

Effect of indium concentration on the internal oxidation of a silver-tin alloy

A VERMA and T R ANANTHARAMAN

Thapar Corporate Research and Development Centre, Patiala 147 001, India

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Abstract. The investigation reported here was undertaken to study the beneficial influence of indium on the internal oxidation behaviour of silver-tin alloys in the context of electrical contact material development. Five compositions of varying indium content, namely Ag-6Sn-xIn ($x=2.0, 2.5, 3.0, 3.5, 4.0$ wt%) were prepared and internally oxidized at different temperatures and oxygen pressure. The kinetics of internal oxidation was studied and an attempt made to correlate the same with microstructure.

Keywords. Electrical contact materials; internal oxidation; silver-tin oxide-indium oxide.

1. Introduction

It has recently been established that silver-cadmium oxide (Ag-CdO) composites are suitable for switching devices operating in the range of 50-5000 amp (Schroder 1987). However, because of the toxic nature of cadmium and the increasingly stricter environmental regulations, silver-tin oxide (Ag-SnO₂) has recently emerged as a possible substitute for Ag-CdO. Ag-SnO₂ has superior erosion resistance and anti-welding characteristics (Sabairi *et al* 1982).

Two manufacturing techniques have generally been adopted for Ag-SnO₂ materials, namely, powder metallurgy (PM) (Yamasaki *et al* 1980) and internal oxidation (IO) (Bohm *et al* 1980). However, the latter process suffers from the problem of high inter-diffusion coefficient of tin in silver. It has been established that a high tin content (> 4 wt%) in silver is not amenable to internal oxidation as it forms an impervious layer of tin oxide inhibiting further diffusion of oxygen in the alloy (Shen and Gould 1987). In order to facilitate internal oxidation, several additives such as bismuth, copper and indium have been tried with different measures of success. Among these only the indium-bearing silver-tin alloy has been commercially exploited to its full potential. Indium prevents the formation of dense oxide bands of SnO₂ and enables oxygen to diffuse at a faster rate into the silver-tin alloy.

The kinetics of the internal oxidation process is given by Wagner's (1959) parabolic relationship viz

$$x^2 = k \cdot t \quad (1)$$

where x is the thickness of the internally oxidized zone after time t and k the scaling constant given by

$$k = 2 \cdot (D_0/v) (N_0/N_m) \quad (2)$$

where D_0 is the diffusion coefficient of oxygen in the alloy; v the oxygen-to-metal atom ratio in oxide, N_0 the oxygen concentration on the surface of alloy and N_m the concentration of the metal to be oxidized.

Equation (2) is based on the solution of the diffusion equation with appropriate boundary conditions and suitable approximations. However, the measured thickness of the oxidized zone and theoretically calculated values differ if the reactive solute also provides significant diffusion. Under these conditions the expression remains parabolic, but the scaling constant also includes the diffusion coefficient of reactive metals. For a given time, the depth of internal oxidation is less than that calculated from (1), and the product enriches the solute in the reacted zone.

Due to enrichment, dense oxide particles in increasingly greater concentration are formed, which reduce the total cross-sectional area available for oxygen diffusion, leading to reduced depth of internal oxidation. However, while dealing with the internal oxidation of ternary alloy systems such as silver-tin-indium, one also has to consider the relative stability of the oxides of solutes. Indium forms a much stabler oxide than tin (free energy of formation of In_2O_3 at 298 K is 198.55 kcal/mol and that of SnO_2 124.2 kcal/mol). Therefore, the uniformly distributed elemental indium will be oxidized at a lower oxygen concentration than would tin. Once the In_2O_3 particles are formed, they become nuclei for the precipitation of tin oxide and may also enhance the rate of precipitation. The insoluble sub-microscopic particles greatly increase the amount of high energy interface regions. It is well established that the diffusion rate along grain boundaries and high energy interface is much higher than within the grain. Thus, the actual depth of internal oxidation will be decided by many competing processes as described above.

It is apparent from the foregoing equations that oxygen pressure, temperature and concentration of active metal influence the scaling constant and hence the overall kinetics of the process. The scaling constant is expressed in terms of activation energy (Q) of the internal oxidation process (GroBe *et al* 1966) through an Arrhenius type of relation viz.

$$k = A \exp -(Q/RT). \quad (3)$$

The activation energy of the process is a fixed quantity for a particular composition and oxygen pressure.

The selection of composition in this work was based on the contact property data reported by different authors and optimum properties found by them in different compositions (Shen and Gould 1987; Honda 1979). It has been established that the maximum indium percentage should be in the range of 2–4 wt% for optimum contact properties. More than 4 wt% indium affects the sticking resistance adversely, whereas < 2 wt% indium is not very effective in facilitating the process of internal oxidation of tin. The optimum tin content for satisfactory performance and processing has been established to be in the range of 4–10 wt% (Honda 1979).

