutile-related tin–molybdenum oxides in which the molybdenum is located at either planar faults or in oxygen depleted surface regions.

## Introduction

A recent study of tin–molybdenum oxides formed by the calcination of precipitates at high temperatures showed that the solids adopt rutile-related structures in which a small amount of molybdenum is incorporated within the tin(IV) oxide lattice [1]. Subsequent examinations by electron microscopy have demonstrated [2] that the dopant molybdenum is located at planar twin boundaries as opposed to being randomly distributed over the cationic sites in the tin(IV) oxide lattice. The presence of molybdenum at the twin boundaries was associated [2] with the migration of molybdenum away from the crystallizing rutile-type phase under the influence of high temperature calcination and its subsequent accommodation in more favourable coordination in the planar faults.

In these respects it is pertinent to note that the surface compositions of other rutile-related solids have recently been shown to be significantly different from the bulk lattice structures [3–7] and it is especially interesting that the surface properties of antimony-doped tin(IV) oxide [3–6] prepared by the calcination of precipitates have been associated with the thermally induced migration of the dopant during the preparative treatment to surface sites.

Although a limited number of tin–molybdenum oxides prepared by solid state reactions and by the calcination of slurries over a restricted range of temperatures have been subjected to surface analysis [8, 9], it is important to note that the nature of mixed metal oxides depends critically on the preparation techniques and that no comprehensive investigation of the surface properties of tin–molybdenum oxides formed by the calcination of precipitates has yet been reported. We have therefore examined the rutile-related tin–molybdenum oxides formed by the calcination of precipitates by X-ray photoelectron spectroscopy to evaluate the extent, if any, of molybdenum migration through the tin(IV) oxide lattice to surface sites.

## Experimental

The tin–molybdenum oxides, with nominal molybdenum concentrations as described in Table I, were prepared by the addition of ammonia in 1 ml aliquots to aqueous solutions of the required proportions of tin(IV) chloride at 70 °C until the cloudy suspensions persisted. The addition of aqueous ammonium molybdate solutions containing the required amounts of molybdenum gave white precipitates which were removed by centrifugation, dried at room temperature and calcined at temperatures between 100 and 1000 °C for 24 h in air. The phase compositions of the samples were determined by powder X-ray diffraction and are described in Table I.

The XPS data were recorded in digital form with a Kratos ES300 spectrometer operating at a base pressure of *ca.* $1 \times 10^{-8}$ torr using Mg K$\alpha$ exciting radiation ($h\nu = 1253.6$ eV). The samples were investigated as fine powders mounted on double-sided Sellotape and examined at room temperature. Quan-

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TABLE I. Tin–Molybdenum Oxides: Details of Preparation, Bulk Phase Composition and Surface Composition

| Sample | Nominal molybdenum content of initial precipitate | Calcination temperature (°C/24 h) | Phase composition[a] | Surface molybdenum content (%) |
|---|---|---|---|---|
| A | 10 | 300 | R | 11 |
| B | 1 | 600 | R | 2 |
| C | 10 | 600 | R | 18 |
| D | 40 | 600 | R | 42 |
| E | 60 | 600 | R + $MoO_3$ | 62 |
| F | 80 | 600 | R + $MoO_3$ | 62 |
| G | 10 | 700 | R | 19 |
| H | 60 | 700 | R | 32 |
| I | 80 | 700 | R + $MoO_3$ | 60 |
| J | 10 | 800 | R | 17 |
| K | 40 | 800 | R | 22 |
| L | 10 | 900 | R | 20 |
| M | 40 | 900 | R | 16 |
| N | 3 | 1000[b] | R | 13 |
| P | 10 | 1000[b] | R | 14 |

[a] As determined by powder X-ray diffraction; R = rutile-type phase. [b] Heated for 14 days.

titative measurements were based on the tin $3d_{5/2}$ and molybdenum $3d_{5/2}$ peaks. All binding energies were referred to a value of 285 eV for the C 1s signal arising from carbon impurity on the sample surfaces before being normalized to the tin $3d_{5/2}$ binding energy of 487.2 eV.

## Results and Discussion

### *Surface Compositions*

The concentration of molybdenum at the surfaces of the mixed oxides are recorded in Table I. Sample A prepared from a precipitate nominally containing 10% molybdenum and heated to 300 °C gave an X-ray photoelectron spectrum showing the bulk and surface compositions to be comparable and indicative of a material in which molybdenum is distributed homogeneously throughout the solid. The result is consistent with the description [1] of sample A, based on X-ray diffraction data, as a highly disordered solid in which the rutile-type phase had not begun to extensively crystallize.

