

THERMODYNAMIC AND KINETIC STUDY OF PHASE TRANSFORMATIONS IN SOLDER/METAL SYSTEMS

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ABSTRACT

Diffusion in both the Pd-Sn and Cu-Sn systems has been investigated using differential scanning calorimetry. Averaged interdiffusion coefficients for the PdSn₄, PdSn₂ and Cu₃Sn intermetallics have been calculated, where equilibrium concentrations in the diffusion couples are assumed. There is a hierarchy within the Pd-Sn system where diffusion is fastest in the most Sn-rich intermetallic. Comparisons within each system, including consideration of the solute diffusion coefficients in pure Sn, provide evidence that in the most Sn rich phase (e.g. PdSn₄) the interstitial diffusion of metal atoms is the dominant reaction mechanism. In contrast, the diffusion coefficient for the Cu-rich phase Cu₃Sn was found to be five orders of magnitude smaller than the solute diffusion coefficient for Cu in pure Sn.

INTRODUCTION

The trend in the microelectronics industry to the use of devices of submicron length scales has increased the need for understanding of the interconnect materials which bond these devices to the board. In traditional attach processes, using a Sn based solder, an intermetallic compound (M_xSn_{1-x}) forms where M is some finishing or plating material, such as Pd, Ni, Cu, Au [1-4]. In some cases, two intermetallics may form during the soldering process and one or both may continue to grow in the solid state. The growth of these alloys takes place presumably by the interdiffusion of the parent phases of M (Pd, Ni, Cu) and Sn. However, it has been observed that in the case of many of these solder/metal diffusion systems that one species diffuses much more rapidly. It is also true that the first phase to form in these systems is always the most Sn rich. To help understand this phase selection and preferred diffusing species, one must turn to a number of studies done concerning the solute diffusion of noble metals and near noble metals in Sn and Pb [5-7]. Researchers found that solutes in the platinum and noble metal groups of the periodic table diffused very rapidly in Sn and Pb. This rapid diffusion was attributed to an interstitial diffusion mechanism. These results have been used previously to explain the first phase selection of the most Sn rich phase [8]. An atom, such as Cu, may diffuse easily into Sn by this rapid, interstitial mechanism, where Sn diffuses in Cu by a slower, substitutional mechanism. An aspect of these systems which has remained unstudied is the possible existence of a continued interstitial diffusion mechanism within the alloys. This is what has been investigated here. Averaged interdiffusion coefficients in a number of alloys of interest have been estimated. These determinations were compared to the solute diffusion coefficients for the relevant systems. Comparisons have resulted in the recognition of the trend in these solder metal systems for a decreasing averaged interdiffusion coefficient as a function of increasing metal content.

EXPERIMENTAL

Diffusion couples of the metals of interest are prepared by two methods, either mechanical co-deformation or physical vapor deposition (PVD, thermal evaporation or DC sputtering). In either case samples are prepared as multilayer stacks, shown schematically in Fig. 1. For the co-deformed diffusion couples, layer thicknesses of the two metals (typically between 1 and 100 microns) are characterized using optical and electron microscopy. In thin film diffusion couples prepared by PVD techniques, layer thicknesses of the two materials (between 20 and 200 nm) were measured using calibrated quartz crystal rate monitors. The as prepared state of all diffusion couples was determined by x-ray diffraction analysis in a standard Θ - 2Θ geometry using Cu-K α radiation.