2. Experimental

Five alloys with compositions $(100 - 6 + x) \text{Ag-6Sn-xIn}$ ($x = 2.0, 2.5, 3.0, 3.5, 4.0$) were melted under vacuum in an induction furnace. The as-cast alloys were rolled in the form of sheets of 4 mm thickness. These sheets were homogenized at 650°C for 15 h. Subsequently, cylindrical pellets of 7.6 mm diameter were punched out of the sheet. Each pellet was cleaned by polishing on 240 grit emery paper to remove

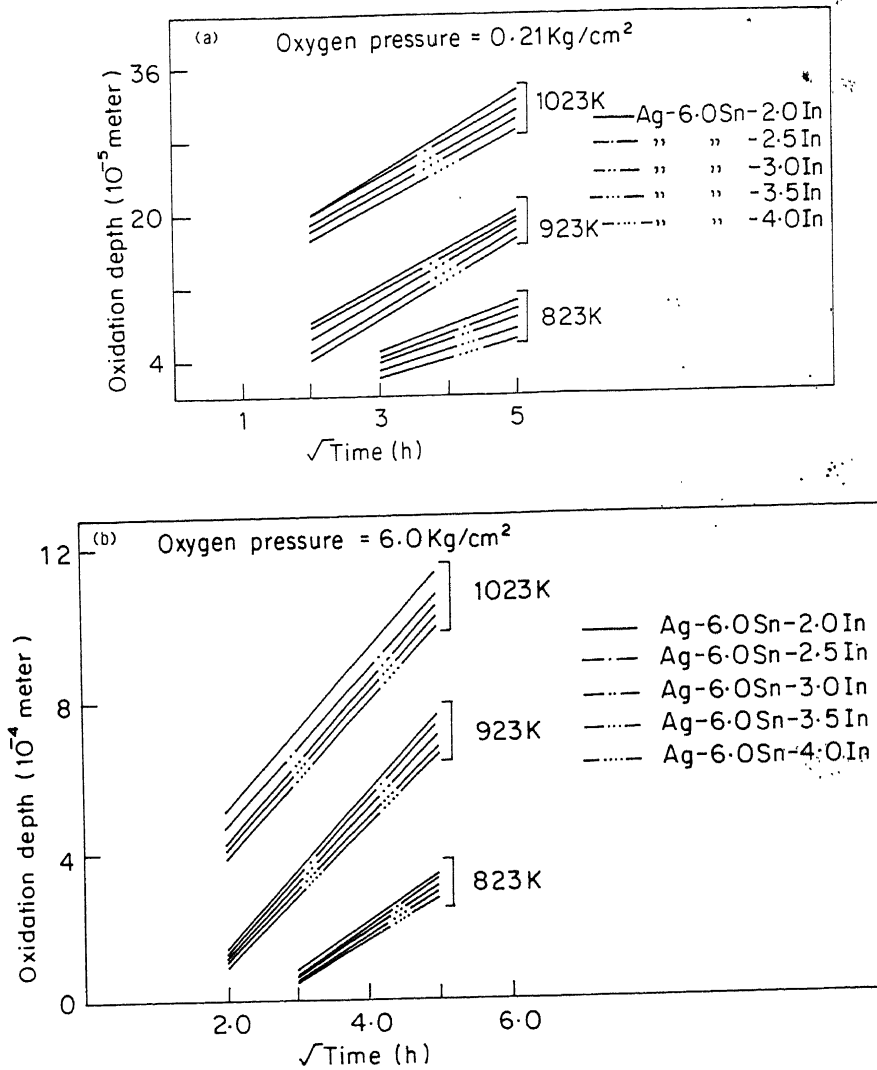


Figure 3. Variation in depth of oxidation with temperature, time and composition. a. oxygen pressure = 0.21 kg/cm^2 , b. oxygen pressure = 6.0 kg/cm^2 .

that the activation energy of the process increases with alloy concentration. This increase may be ascribed to the reduction in the fractional volume of silver available for oxygen to diffuse as the volume percentage of alloying elements increases. Further, oxides being very dense, the rate of diffusion of oxygen through oxides is comparatively negligible.

