Oxidation of thin films of tin at room temperature in hydrogen sulphide atmosphere

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Abstract. The oxidation of thin films of tin at room temperature in an atmosphere containing 10% H_2S and 90% air has been studied by measuring the changes in resistance of thin films. Morphological studies have also been carried out using optical and scanning electron microscopes. Reaction kinetics change from logarithmic law at ordinary atmospheres to a power law in the presence of H_2S. The basis of formation of sulphide along with the oxide is explained, the former growing on a lower layer and the latter on an upper layer.

Keywords. Oxidation; tin; hydrogen sulphide; thin films; resistance change.

1. Introduction

Hydrogen sulphide is a naturally occurring gas forming part of the sulphur-cycle (Minster 1963). Owing to its highly corrosive nature, H_2S testing on metals and alloys is of industrial importance. Tin is a metal of widespread use in external atmosphere mainly as a sacrificial coating on metals. Extensive studies on the oxidation of tin have been carried out by Boggs and coworkers (Boggs *et al* 1961a, b, 1963, 1964a; Boggs 1961c, 1964b). Chan duc Thiep *et al* 1977a, b employed the selective Mössbauer spectroscopy method to study the oxidation mechanism of thin films of tin deposited on glass. The formation of sulphur containing mixed films on tin was discussed by Gabe (1977). The present paper contains investigations about the effect of H_2S on the oxidation of thin films of tin at constant relative humidities ($\approx 85\%$) and at room temperature (≈ 303 K).

2. Experimental

The oxidation rate was followed by measuring the rate of increase of resistance of thin films (900 Å) of tin (99·999%) which had been evaporated on to optically plane glass substrates at room temperature. Thick electrode films of tin were previously deposited at the ends of the glass substrates, which were cleaned by chemical and ion-bombardment methods. All evaporations were carried out in a conventional vacuum line at pressures greater than 10^{-5} torr. The films and electrodes were evaporated from a molybdenum boat.

After measuring the resistances, the films coated in the same pump-down were quickly transferred to an enclosed glass chamber (Muneera *et al* 1983) evacuated to a pressure of 10^{-2} Torr. The required amount of air was then admitted into the chamber followed by 10% by volume of dry H_2S stored in a reservoir. The relative humidity inside the chamber was assessed using a dry and wet thermometer

assembly. Resistances of the films were measured at regular intervals for several hours using a vernier potentiometer of accuracy 10^{-6} v. div^{-1}. After about ten days, the films were taken out and photographed. Both optical and scanning electron microscopes were used to study the structure of the oxide films formed. Resistance could not be measured for longer periods due to the failure of metal contacts used for external connections. Studies with higher percentage of H_2S were also not possible because of the vigorous attack by the highly corrosive gas on the metal contacts used.

3. Results and discussion

The change in resistance of the thin film can be related to the oxide thickness (Hunt and Ritchie 1972). If the evaporated thin film is regarded as a thin isotropic metal sheet which oxidises on one surface only and obeys Ohm's law, then it follows that the film resistance R and the oxide thickness X are related by the equation

$$x = \frac{\phi \rho l}{\omega} \left(\frac{1}{R_0} - \frac{1}{R} \right),\tag{1}$$

where ϕ is the thickness of the oxide, derived from unit thickness of metal, ρ is the resistivity of the metal film, l is the length of the film between contacts, ω is the width of the film and R_0 is the resistance of the film prior to oxidation. In deriving this equation it has been assumed that the resistivity of oxide formed is very much larger than that of the metal. This condition is satisfied in the present studies as the oxide and sulphide formed on the thin film of tin at room temperature are amorphous (Bound and Richards 1939; Hart 1952; Britton and Bright 1957; Boggs *et al* 1961b; Raymond and Donald 1955). From (1) it is clear that the oxide thickness x is proportional to $-1/R$.

The oxidation of tin at room temperature obeys a direct logarithmic rate law (Tamman and Köster 1922; Katz 1956; Britton and Bright 1957; Gabe 1977). With the introduction of 10 % H_2S, the oxidation rate changed from a direct logarithmic law to a power law of the form

$$x^n = kt,\tag{2}$$

where x is the oxide thickness and k and n are constants. This is evident from the plot of log $1/R$ vs log t in figure 1.

The surface structures developed on the film after about ten days of exposure to H_2S + air atmosphere are shown in figures 2–8. There are two types of nucleation centres: the slightly large bright centres and the more distributed form of fine grains or powdery nuclei (figure 2). Some of the former grow into larger growth centres near the edges of the films (figures 3–5). They are different from the wheel-shaped or dendritic growth centres (Boggs *et al* 1961b; Muneera *et al* 1983) observed on films exposed to normal atmospheres (figures 9–10). Figure 6 shows the larger growth centre along with the other nucleation centres. Growth centres under different stages of growth are observed on the same specimen.