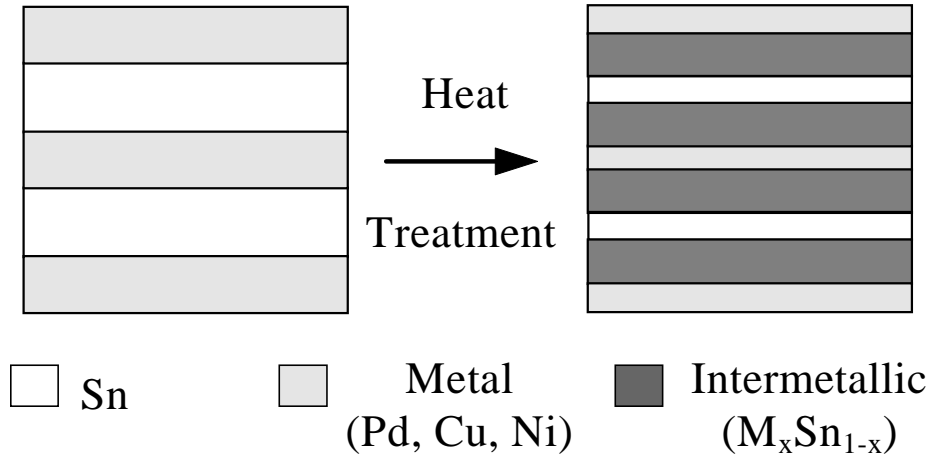


Figure 1- Schematic of a solder/metal diffusion couple. The as prepared samples for this investigation consisted of multilayers stacks where there were 10 or more layers of each metal. The diffusion couples were reacted in a differential scanning calorimeter where the growth of the intermetallic compounds was monitored by measuring the heat flow.

After sample characterization, the diffusion couples were cut up and hermetically sealed in Al pans. Sealing took place in an Ar atmosphere of 10 kPa. A series of three identical differential scanning calorimetry (DSC) runs were performed. In most cases, the runs consisted of heating the sample at 20K/min to a desired isotherm temperature and annealing the sample for 20-30 minutes. However, some samples were heated a second time to a higher temperature to ensure a complete reaction of the diffusion couple. In either case, the third run was subtracted from the first to obtain a plot of heat flow versus time for the sample.

By using differential scanning calorimetry to measure the heat flow, dH/dt , we directly monitor solid state reactions to form intermetallic compounds. For the case of one dimensional growth of an intermetallic layer in a planar geometry, the heat flow, dH/dt , is directly proportional to the reaction rate, dx/dt [9]:

$$\frac{dH}{dt} = \frac{A \rho \Delta H_r}{M} \frac{dx}{dt} \quad (1)$$

where M , ρ , and ΔH_r are, respectively, the molar mass, density (both specific to the growing intermetallic phase), and the heat of reaction. The last parameter, A , is the interfacial area which is calculated from measurements of layer thicknesses. Also, for some temperature range where an intermetallic is observed to grow, one may expect that the reaction kinetics are governed by *diffusion limited growth*:

$$\frac{dx}{dt} = \frac{k^2}{2x} \quad (2)$$

where x is the thickness of the growing intermetallic and k^2 is the temperature dependent *reaction constant*.

By performing an anneal with the differential scanning calorimeter at a given temperature, the reaction constant at that temperature may be determined. Integrating Eq. 1 and 2, one finds that:

$$k^2 = \left(\frac{M}{A \rho \Delta H_r} \right)^2 \frac{H^2}{t} \quad (3)$$

Thus, by first integrating measurements of the heat flow as a function of time to obtain the integrated heat flow, H , and plotting H^2 versus time, the reaction constant, k^2 , may be calculated. In a similar fashion, estimates of k^2 can be determined at all temperatures of a constant heating rate DSC curve [9]. At any given temperature, where diffusion limited growth is observed, the reaction constant may be

related to the *averaged interdiffusion coefficient* for the growing intermetallic, \bar{D}

$$[10]: k^2 = 2G_\beta \Delta C \bar{D} \quad (4)$$

where ΔC is the concentration gradient across the growing intermetallic layer and G_β is related to the concentration differences across the interfaces between the growth and parent phases.

RESULTS AND DISCUSSION

Pd-Sn System

Two reactions have been investigated within the Pd-Sn system. The first reaction, detailed in a previous report [11], is $\text{Pd} + \text{Sn} \rightarrow \text{PdSn}_4$, ΔH_r . The second reaction which will be discussed here is $\frac{1}{2}(\text{Pd} + \text{PdSn}_4) \rightarrow \text{PdSn}_2$, ΔH_r . Sputter deposition was used to fabricate thin film Pd/Sn diffusion couples in the stoichiometry of the PdSn_2 phase. The as prepared x-ray diffraction profile of one of these samples appears in Fig. 2. Bragg peaks are identified that correspond to Pd, Sn, and two intermetallics, PdSn_4 and PdSn_2 .