The XPS data recorded from the dehydrated rutile-related solids B and C containing low concentrations of molybdenum and calcined at 600 °C showed some molybdenum enrichment of the surfaces suggesting that molybdenum migration to the superficial regions begins at temperatures between 300 and 600 °C. However, the difference between the concentrations of molybdenum within the bulk and at the surface of the tin–molybdenum oxides D and E formed by the calcination at 600 °C of precipitates nominally containing 40 and 60% molybdenum was small. Given that the photoelectrons recorded from molybdenum in oxygen coordination escape from within *ca.* 20 Å of the surface [10, 11] the results may reflect the smaller particle sizes, *ca.* 50 Å, of these materials which were also shown [1] by X-ray diffraction to be less crystalline than samples prepared from precipitates containing lower concentrations of molybdenum and heated to similar temperatures. The detection of only 62% molybdenum at the surface of sample F, formed by calcination of a precipitate containing 80% molybdenum at 600 °C, may reflect the low surface area of the highly crystalline large particle molybdenum(VI) oxide phase which was identified by X-ray diffraction and scanning electron microscopy [1]. Analogous results have been obtained [4] during XPS studies of biphasic tin–antimony oxides containing a rutile-type phase and antimony oxide.

The concentrations of molybdenum in the surface regions of the samples H and I which had been calcined at 700 °C were also found to be less than those in the precipitates from which they were formed. However, these results may be associated with the loss of molybdenum as volatile molybdenum(VI) oxide at this higher temperature [1], indeed it is relevant to note the identification by X-ray diffraction of considerable quantities of condensed molybdenum trioxide on cool regions of the apparatus at the end of the calcination experiments. Although in sample I this may be associated with the volatilization of the discrete molybdenum(VI) oxide phase in the biphasic solid, the quantity of molybdenum lost from the monophasic rutile-type sample H is greater than that which could have been present as molybdenum trioxide. The result is consistent with the loss of molybdenum from the rutile-type phase H which, despite its amenability to accommodation in the poorly crystalline rutile-

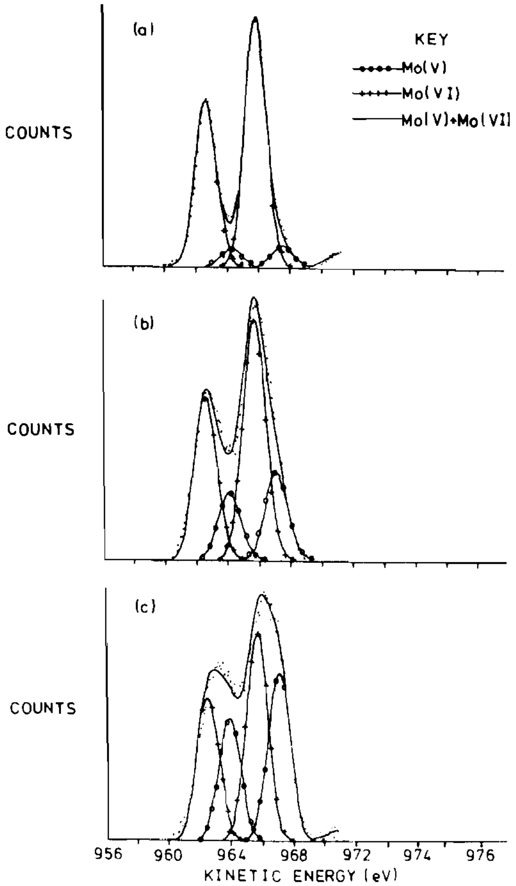

Fig. 1. X-ray photoelectron spectra recorded from (a) molybdenum(VI) oxide; (b) a tin–molybdenum oxide prepared by heating a precipitate containing 40% molybdenum at 600 °C (sample D); (c) a tin–molybdenum oxide prepared by heating a precipitate containing 40% molybdenum at 800 °C (sample K).

related solids formed at lower temperatures, is not tolerated by the more crystalline rutile-type phase formed at higher temperatures. This process is well illustrated by a comparison of the XPS data recorded from the monophasic rutile-related solids D, K and M which nominally contained 40% molybdenum and which were heated at 600, 800 and 900 °C. The results show that the surface molybdenum concentrations decrease from *ca.* 42% to *ca.* 16% as the mixed oxides adopt more crystalline rutile-type structures following calcination at increasingly higher temperatures. The results are therefore quite consistent with a system in which increasing crystallization of the rutile-type phase at increasing temperatures induces the segregation of molybdenum to the surface where it nucleates as molybdenum(VI) oxide which volatilizes at elevated temperatures.