The various chemical reactions which can take place when the film is kept in an atmosphere containing 10% H_2S and 90% air are as given below (Boggs *et al*
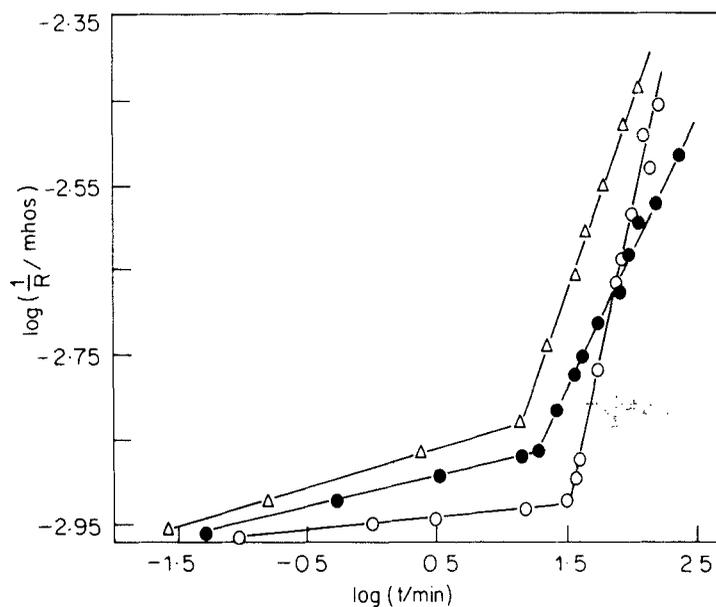
Figure 1. Plot of log $1/R$ vs log t. The oxidation rate for the initial period is different as observed usually.
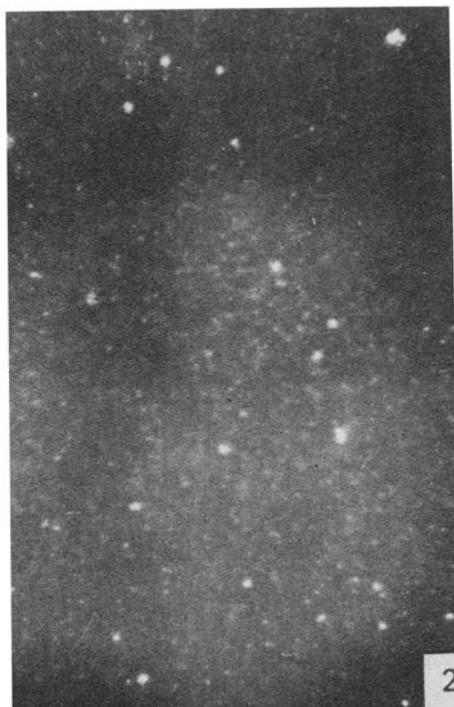

Figure 2. The two types of nucleation centres observed on a film kept in 10% H_2S + air atmosphere for about ten days ($\times$ 220).
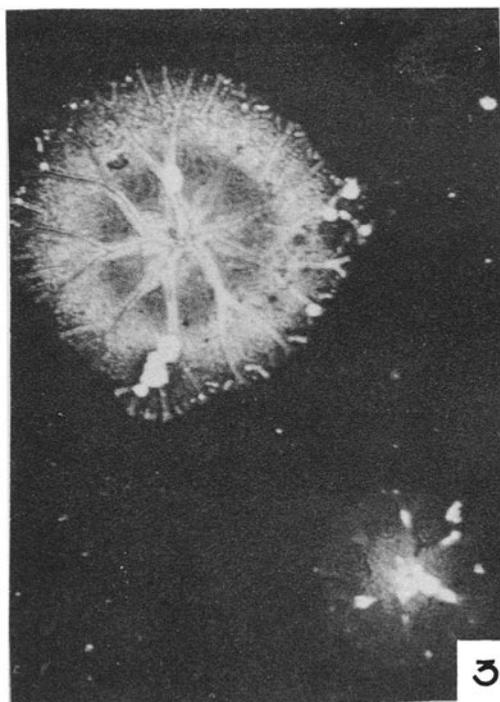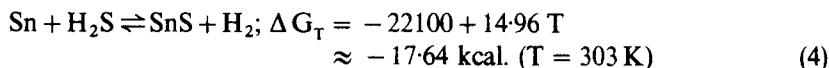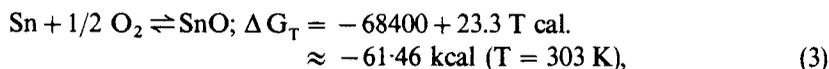
Figure 3. Optical micrograph of the wheel-shaped dendrites seen at the edges of the film (× 480).