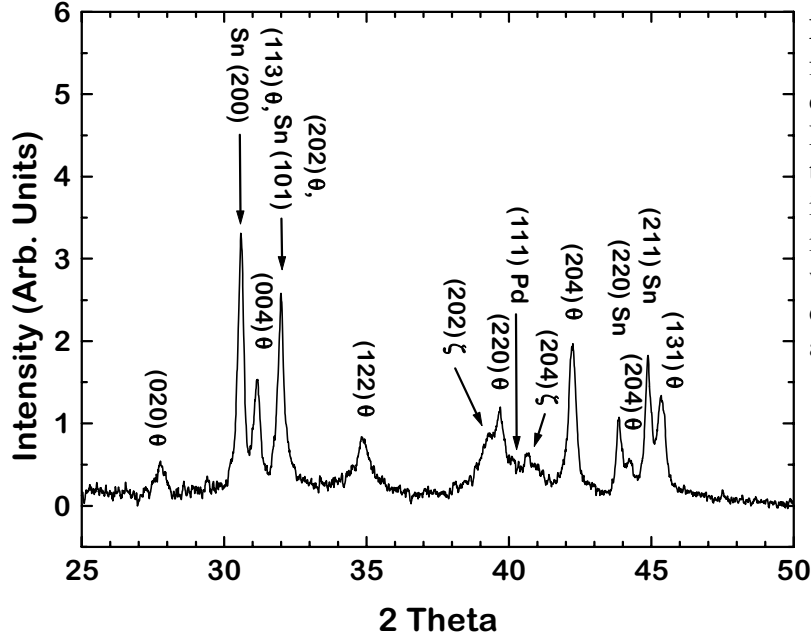


Figure 2- X-ray diffraction profile for an as prepared Pd/Sn diffusion couple of overall stoichiometry PdSn_2 prepared by sputter deposition. Peaks are labeled with Miller indices corresponding to the phases identified. Two intermetallic phases were present in the as prepared diffusion couple: PdSn_4 (labeled θ) and PdSn_2 (labeled ζ).

Samples were annealed at room temperature until it became apparent from x-ray diffraction data that PdSn_2 was growing at the expense of PdSn_4 . At this point, samples were heated in a differential scanning calorimeter. Figure 3 is a plot of heat flow versus time for a sample that was heated to 380K, annealed there for 20 minutes and then heated to 560K. By heating the sample in this manner, we could obtain reaction constants at the middle isotherm temperature, and still observe a complete reaction of the diffusion couple. Integration of the scan shown in Fig. 3 for times between 4 and 44 minutes yields a heat of reaction of -19.6 kJ/mol. This value may be compared with a calculation for ΔH_r made from literature values of elemental heats of formation [12-13]. This calculation, for the reaction $\frac{1}{2}(\text{Pd} + \text{PdSn}_4) \rightarrow \text{PdSn}_2$, resulted in $\Delta H_r = -20.8 \pm 0.2$ kJ/mol. A total of seven DSC runs were performed and values of ΔH_r calculated for each run were between -11.7 and -19.6 kJ/mol. The difference between the heat of reaction obtained for an individual DSC run and the literature value was taken to be a quantity representing the amount of pre-existing PdSn_2 in our diffusion couples. Thus, this heat difference could be added to the integrated heat flow, H , to correct for the initial growth layer of PdSn_2 .

With this correction made, values of the reaction constant were calculated for the growth of PdSn₂. It was found that the logarithm of these values of k^2 varied linearly with inverse temperature, consistent with thermally activated, Arrhenius growth:

$$k^2 = k_o \exp(-E_a/k_b T) \quad (5)$$

where k_b is Boltzmann's constant, k_o is the pre-exponential factor and E_a is the activation energy. Figure 4 is a plot of the logarithm of k^2 versus inverse temperature times one thousand. The straight line in Fig. 4 is a fit which resulted in a value of $E_a = 0.74$ eV for the activation energy. This value is quite similar to the activation energy obtained for diffusion in the PdSn₄ alloy, $E_a = 0.77$ eV [11].