Scanning electron micrographs (SEM) were taken along the direction of oxygen diffusion for all compositions. Micrographs 7a and 7b show the size and shape of the oxide dispersion at 0.21 kg/cm^2 and 6.0 kg/cm^2 respectively. These micrographs have been taken at equal distances from the surface in view of the gradual coarsening of oxides from the surface to the bulk. It may be noted that coarsening of oxide particles occurs as the indium percentage is varied over the range of 2-

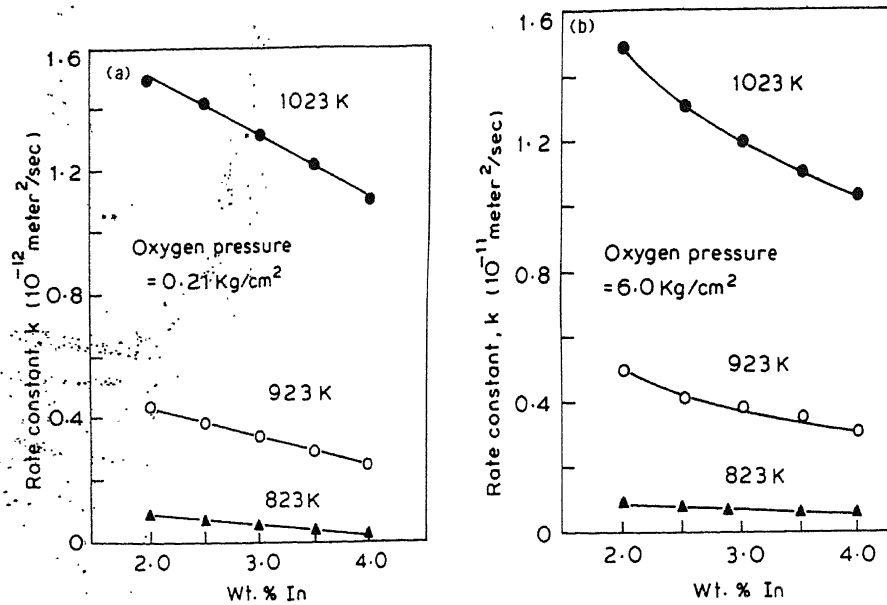


Figure 4. Variation in rate constant with composition and temperature. a. oxygen pressure = 0.21 kg/cm², b. oxygen pressure = 6.0 kg/cm².

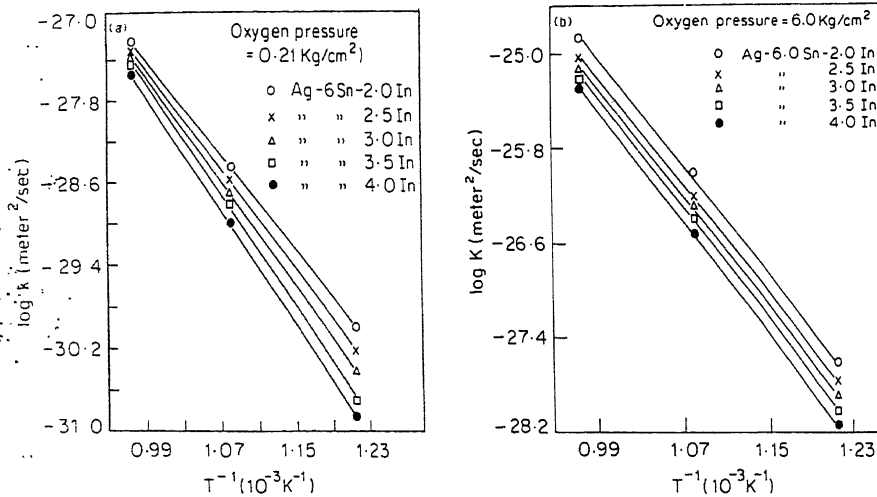


Figure 5. Log K vs $(1/T)$ plot for Ag-6Sn-xIn ($x=2.0, 2.5, 3.0, 3.5, 4.0$) alloy. a. oxygen pressure 0.21 kg/cm², b. oxygen pressure 6.0 kg/cm².

4 wt%. It is also apparent from the micrographs that the fractional volume of silver is substantially reduced over the compositional range. It is quite likely that oxides are enriched with increase in indium concentration. However, this could not be confirmed in the absence of an energy-dispersive spectrometer. A thin (1–2 μ m) oxide-free silver layer following internal oxidation is observed in all the samples.