1961 a, b, c; Gabe 1977). The relevant thermodynamical data are obtained from Kubaschewski *et al* (1967)

$$Sn + 1/2\ O_2 \rightleftharpoons SnO; \Delta G_T = -68400 + 23.3\ T\ cal.$$
$$\approx -61{\cdot}46\ kcal\ (T = 303\ K), \tag{3}$$

$$Sn + H_2S \rightleftharpoons SnS + H_2;\ \Delta G_T = -22100 + 14{\cdot}96\ T$$
$$\approx -17{\cdot}64\ kcal.\ (T = 303\ K) \tag{4}$$

Thermodynamically the greater possibility of reaction is the one in which there is maximum decrease in free energy change. Thermodynamic equilibrium will not be attained for short periods of oxidation and at room temperature, the conditions under which the present studies are made. In such cases the reaction kinetics determine the possibility of occurrence of a particular chemical reaction. It has been reported that the oxide formed on tin at room temperature is SnO (Boggs *et al* 1961 a, b, 1963; Gabe 1977). Therefore considering the higher partial pressure of O_2 (143·64 mm of Hg) and greater electron affinity of sulphur, both SnO and SnS are expected to form, although the free energy change associated with reaction (4) is less than that with reaction (3).

The oxidation of tin at room temperature takes place by the outward migration of cations (Boggs *et al* 1961). In the presence of 10% H_2S and 90% air, both hydrogen sulphide and oxygen are expected to be adsorbed on the surface. Because of the higher partial pressure of oxygen, it seems reasonable that SnO is formed first and grows by
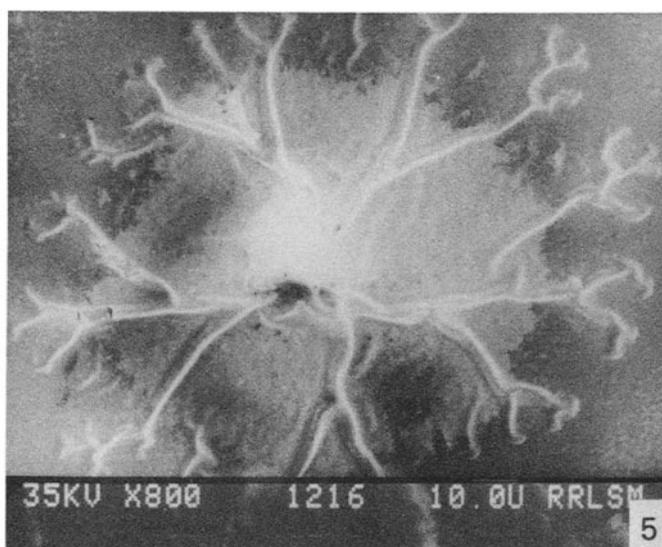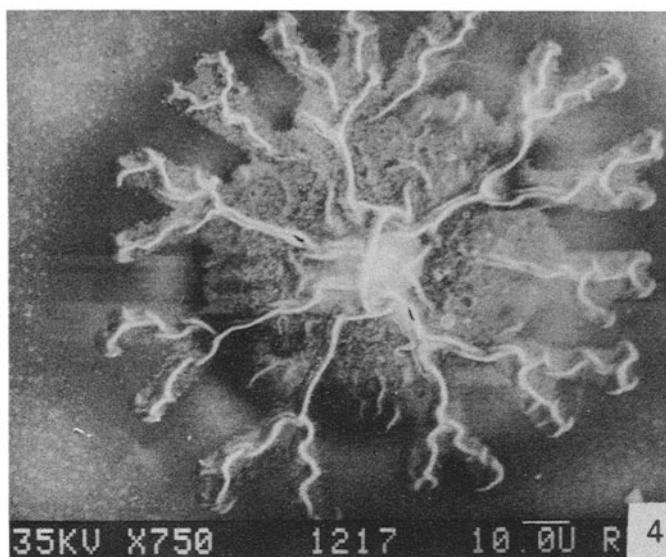
Figures 4–5. SEM of the rosette-shaped dendrite in which the lower sulphide layer **4.** also grows into branches following the upper oxide dendrites and **5.** forms a circular bed for the radiating oxide dendrites.