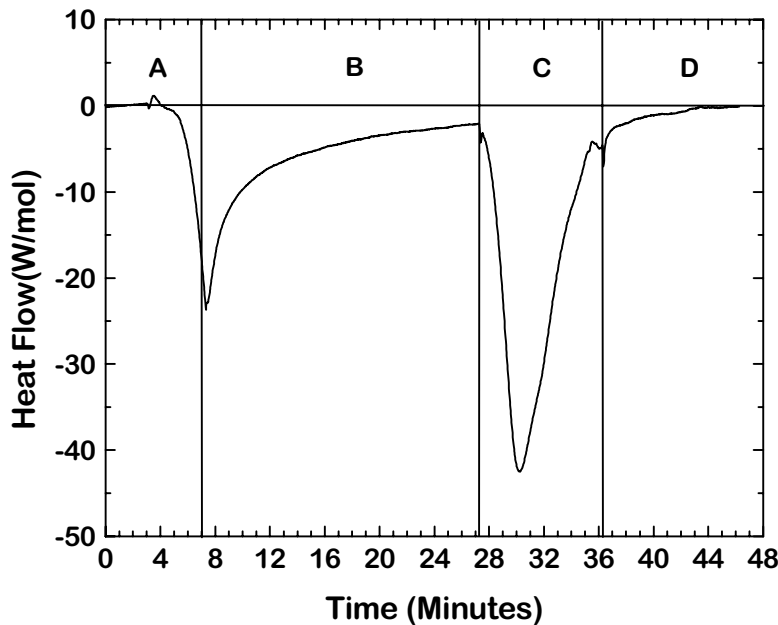
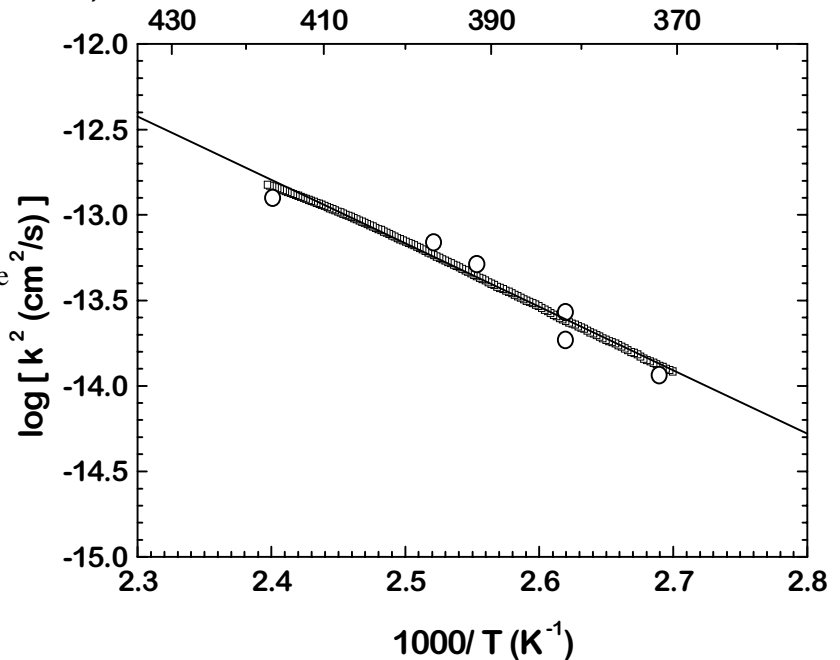


Figure 3- A plot of heat flow versus time for a Pd/Sn multilayer prepared by sputter deposition. The sample was prepared with 40 nm Pd layers and 146 nm Sn layers. This differential scanning calorimetry scan consists of (A) an initial isotherm and heating at 20K/min to 380K, (B) a twenty minute isotherm at 380K, (C) heating at 20K/min to 560K, and (D) a fifteen minute final isotherm at 560K

Figure 4- A plot of the logarithm of the reaction constant, k^2 , versus inverse temperature times one thousand. These are values of k^2 determined by differential scanning calorimetry (O-from isotherm data and overlapping -constant heating rate data) for the reaction $\frac{1}{2} (\text{Pd} + \text{PdSn}_4) \rightarrow \text{PdSn}_2$. The straight line fit shown here resulted in an activation energy of $E_a = 0.74$ eV.



