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Diffusion in the CuSn binary system: application to Nb_3Sn composites

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Non-parabolic growth of intermediate phases in CuSn binary diffusion couples has been observed at 220° C. The deviation from parabolic behaviour may be attributed to grain boundary diffusion. Diffusion coefficients for both the ϵ-(Cu_3Sn) and η-(Cu_6Sn_5) phases are typically of the order of 2×10^{-11} cm^2 sec^{-1}, and are in general agreement with other published values.

1. Introduction

In this article we report on the kinetics of low temperature diffusion in CuSn binary diffusion couples. This study was motivated by the necessity of understanding Sn diffusion during the manufacture of "external-tin" processed Nb_3Sn multifilamentary superconductors [1, 2]. In the external-diffusion process a drawn Nb–Cu composite is electroplated with Sn, which must then be diffused into the bulk of the composite to undergo a solid state reaction with Nb to form Nb_3Sn. It is during the early stages of the diffusion anneal that most of the manufacturing problems are encountered. The first stage involves a diffusion anneal at a temperature below the melting point of Sn. This serves primarily to reduce the overall Sn thickness on the surface of the composite before the remaining Sn becomes molten. The problems of Sn flow and coalescence are much less severe when the Sn thickness is reduced.

Diffusion was studied at 220° C by observing the time dependence of the growth of the intermediate phases in the CuSn system. From this data the interdiffusion coefficients for growth of the ϵ-phase (Cu_3Sn) and the η-phase (Cu_6Sn_5) were measured, and non-parabolic growth behaviour was observed. A change in the η-phase growth morphology associated with Sn melting was also observed.

2. Experimental details

The mechanical fabrication of external-diffusion processed composites has been discussed in great detail previously [3, 4]. Nb–Cu composites and oxygen-free high conductivity Cu wires varying in diameter from 0.25 mm (0.01 in.) to 0.76 mm (0.03 in.) were Sn-plated from a commercial stannous fluoborate plating formulation. The thickness of the Sn plate varied from 18 μm on the 0.25 mm wire to 51 μm on the 0.76 mm wires. The wires were found to be plated uniformly both lengthwise and circumferentially, as far as could be ascertained by mechanical measurement of the as-plated diameter and by optical microscopy.

The formation of intermediate phases in CuSn diffusion couples was observed by metallographic analysis of ground and polished sections taken in the direction transverse to the wire axis. Light etching with $FeCl_3$-saturated methanol was effective in delineating the low temperature phases. Determination of phase thicknesses was made by optical microscopy and scanning electron microscopy. In general the phase thickness at a given time was determined from the average of 40 individual points measured circumferentially around a wire.

Annealing heat treatments were carried out in a vacuum of 1.3×10^{-4} Pa (1×10^{-6} mm Hg) in a furnace temperature regulated to ± 3° C. The usefulness of pre-annealing prior to Sn plating in order to reduce Kirkendall porosity has been discussed previously [5], as has the role of oxygen in preventing Sn coalescence when its melting point (232° C) is exceeded [6, 7].

3. Results and discussion

At temperatures below 250° C there exist four phases in the CuSn binary system: the Cu and Sn

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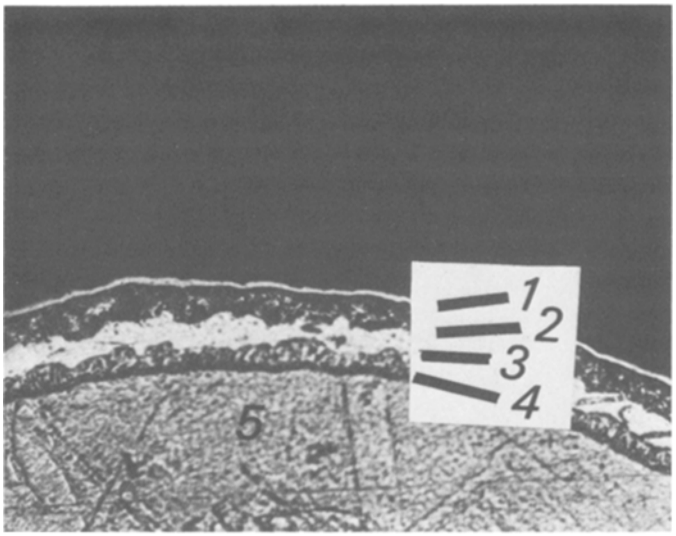


Figure 1 An optical micrograph revealing the growth of the ϵ and η phases after 112h at 220° C. The layers are: 1. electroplated nickel; 2. remaining tin; 3. η-phase; 4. ϵ-phase; and 5. α-bronze. The total thickness of layers 2, 3 and 4 is 20 μm.

terminal solid solutions and two intermediate phases, ϵ-(Cu_3Sn) and η-(Cu_6Sn_5). The extent of solid solubility for either Cu or Sn is quite limited at these temperatures. The solubility of Sn in α-Cu is less than 4 at% at 250° C and is reduced to almost zero at 100° C. In the Sn solid solution the solubility of Cu reaches a maximum of 0.01 at% at the eutectic temperature, 227° C. The η-phase undergoes a structural transformation at 180° C, but for our purposes this need not be considered [8].