outward migration of cations. From SEM and optical microscopic studies, it can be concluded that at sites where SnO grows into 'radially symmetric dendrites', the sulphide forms a layer beneath the oxide layer (figures 3–5). The oxide and sulphide together forms 'wheel-shaped' (figure 3) or 'rosette shaped' (figures 4–5) dendrites at these sites. Even at other sites where SnO forms comparatively smaller growth centres the powdery or fine-grain like SnS is observed on a lower layer (figures 2, 6). Therefore
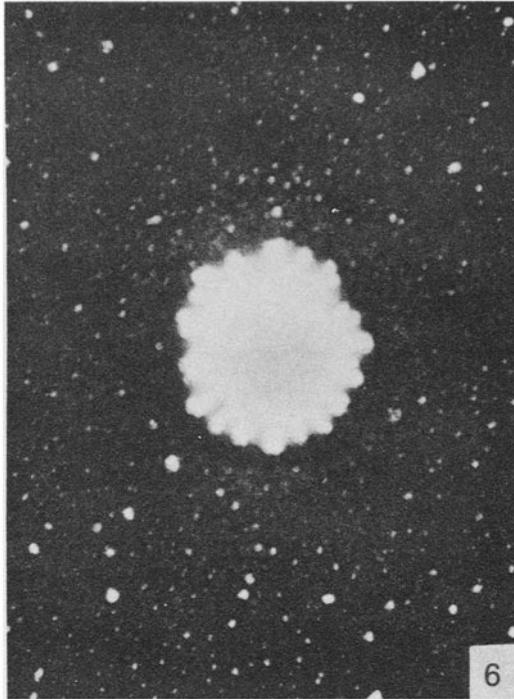
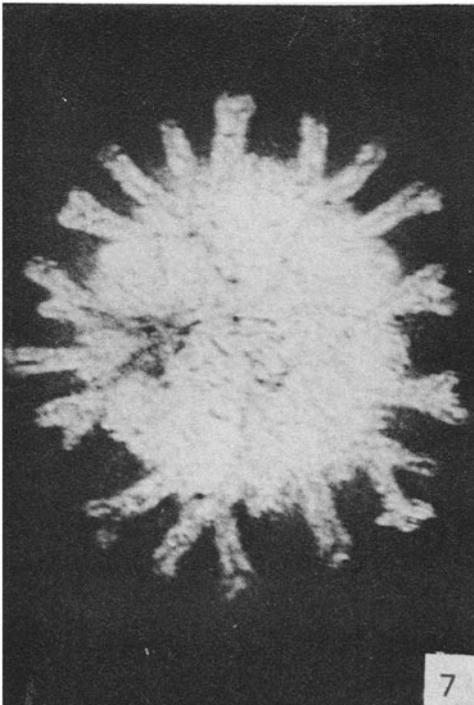**Figure 6.** The larger growth centre along with the two types of nucleation centres (× 220).

Figure 7. Optical micrograph of figure 4 under transmitted light showing podia-like extensions at the boundary (× 540).
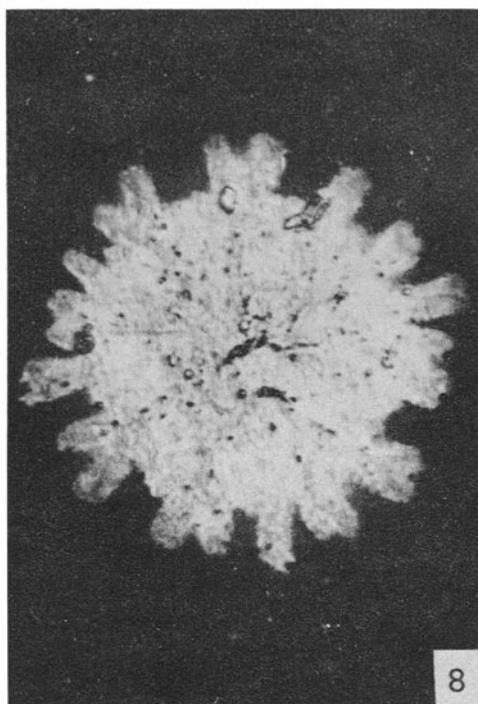
Figure 8. Later growth stage of a pattern similar to that shown in figure 7 (× 500).
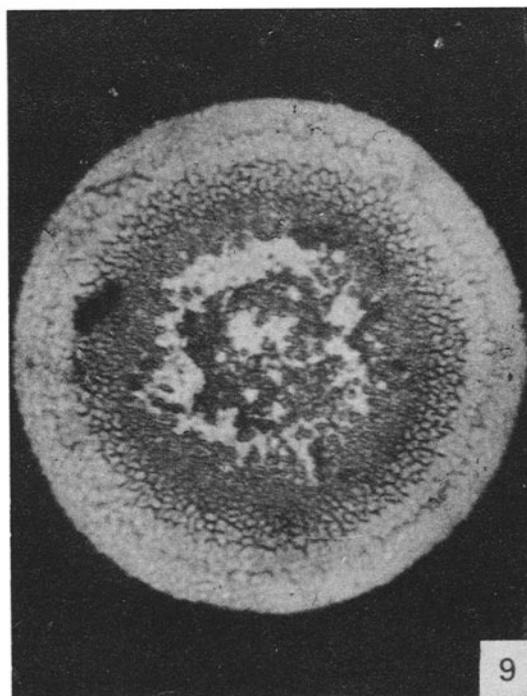

