A survey of the liquidus surface and invariant reactions involving liquid has been made for solidification in the ternary Sn-Ag-Sb system. Differential thermal analysis and electron-beam microprobe analysis were used to measure liquidus temperatures and determine the composition of solid phases resulting from solidification. A liquidus projection and the composition of the phases coexisting at the two observed invariant reactions were determined. Ternary alloys based on the Sn-Ag-Sb system have been used as thermal fatigue-resistant solders where high heat loads must be dissipated. An analysis of the properties encountered from such solders is presented, based on the phase constitution resulting from the solidification behavior reported here.

**Key words:** Sn-Ag-Sb liquidus projection, solder alloys, Sn-Ag-Sb solders.

**INTRODUCTION**

The introduction of high-strength solders based on ternary alloys found in the tin-rich corner of the Sn-Ag-Sb system has attracted attention in cases where thermal fatigue is a problem. In these applications silicon chips are bonded to metallic substrates in which high heat loads may be dissipated. Such solders have the high tensile strength and low ductility that can be associated with resistance to thermal fatigue and to the resultant degradation of heat transfer during power cycles.

One alloy of this type which has been awarded a patent because of its unique wetting and thermal fatigue resistance is alloy J, which contains 65% (by weight) tin, 25% silver and 10% antimony. The development of alloy J has been conducted without knowledge of equilibrium solidification temperatures or the phase distribution expected in this ternary system. While it has been recognized that large temperature differences can be expected in these alloys between the onset of solidification and final freezing, no information on the ternary liquidus surface appears in the literature. A study of the distribution of phases at low temperature has been made by Cheng, although he did not investigate equilibria involving liquid. Since the onset of solidification and the phase distribution expected from freezing of liquid are central to behavior of solders, an investigation of the nature of the liquidus surface in the ternary Sn-Ag-Sb alloys seems appropriate.

We report here a preliminary survey of the main features of the liquidus surface. We have given special attention to identification of the four-phase invariant reactions involving liquid and to a determination of the composition of the solid phases partaking in these reactions. The results can be used to generate an outline of the liquidus surface and the composition of the phases coexisting in the two invariant equilibria. Although a detailed determination of isothermal contours on the liquidus surface was not made, sufficient information about the initiation and completion of freezing was obtained to be of considerable use in the analysis of Sn-Ag-Sb solders.

**EXPERIMENTAL TECHNIQUE**

The data collected during solidification were thermal arrests that could be used to determine the onset of primary, secondary and tertiary solidification, and chemical analyses of the solid phases with an electron-beam microprobe. Metallographic examination of the microstructures was used to identify the solid phases, and, especially, to identify the phase produced by primary freezing. Composition of the solid at the invariant points as determined by altering the composition of the liquid of the specimens in a systematic fashion until only a single thermal arrest at the temperature of the invariant reaction was observed.

The specimens were made from pure metals of 99.99% nominal purity obtained from Cominco Electronic Materials of Spokane, Washington. Predetermined quantities of each metal were weighed to an accuracy of 0.05 gram to obtain approximately 100 grams of a specimen of known compo-
sition. To minimize oxidation and loss of the more volatile antimony, the tin and silver were melted first. Melting was carried out under argon in a graphite crucible made from grade 780GL graphite obtained from AIRCO, Inc. The interior of the crucible was a cylindrical cavity 75 mm long and 25 mm i.d. The argon atmosphere was maintained during melting by directing a stream of argon into the cavity, which was approximately half-filled with the specimen and half with argon. The antimony was added when the tin and silver had melted and the temperature was estimated to be 50 to 100 degrees above the liquidus temperature. The liquid was stirred vigorously with a graphite rod; it was then allowed to solidify around a graphite sleeve into which the thermocouple for thermal analysis could be inserted. No loss of antimony vapor was detected visually during melting, and the oxide-free surface obtained after solidification was used as an indication that metal loss during melting had been minimal. No bulk chemical analyses were made after melting.

Thermal arrests were made by differential thermal analysis of these specimens. They were contained in the graphite melting crucibles, which in turn, were held within a closed silica tube in a furnace. The silica tube was evacuated and backfilled with argon before the specimens were muted at the start of the thermal analysis. The reference for the differential analysis was a cylindrical rod of nickel which had roughly the same heat capacity as the specimen. Chromel-alumel thermocouples were used; they were calibrated with pure metals at the melting point of tin (231.97°C), cadmium (321.11°C), zinc (419.58°C) and aluminum (660.37°C). During thermal analysis a cooling rate of approximately 1 1/2 °C/min was maintained. The dc millivolt signal from the differential thermocouple was stored at 30 second intervals in a HP3497A Data Acquisition/Control Unit, which itself was controlled by a HP87XM computer. The millivolt data were converted to temperature, T, and differential temperature, θ, and graphed in a HP9872C Plotter, most importantly as curves of derived inverse differential, dθ/dT, vs. temperature. Thermal arrests were prominent on these graphs and could easily be resolved from the background, since in many instances dθ/dT tends to infinity as a latent heat is evolved.

Initial identification of solid phases resulting from freezing of each specimen was made from chemical analysis with a Cameca MBX electron-beam microprobe. All phases present were found to be those which appear in one of the three binary systems. The composition of the secondary solidification showing the onset of simultaneous freezing of two solid phases. These points should fall on the liquidus valleys of Fig. 1. The second listed thermal arrest is that of secondary solidification, showing the onset of simultaneous freezing of two solid phases. The composition of the liquid participating in the four-phase invariant reactions is easily identified because a thermal arrest at this temperature appears in the cooling curves of several different specimens. We made an initial estimate of the composition of the liquid that freezes at each invariant point, and obtained a thermal arrest curve of a liquid made to have this estimated composition. Thermal arrest curves from the first estimates showed secondary peaks because we did not correctly guess the invariant composition. We then adjusted the composition until the thermal arrest curve revealed only a primary peak at the (previously-determined) temperature of the invariant reaction. This is believed to indicate that the liquid had been correctly made up to the invariant composition.

Composition of the solid phases resulting from invariant freezing is also difficult to measure because failure to attain equilibrium during freezing is characteristic of this system. Since each solid phase can appear to have several analyses, depending where the microprobe beam strikes, it is difficult to know which location was in equilibrium with the invariant liquid. In an attempt to attain equilibrium, specimens were held for 32 days in evacuated silica capsules at a temperature just below the invariant temperature (a 224°C anneal for the invariant at 235°C, a 364°C anneal for the invariant at 378°C). Composition of the phases present was determined with the microprobe after these anneals. This was only partially successful in revealing the equilibrium composition because solidification over a range of temperature had produced a corresponding range of composition for the solid phases. This range was not completely eliminated by long holding. In addition, partial melting of one specimen was encountered due to the unexpected presence of nonequilibrium liquid. Nevertheless, the compositions given in Table II are our best estimates. These compositions are also consistent with corresponding binary invariant points readily available from phase diagrams published in the ASM Handbook.³

DATA AND RESULTS

The composition of the twenty-one mixtures studied and the temperature of the thermal arrests are shown in Table I. The first-listed thermal arrest temperature is the liquidus temperature observed; a three dimensional plotting of these should comprise the liquidus surface. Our estimate from these data of the appearance of the liquidus projection is shown in Fig. 1. The second listed thermal arrest is that of secondary solidification, showing the onset of simultaneous freezing of two solid phases. These points should fall on the liquidus valleys of Fig. 1, which are lines at which surfaces of primary solidification intersect. The composition of the liquid at the onset of secondary freezing is not known, however, so the intersection of the liquidus surfaces cannot be determined from secondary thermal ar-