Isothermal diffusion studies were performed at 220° C by observation of the change in thickness of the ϵ and η phases for times varying from one to 180h. A typical optical photomicrograph of the four phases is shown in Fig. 1. The measured thicknesses of the phases are plotted on a log–log scale in Fig. 2. From these data it was observed that the phases grow according to the equation

$$\Delta x = kt^{1/n} \qquad (1)$$

where Δx is the respective phase thickness, t the time, and k and n growth constants. The exponential factor n was calculated to be 2.53 for the ϵ-phase and 2.51 for the η-phase. Usually the diffusional growth of intermediate phases follows a parabolic law behaviour in which $n = 2$. Any deviation from parabolic behaviour is an indication that some mechanism other than bulk diffusion is governing the growth kinetics.

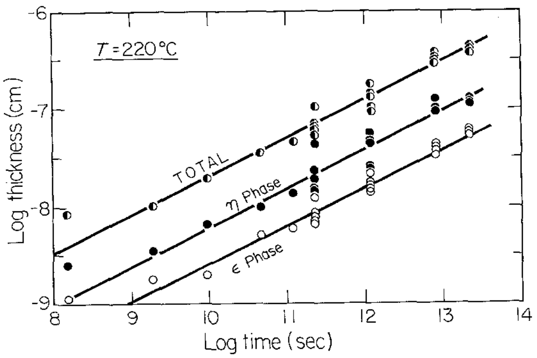


Figure 2 Measured thickness of the ϵ- and η-phases plotted against time. The linearity was determined by a least-squares best fit.

A question arises as to whether the diffusion interface in a small diameter wire is sufficiently non-planar to cause the observed deviations from parabolic behaviour. This question was answered using a diffusion analysis program employing finite element methods and capable of handling both planar and non-planar geometries. The growth rates of the intermediate phases were determined using diffusion data appropriate at 220° C. In both cases growth rates were found to be closely parabolic over 200h of diffusion time. The occurrence of non-parabolic behaviour greatly complicates the determination of the interdiffusion coefficients. If we follow the analysis of Wagner [9] for instance, but allow for the occurrence of non-parabolic growth, then a time dependent expression for the diffusion coefficients of the form

$$D^{\epsilon} = \frac{\Delta x^{\epsilon}}{nt\Delta N^{\epsilon}_{Sn}}(f_{\epsilon\epsilon}\Delta x^{\epsilon} + f_{\epsilon\eta}\Delta x^{\eta}) \qquad (2)$$

and

$$D^{\eta} = \frac{\Delta x^{\eta}}{nt\Delta N^{\eta}_{Sn}}(f_{\eta\epsilon}\Delta x^{\epsilon} + f_{\eta\eta}\Delta x^{\eta}) \qquad (3)$$

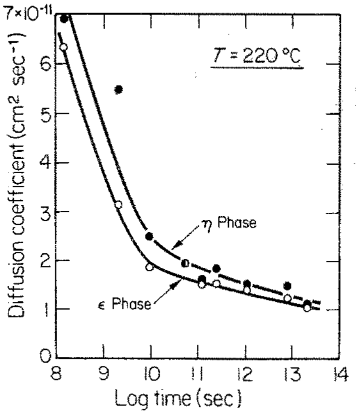


Figure 3 Interdiffusion coefficients for the ϵ- and η-phases plotted against time.

results. These are identical to the expressions obtained by Gurov *et al.* [10] with the exception that we have included the molar volumes of the phases in the analysis (see Equations 5 and 6). D is the interdiffusion coefficient, Δx the phase thickness, ΔN_{Sn} the homogeneity range of the phase, n is the previously defined growth constant and t time. The other terms are defined as follows:

$$f_{\epsilon\epsilon} = N^{\epsilon}_{Sn}(1-N^{\epsilon}_{Sn}) \tag{4}$$

$$f_{\epsilon\eta} = N^{\epsilon}_{Sn}(1-N_{Sn})\frac{V^{\epsilon}_{m}}{V^{\eta}_{m}} \tag{5}$$

$$f_{\eta\epsilon} = N^{\epsilon}_{Sn}(1-N_{Sn})\frac{V^{\eta}_{m}}{V^{\epsilon}_{m}} \tag{6}$$

$$f_{\eta\eta} = N^{\eta}_{Sn}(1-N^{\eta}_{Sn}). \tag{7}$$

The N_{Sn}s are the Sn concentrations, and the V_ms are the molar volumes of the respective phases. Equations 2 and 3 were derived by assuming non-parabolic growth and substituting the transformation $\lambda = x/t^{1/n}$ for the usual Boltzmann transformation $\lambda = x/t^{1/2}$ [9].

The calculated interdiffusion coefficients are plotted in Fig. 3. The interdiffusion coefficients are of the order of 1×10^{-11} cm² sec⁻¹ and 3×10^{-11} cm² sec⁻¹ for the ϵ and η phases, respectively. These results compare favourable with those of Starke and Wever [11], who obtained values of 3.7×10^{-11} cm² sec⁻¹ for the ϵ-phase and 2.2×10^{-11} cm² sec⁻¹ for the η-phase at 210° C. The relative magnitudes of the coefficients are however reversed. It should be pointed out that one of the major uncertainties in calculating the diffusion coefficients are the ranges of homogeneity of the phases. We chose 1.0 at% and 2.0 at% for the ϵ- and η-phases, respectively [12].