The form of k^2 found for the growth of the two intermetallic phases, PdSn₄ and PdSn₂, may be used to calculate an averaged interdiffusion coefficient. Assuming equilibrium concentrations in our diffusion

couples [14], Eq. 4 and 5 may be used to obtain:

$$\tilde{D} = D_o \exp(-E_a/k_b T) \quad (6)$$

with $D_o = 1.4 \text{ cm}^2/\text{s}$ and $E_a = 0.77 \text{ eV}$ for **PdSn₄** and $D_o = 2.8 \times 10^{-4} \text{ cm}^2/\text{s}$ and $E_a = 0.74 \text{ eV}$ for **PdSn₂**. These forms of the averaged interdiffusion coefficients are plotted in an Arrhenius fashion in Fig. 5. of Pd in pure Sn. It would be most interesting to compare averaged interdiffusion coefficients for the alloys in this system with a solute diffusion coefficient for Pd in Sn. This is a quantity that, to our knowledge, has never been measured. However, using a semi-empirical relation found in the literature [15], an estimate for the solute diffusion coefficient along the (100) axis of Sn was made for 303K (c.f. Fig. 5). A hierarchy of diffusion in this system is indicated, with diffusion in the most Sn rich phase being the fastest of those measured and closest to that of the interstitial diffusion of Pd in pure Sn.

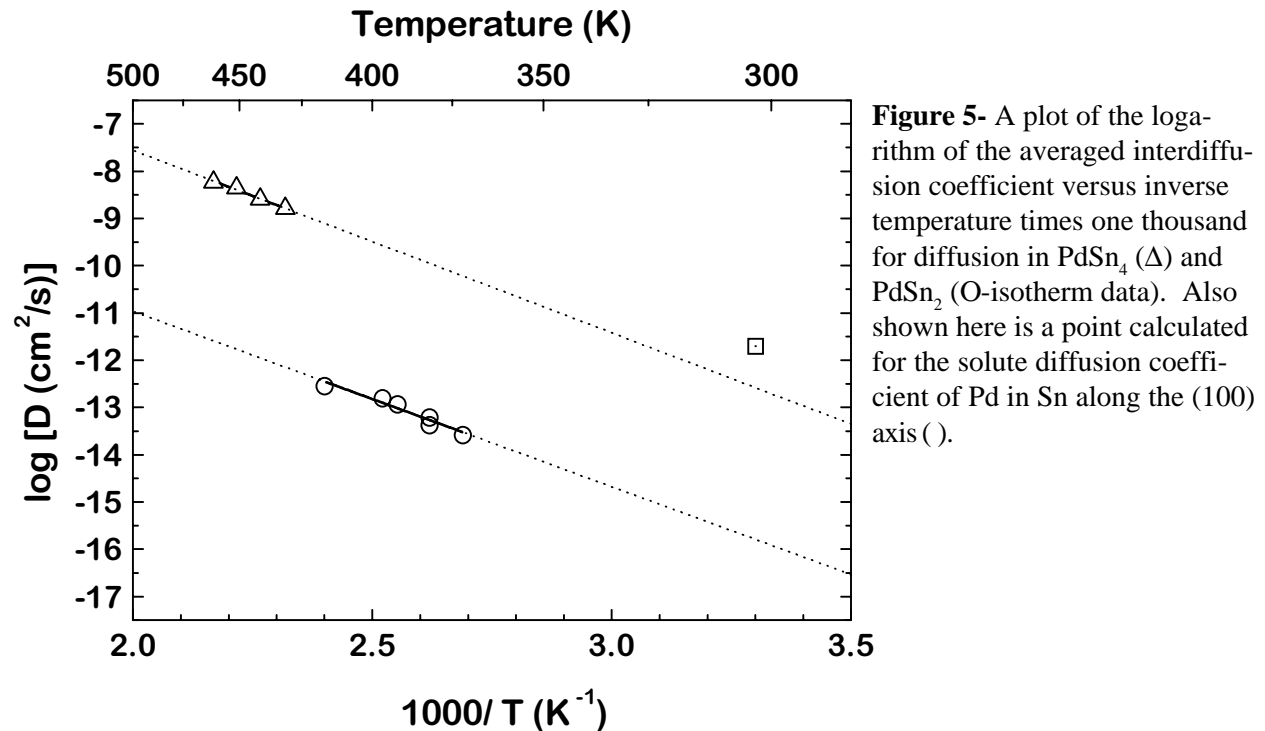


Figure 5- A plot of the logarithm of the averaged interdiffusion coefficient versus inverse temperature times one thousand for diffusion in PdSn₄ (Δ) and PdSn₂ (O-isotherm data). Also shown here is a point calculated for the solute diffusion coefficient of Pd in Sn along the (100) axis (□).