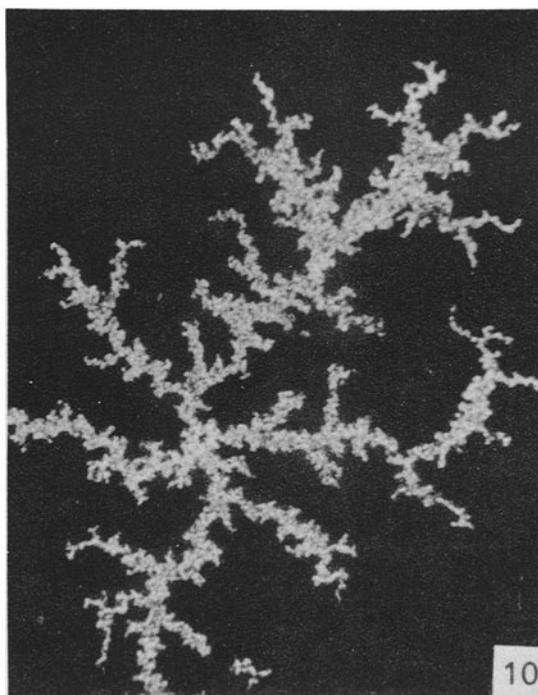**Figure 9.** Wheel-shaped growth centre observed on a film kept in normal atmosphere (× 1440).

Figure 10. The dendritic growth of oxide observed on the film kept in normal atmosphere (× 200).

SnS is presumed to form between the metal and the oxide layer, *i.e.*, at the oxide-metal interface. It must grow by the inward migration of sulphur through the oxide layer reacting with cations and electrons at the sulphide-oxide interface. The presence of sulphur in the oxide remarkably enhances the cation diffusivity (Wooten and Birks 1972; Lawless 1974). The oxidation rate is therefore increased to that of a power law when 10% H_2S is introduced.

The radially symmetric dendrites may be formed in a way similar to that of the dendrites found at low oxygen pressures (Boggs *et al* 1961b). These structures are commonly observed near the edges of the films where the chance of finding high density of grain-boundaries is greater. Although the partial pressure of oxygen is considerably high, the presence of H_2S and the higher electron affinity of sulphur leads to an initial adsorbed layer of variable oxygen concentration. The 'wheel-shaped' or 'rosette shaped' dendrites grow laterally in radial directions (see the small growth centre in figure 3). The areas between adjacent primary branches become depleted in oxygen as oxygen in the adsorbed layer is consumed during the formation of radiating branches. These branches grow outward into areas richer in oxygen uniformly forming secondary and tertiary branches and a well-defined radially symmetric circular pattern is obtained. The sulphide layer also grows laterally forming a circular bed for the radiating dendrites (figure 5). In figure 3 the sulphide layer formed below the radially symmetric dendrite forms a rim at its boundary. In certain cases (figure 4) the sulphide layer also grows into branches following the oxide dendrites. When viewed under transmitted light using an

optical microscope, figure 4 appears as shown in figure 7. The distinction between oxide and sulphide layer is less clear in figure 7. At the boundary of the growth centre, the oxide and sulphide together form 'podia'-like extensions (figures 7, 8). The tips of the branches seem to have thickened. With further oxidation, the area between podia-like extensions get filled up gradually (figure 8).

4. Conclusion

With the presence of 10% H_2S, the rate equation changes from a logarithmic law to a power law, indicating an increase in oxidation rate. This is explained on the basis of formation of sulphide along with the oxide, the former growing on a lower layer and the latter on the upper layer. The oxide and sulphide together forms 'wheel-shaped' or 'rosette-shaped' dendrites at the edges of the film.

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