In these respects it is relevant to note that the surface compositions of the solids C, G, J and L which were prepared by heating precipitates nominally containing 10% molybdenum at temperatures between 600 and 900 °C are all similar. It seems therefore that in these materials the thermally induced segregation of molybdenum from the bulk to the surface and its volatilization as $MoO_3$ maintains a surface concentration of *ca.* 18% molybdenum.

TABLE II. Molybdenum Binding Energies in Tin–Molybdenum Oxides

| Sample | Binding energies (eV) | | Mo(VI):Mo(V) ratio |
|---|---|---|---|
| | Mo(VI) | Mo(V) | |
| A | 232.9 | 231.5 | 1.78 |
| B | 232.4 | 231.1 | 2.59 |
| D | 232.9 | 231.5 | 2.77 |
| E | 232.9 | 231.4 | 6.86 |
| F | 232.9 | 231.4 | 9.6 |
| G | 233.2 | 231.8 | 1.33 |
| H | 234.4 | 232.0 | 1.42 |
| I | 233.0 | 231.4 | 6.12 |
| J | 233.0 | 231.6 | 1.39 |
| K | 232.8 | 231.4 | 1.24 |
| L | 232.9 | 231.6 | 1.19 |
| M | 233.0 | 231.6 | 1.26 |
| P | 232.5 | 231.2 | 0.81 |
| Q | 232.7 | 231.3 | 1.27 |
| $MoO_3$ | 233.0 | 231.4 | 8.0 |

It is also important to mention that the XPS data recorded from the highly crystalline rutile-related samples N and P, which were heated at 1000 °C for 14 days, show that the surface molybdenum concentration undergoes continued depletion when calcination is continued at elevated temperatures. Given that electron microscopy and X-ray microanalysis failed to detect any molybdenum in tin–molybdenum oxides calcined at 1000 °C in any areas of the bulk matrix other than at the planar twin boundaries [2] it would seem that the process of thermally induced migration of molybdenum from the bulk to the surface or the planar defects continues until the reservoir of molybdenum in the crystallising rutile-related matrix is exhausted.

### *Cationic Oxidation States at the Surface*

The XPS spectra recorded from all the tin–molybdenum oxides showed tin $3d_{5/2}$ binding energies of 487.2 eV characteristic of tin(IV) in tin(IV) oxide. The molybdenum $3d_{5/2}$ envelope in the XPS spectra recorded from molybdenum(VI) oxide and the tin–molybdenum oxides was best fitted to two overlapping peaks (Fig. 1) whith binding energies (Table II) which are similar to those which have been attributed [9, 12] to molybdenum(VI) and molybdenum(V). Whilst molybdenum(VI) was generally the predominant species, the amounts of molybdenum(V) in the surface layers depended on the molybdenum concentration in the original precipitates and the calcination temperatures. The detection of molybdenum(VI) in the tin–molybdenum oxides is not too surprising given that the solids were prepared from reactants containing molybdenum(VI). However, the identification of molybdenum(V), which was initially detected [4] by ESR, at the surface of both molybdenum(VI) oxide and the tin–molybdenum oxides is interesting and may reflect the reduction of molybdenum(VI) to molybdenum(V) as a result of oxygen loss during the calcination of the solids. Indeed, a comparison of the XPS data recorded from the rutile-related solids B and D formed at 600 °C with that obtained from the rutile-type samples G, H, J, K, L and M which had been heated at higher temperatures shows the molybdenum(V) component to increase with increasing calcination temperature. Given the octahedral environment of cations in the rutile-type structure and the preference of molybdenum(VI) for non-octahedral coordination [13, 14], the XPS results, taken together with the X-ray diffraction [1] and electron microscopy [2] data, reflect the migration of molybdenum(VI) away from the crystallizing rutile-type phase to the planar twin boundaries and to surface sites there where they can obtain more favourable coordination. Continued thermal treatment then induces reduction to molybdenum(V) as a result of oxygen loss.

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