Cu-Sn System

The Cu-Sn system is one in which interstitial diffusion has been observed [16]. Also, this is a well studied system in terms of the reaction of Cu with both pure Sn [17-19] and Sn-Pb solder [20-21]. We have estimated an averaged interdiffusion coefficient for the Cu₃Sn intermetallic from our measurements of reaction constants [17]. Figure 6 is a plot of the logarithm of these measurements for the averaged interdiffusion coefficient, and the solute diffusion coefficient of Cu in Sn in the (100) direction [16] versus inverse temperature. It is evident from Fig. 5 that in this Cu-rich phase of Cu₃Sn the averaged interdiffusion coefficient is much smaller than the solute diffusion coefficient and most likely not representative of the rapid, interstitial mechanism of Cu in pure Sn.

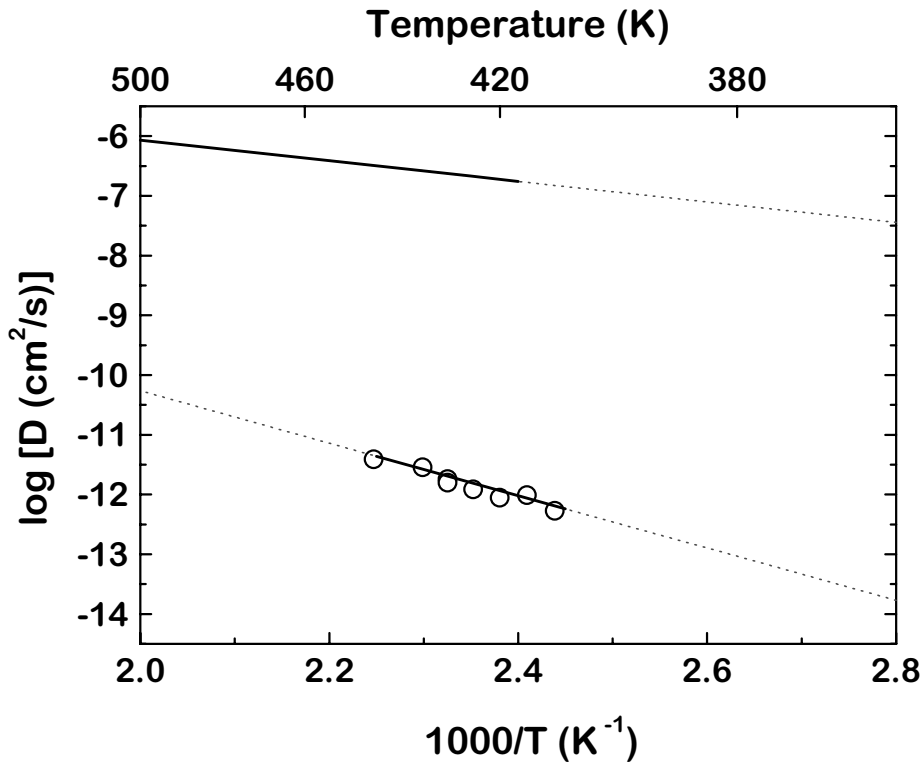


Figure 6- A plot of the logarithm of the diffusion coefficient versus inverse temperature for: (O) the averaged interdiffusion coefficient for Cu_3Sn [17], and the solute diffusion coefficient of Cu in Sn (100 axis) [16]. The solid dark lines indicate the temperature regions where the respective diffusion coefficients were measured.

CONCLUSIONS

From measurements made by differential scanning calorimetry, diffusion in two phases of the Pd-Sn system (PdSn_4 and PdSn_2) and one phase of the Cu-Sn system (Cu_3Sn) has been investigated. Averaged interdiffusion coefficients for all three intermetallics have been calculated, where equilibrium concentrations in the diffusion couples are assumed. There is a hierarchy within the Pd-Sn system, where diffusion is fastest in the most Sn-rich intermetallic. Also, the similar activation energies for diffusion in these Sn-rich Pd-Sn alloys indicates that the basic diffusion mechanism in PdSn_4 and PdSn_2 may be similar. Comparisons within each system, including consideration of the solute diffusion coefficients in pure Sn, provide evidence that in Sn rich phases (e.g. PdSn_4) the interstitial diffusion of metal atoms is the dominant reaction mechanism. On the other hand, the diffusion coefficient for the Cu-rich phase Cu_3Sn was found to be five orders of magnitude smaller than the solute diffusion coefficient for Cu in pure Sn.

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