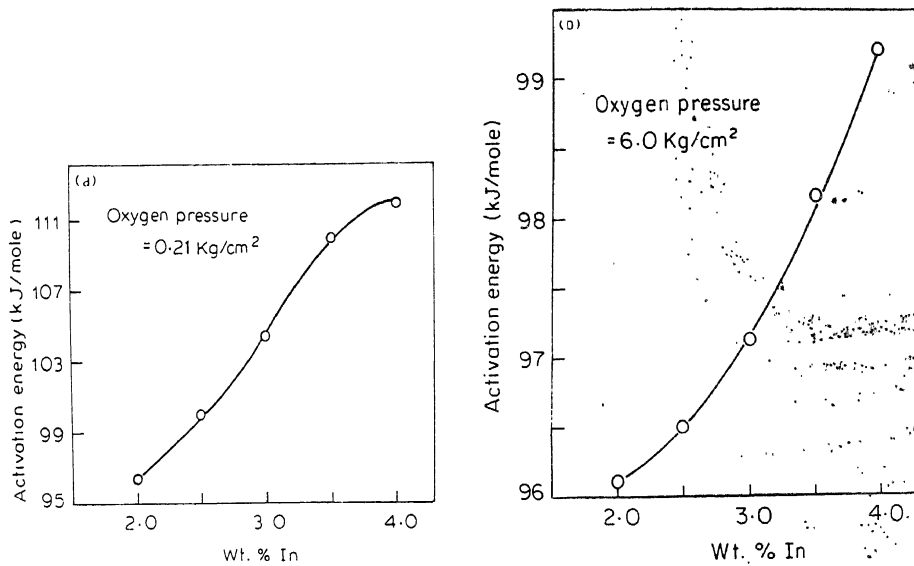


Figure 6. Variation of activation energy of internal oxidation process for Ag-6Sn-xIn ($x=2.0, 2.5, 3.0, 3.5, 4.0$) alloys. a. oxygen pressure 0.21 kg/cm², b. oxygen pressure 6.0 kg/cm².

The mechanism of formation of these layers has been attributed to the onset of diffusion creep owing to the formation of bulky oxides (Machert 1986). This observation gives support to the idea of enrichment of oxides as the indium content is increased.

The difference in size of oxide particles at different oxygen pressures is evident in the scanning electron micrographs. At lower oxygen pressure (0.21 kg/cm²) the size of oxide particles is coarser than at higher oxygen pressure. This can be attributed to the modified nucleation and growth kinetics of oxide particles at higher oxygen pressure. Due to a steeper oxygen concentration gradient, the oxidation front moves at a faster rate. As the oxide front sweeps through the alloy, it nucleates oxide particles and before these nucleated oxide particles have an opportunity to grow by the counter diffusion of oxide elements, fresh nucleation takes place ahead of the previous nucleation site. However, at lower oxidation pressure, the rate of advancing oxidation front is reduced and consequently the growth of oxide particles is appreciable. Further, since the heat of formation of tin oxide (SnO₂) and indium oxide (In₂O₃) at 298 K is -124.2 and -198.55 kcal/mole, respectively, it is quite likely that indium oxide acts as nucleating agent for the growth of the tin oxide.

Table 1 gives the physical properties relevant for the characterization of electrical contact materials. The trend in change of electrical conductivity with volume fraction of oxides is in conformity with the law of mixtures. However, the theoretical values do not match with experimental results. This discrepancy may arise due to two reasons. Firstly, if the enrichment of oxide does take place, the volume fraction of silver is correspondingly reduced. Secondly, the precipitation of oxides changes the scattering characteristics of silver. Both these effects impair the conductivity values. It may be noted that the hardness value does not increase in step with the increase in volume fraction of oxides. This behaviour may be

