Internal oxidation of rapidly solidified silver–tin–indium alloy powders

A. VERMA, T.R. ANANTHARAMAN
Thapar Corporate Research and Development Centre, Patiala 147001, India

The internal oxidation behaviour of rapidly solidified silver–tin–indium (Ag–Sn–In) alloy powders is described. Internal oxidation of Ag–Sn–In alloy has gained importance in view of the possible replacement of toxic silver–cadmium oxide (Ag–CdO) material by a better property silver–tin oxide (Ag–SnO₂) electrical contact material. Rapidly solidified Ag–Sn–In alloy powders of composition Ag–6.0Sn–3.0In were prepared by gas atomization. The important characteristics of alloy and powders, from the point of view of internal oxidation, were determined. The powders were internally oxidized and subsequently processed by conventional powder metallurgy techniques. The important physical properties, such as electrical conductivity, hardness, density and microstructure, were determined. The physical properties, especially the microstructure and rate of internal oxidation, were compared with the materials prepared by the conventional internal oxidation route.

1. Introduction

Various facets of internal oxidation of silver-based binary alloys have been studied by many researchers [1–3]. The process basically involves diffusion of oxygen through an alloy consisting of a noble and one or more less noble component(s). Formation of oxides of less noble component(s) takes place in situ, if its free energy of oxide formation is lower than that of the noble metal. The kinetics of the process for a binary system has been worked out by Rhines et al. [4]. The results of these studies have been used to develop various silver–metal oxide electrical contact materials, such as silver–cadmium oxide, silver–tin oxide, silver–indium oxide, etc. However, internal oxidation of materials is intrinsically slow and results in a non-uniform dispersion of oxides as well as an oxide-free zone, also called a denuded zone, in the centre.

In order to overcome some of these problems with varying degree of success, internal oxidation of alloyed powder (IOAP) of various silver-based alloys has been tried [5]. IOAP not only shortens the total time for internal oxidation by virtue of the reduced distance that oxygen has to diffuse, but also results in a more uniform microstructure. The present work was carried out with a view to quicken the process of oxidation further and to obtain a finer and more uniform dispersion. Rapidly solidified powder of composition Ag–6.0Sn–3.0In has been studied in view of its commercial importance as electrical contact material. Needless to say, rapid solidification leads to small grain size materials of more uniform composition [6]. A higher percentage of grain-boundary area is expected to facilitate faster diffusion of oxygen and hence to expedite the process of internal oxidation.

The role of indium in this alloy is to facilitate the internal oxidation of tin. It has been established that a tin content of more than 4 wt % is not amenable to internal oxidation because an impervious layer of tin oxide is formed, inhibiting further diffusion of oxygen [7]. Because indium forms a much stabler oxide than tin (free energy of formation of In₂O₃ at 298 K is −830.93 kJ mol⁻¹ and that of SnO₂ is −519.77 kJ mol⁻¹), the uniformly distributed elemental indium becomes oxidized at a lower oxygen concentration than tin. The In₂O₃ particles become nuclei for the precipitation of tin oxide and may also enhance the rate of precipitation. These insoluble submicroscopic particles greatly increase the amount of high-energy interface region, thereby enhancing the diffusion of oxygen.

2. Experimental procedure

The flow chart of the adopted process route is given in Fig. 1. Alloy of composition Ag–6.0Sn–3.0In was prepared by vacuum resistance melting. The alloy melt was atomized in an atomizer consisting of an annular nozzle design of convergent–divergent geometry. The throat to exit ratio of the nozzle was designed to be 1:4. Atomization was carried out in a nitrogen atmosphere at 1.5 MPa pressure. The atomization conditions, such as nozzle position and optimum range of gas pressures, etc., were optimized using lead–tin alloy. The atomized powders were sieved through 150 mesh (ASTM) size sieve. The morphology of the powder was determined by scanning electron microscopy (SEM). The size distribution and microstructure of the atomized powder were determined by embedding them in Perspex™ thermoplastic.

In order to select the internal oxidation (IO) temperature, the melting point of the alloy composition was evaluated by differential scanning calorimetry.
3. Results and discussion

It was earlier established [8] through X-ray studies that the combined percentage of tin and indium in Ag-6.0Sn-3.0In had terminal solubility in silver. The DSC scan of the alloy (Fig. 2) helped in determining the melting point of the alloy (1108.6 K) and thereby choosing a proper internal oxidation temperature.

(DSC). The internal oxidation behaviour of the representative sample was studied using a thermal gravimetric analyser (TGA). The powders were heated in air at the rate of 20 K min$^{-1}$ to 1023 K followed by isothermal heating for 2 h at 1023 K. In order to compare the internal oxidation behaviour of the rapidly solidified atomized powders with the powders of coarser grain size, a small volume of powder was taken and heated in vacuum at 773 K for 24 h to bring about grain growth. The powder mass was well dispersed during this process to avoid sintering. The thermogram of these powders was determined in the same way as for the rapidly solidified atomized powders.

The morphology and microstructure of the atomized powder were determined. Having determined the time for internal oxidation by TGA, the complete mass of powder was internally oxidized at the same temperature, for durations longer than that determined by TGA, because of the denser packing of powders in the furnace. The internally oxidized powders were consolidated in the shape of cylindrical pellets of dimensions 16 mm diameter and 4 mm height. The consolidation was carried out in a double-acting hydraulic press at 618 MPa pressure. The green density of the pellets was determined by a dimensional method. The pellets were sintered in air at 1173 K for 1.0 h and density of the pellets was determined. The pellets were re-pressed at 1235 MPa pressure to improve the density. Re-pressed pellets were annealed at 973 K for 30 min. Electrical conductivity, hardness, density and microstructure of the annealed pellets were then evaluated. In order to determine the compositional variation from point to point, an X-ray line trace was taken using an energy dispersive spectrometer (EDS).