The occurrence of non-parabolic growth is usually taken as an indication that bulk diffusion is not the governing process and that some other mechanism determines the rate of phase growth. In this case, the alternative mechanism is probably grain boundary diffusion. This hypothesis is supported by the observation of radially-oriented columnar grains in the ϵ-phase, as shown in Fig. 4, and by the general observation that, at sufficiently low temperatures, grain boundary diffusion becomes significant in many systems [13–15].

As expected, the growth morphologies of both phases are planar during solid state diffusion at 220° C. If the diffusion process occurs at a temperature above the melting point of Sn (232° C) then a marked change in the growth morphology

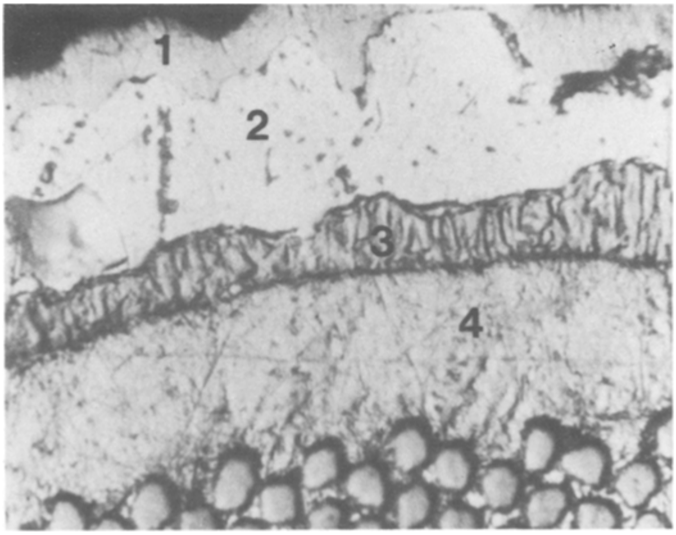
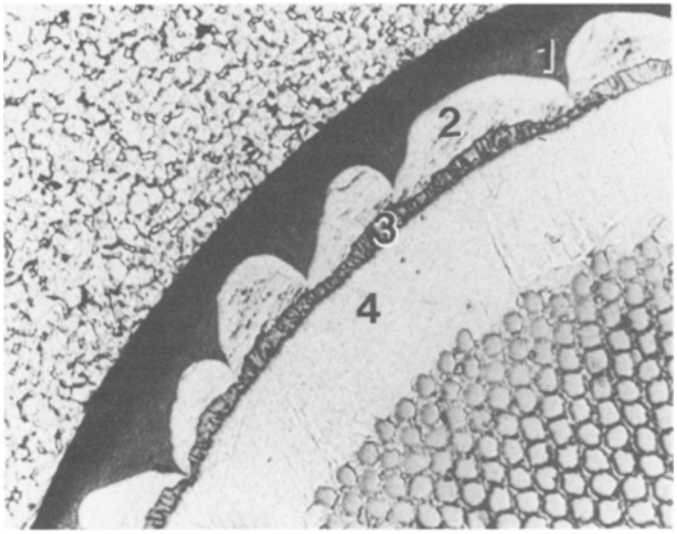


Figure 4 Columnar grain structure in the ϵ-phase (number 3) is shown. The ϵ-phase is approximately 5 μm thick and the etchant was $FeCl_3$ in methanol.



igure 5 The hillocked morphology eveloped by the η-phase as it grows nto the molten Sn. The layers are: 1. esidual tin; 2. η-phase; 3. ε-phase; nd 4. α-bronze. The total thickness f layers 1, 2 and 3 is approximately 0 μm.

of the η-phase occurs. The η-phase front growing into the liquid Sn develops a hillocked structure that repeats regularly around the circumference of the wire, and shown in Fig. 5. At 250° C those hillocks grow quite rapidly, and on reaching the surface force the remaining molten Sn into the valleys between them. We have observed this to be beneficial in the fabrication of larger diameter, > 0.5 mm (0.020 in.), external-diffusion processed composites. The hillocked formation tends to retard the downward flow of molten Sn on the surface of the wire during the early stages of the diffusion anneal. This aids in promoting a homogeneous Sn distribution around the circumference of the composite.

4. Conclusion

The interdiffusion coefficients for the ε- and η-phases in the CuSn system are approximately 1×10^{-11} cm^2 sec^{-1} and 3×10^{-11} cm^2 sec^{-1} respectively. The growth of intermediate phases in the CuSn binary system at 220° C is a non-parabolic process. Due to the columnar grain structure observed in the ε-phase and the rather low diffusion temperature involved, a grain boundary diffusion effect is suggested. During diffusion at 250° C the η-phase develops a hillocked structure which acts to retard downward Sn flow and may be advantageous during the homogenization annealing of large diameter external-diffusion processed composites.

Acknowledgements

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