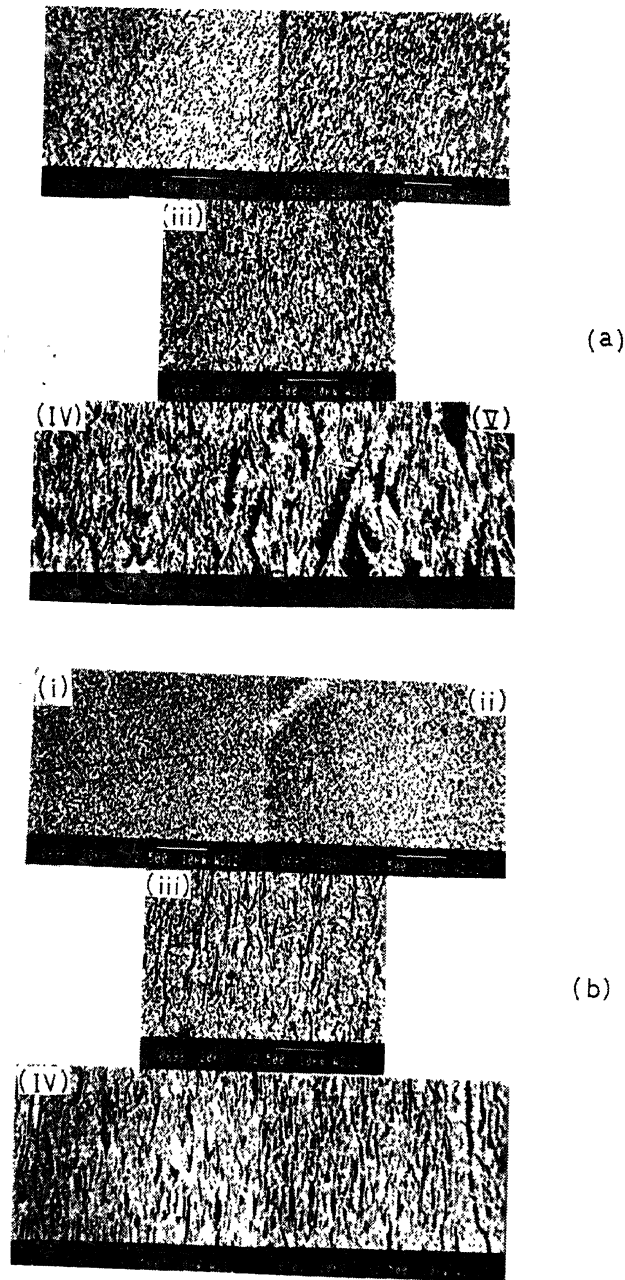


Figure 7. Scanning electron micrographs taken along the moving oxygen front for Ag-6Sn-xIn ($x = 2.0, 2.5, 3.0, 3.5, 4.0$) alloys. a. oxygen partial pressure 0.21 kg/cm^2 . b. oxygen partial pressure 6.0 kg/cm^2 .

accounted for the coarsening of oxide particles with increased volume fraction (see micrographs 7a and 7b). Coarsening of oxides leads to increase in interparticle spacing and a consequent decrease in barriers arresting the motion of dislocations. The difference in hardness values between samples oxidized at different oxygen

Table I. Physical properties of internally oxidized Ag-6Sn-xIn ($x = 2.0, 2.5, 3.0, 3.5, 4.0$) at 1023 K for 25 h at the depth of 0.05 mm from surface.

Alloy composition (wt %)	Composition* after internal oxidation (wt %)	Volume percentage* of tin oxide	Volume percentage* of indium oxide	Total volume percentage* of oxide	Electrical conductivity (% IACS)	Hardness (HV0.1) internal oxidation at 0.21 kg/cm ² oxygen pressure	Internal oxidation at 6.0 kg/cm ² oxygen pressure
92.0Ag-6.0Sn-2.0In	90.0Ag-7.6SnO ₂ -2.4In ₂ O ₃	10.52	3.30	13.91	—	102.8 ± 0.8	109.2 ± 2.9
91.5Ag-6.0Sn-2.5In	89.4Ag-7.6SnO ₂ -3.0In ₂ O ₃	10.49	4.22	14.71	73.0	107.4 ± 1.1	110.4 ± 2.0
91.0Ag-6.0Sn-3.0In	88.8Ag-7.6SnO ₂ -3.6In ₂ O ₃	10.46	5.05	15.51	69.0	108.2 ± 3.1	114.6 ± 5.7
90.5Ag-6.0Sn-3.5In	88.2Ag-7.6SnO ₂ -4.2In ₂ O ₃	10.43	5.88	16.31	65.0	110.8 ± 2.6	115.3 ± 3.8
90.0Ag-6.0Sn-4.0In	87.6Ag-7.6SnO ₂ -4.8In ₂ O ₃	10.41	6.70	17.11	62.0	111.0 ± 2.6	117.0 ± 4.8

*Percentages based on chemical analysis.

pressures may also be explained by the easier movement of dislocations in coarser microstructures.

4. Conclusion

The following points emerge from the present study of the role of indium in the internal oxidation of a silver-tin alloy under different process conditions:

(i) Ag-6Sn-xIn ($x = 2.0, 2.3, 3.0$ wt%) alloys are single phase and amenable to the internal oxidation process. Higher percentage of indium does not facilitate the internal oxidation process. For indium concentrations exceeding 3 wt%, coarsening of oxide particles occurs, which may not be favourable from the point of view of contact properties.

(ii) Higher oxygen pressure remarkably increases the rate of internal oxidation and leads to refinement of the dispersed oxide. The former is relevant from the view point of application, while the latter is likely to impart better anti-welding and anti-erosion properties to the product.

(iii) Although internal oxidation at higher partial pressure of oxygen leads to refinement of dispersoids, the hardness values do not increase appreciably. This is desirable in the context of making the required shapes.

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