The Effect of Antimony on Sintering of Silver in the Initial Stage

P. Y. Y. MAAK AND K. T. AUST

A previous study by Takahata et al.\(^1\) gave some indication that the addition of a solute (1.16 wt pct) to spherical silver powder increased the shrinkage rate at 800 and 850°C in the early stage of sintering (up to about 0.5 pct shrinkage). However, the difference in shrinkage between the pure Ag and Ag-Sb powders was quite small in this initial stage. It was possible, therefore, that this result may have been partly associated with experimental error in measuring shrinkage (about ±0.0018 maximum) and in determining the true origin of the isothermal shrinkage curves. It was evident that further studies at lower temperatures would be required before unequivocal statements could be made regarding this early stage of sintering.

In the present study, the effect of Sb (1.16 wt pct) on the sintering kinetics of Ag in the early stage was investigated using lower sintering temperatures (700 to 800°C) and shorter sintering times (up to 3 to 4 h) in argon atmosphere. The material characteristics, preparation of specimens for the sintering studies, shrinkage measurements and metallographic study of the sintered specimens are described in Ref. 1.

Isothermal shrinkage curves of \(\Delta L/L_0\) vs sintering time \((t)\) are shown in Fig. 1 for specimens sintered at 700, 740, and 780°C and in Fig. 2 for the data at 720, 760 and 800°C. These curves indicate that the Ag-Sb alloy shrinks at a faster rate than the pure Ag in the first 10 to 20 min of sintering at the same temperature. However, with continued sintering at the higher temperatures the rate of shrinkage of the alloy powders decreased. This puzzling behavior is similar to that of some other systems wherein the isothermal shrinkage values are based on a B.A.Sc. thesis of P. Y. Y. Maak, University of Toronto, 1977.

P. Y. Y. MAAK and K. T. AUST are Graduate Student and Professor, respectively, Department of Metallurgy and Materials Science, University of Toronto, Toronto, Canada M5S 1A4. The present work is based on a B.A.Sc. thesis of P. Y. Y. Maak, University of Toronto, 1977.


Fig. 1—Shrinkage vs sintering time at 700, 740, and 780°C for Ag and Ag-Sb.

der decreases more rapidly than that of the silver, dropping to nearly zero, as was observed by Takahata et al. This latter effect was interpreted in terms of a decrease of the grain boundary self diffusion of Ag by Sb. After about 200 min of sintering at 800°C, the shrinkage ($\Delta L/L_0$) of the Ag is greater than that of the Ag-Sb as was also found previously. The cross-over of the shrinkage curves of Ag and Ag-Sb occurred at about 1.5 pct shrinkage after sintering for about 200 min at 800°C (Fig. 2). Takahata et al. observed this cross-over to occur at about 0.5 pct shrinkage after sintering for the same time and temperature. Further studies are required to determine the reason for this different behavior in the two studies.

A summary of the sintering data obtained for the Ag and Ag-Sb samples after 3 or 4 h sintering is given in Table I. The density measurements gave results similar to those obtained for the shrinkage. The Ag-Sb specimens display a greater densification than the Ag specimens for the same sintering temperature and time, until after 4 h at 800°C the extent of densification was reversed in the Ag-Sb and Ag.

Table I also shows the average neck radius ($x$) from more than 50 measurements for each specimen, calculated at 95 pct confidence limits. These values were obtained from SEM photographs of specimens prepared by the pore replica method of Lee et al. This technique of three-dimensional replication of the pore structure of silver powder samples has proved a precise means for measuring sintering parameters such as neck size. Typical SEM pictures of the pore replicas from the sintered Ag and Ag-Sb samples are shown in Fig. 3. From the $x$ values in Table I it appears that for the same sintering conditions the neck radii of Ag-Sb are smaller than those of Ag, i.e., Sb decreases the neck growth rate of silver. (It should be noted that neck radii of curvature values estimated from optical microstructures show the same trend.) Since surface diffusion should dominate neck growth of Ag in this early stage of sintering, the present results indicate that the surface mass transport of the Ag is depressed by the presence of Sb. A solute (Sb) may reduce the surface mass transfer coefficient by reducing the surface energy and/or the surface diffusion coefficient. A comparison of the neck size and shrinkage data in Table I clearly shows that Sb inhibits the very early surface diffusion neck growth, giving more shrinkage with the resultant higher driving force and smaller neck size.

In the absence of pressure, sintering is driven by surface curvature or rather, by the difference in surface curvature ($K$) between sources and sinks. Grain boundary diffusion appears to be the dominant densification mechanism in the initial stage of sintering of Ag. The following equation derived by Ashby was used to describe the curvature driving force ($K$) for a grain boundary diffusion source in the initial stage of sintering of an aggregate of spheres:

$$K = \left(\frac{1}{\rho} - \frac{1}{x}\right)$$

where $\rho' = \rho/2(a - x)$ and $a$ is the particle radius.

The various $K$ values calculated from Eq. [1] using the measured $x$ values and a particle radius of 21 um are given in Table I. The $K$ values for the Ag-Sb are greater than those of Ag for the same sintering time and temperature. A greater driving force may account for the enhanced shrinkage rate of the Ag-Sb, as compared to Ag, in the first 10 to 20 min of sintering (Figs. 1 and 2). With higher sintering temperatures, and longer sintering times (e.g., 3 and 4 h at 800°C), the $K$ values in Table I for both the Ag and Ag-Sb de-