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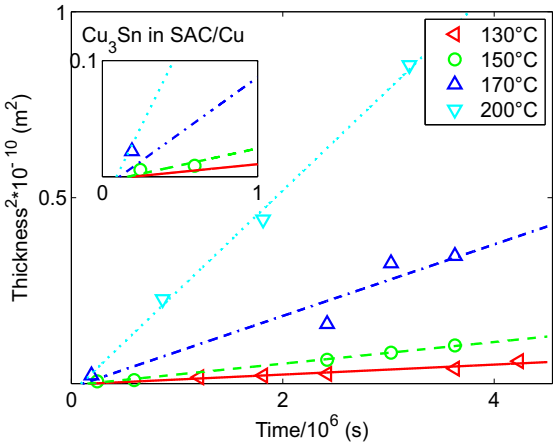

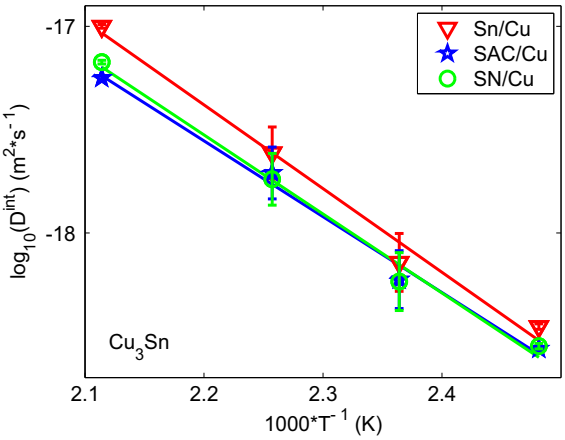

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Investigation of the diffusion behavior in Sn-xAg-yCu/Cu solid state diffusion couples

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Abstract:

The interfacial reactions and growth behavior of the Cu_3Sn and Cu_6Sn_5 phases in Sn-3.0%Ag-0.5%Cu/Cu and Sn-3.5%Ag-0.7%Cu/Cu diffusion couples were investigated at 130°C, 150°C, 170°C and 200°C and compared with those in binary Sn/Cu diffusion couples using identical experimental conditions. The Ag solubility in the Cu_3Sn and Cu_6Sn_5 phases was found to be quite small. The parabolic growth constants of Cu_3Sn and Cu_6Sn_5 in Sn-xAg-yCu/Cu diffusion couples were calculated. A transient stage for the growth of Cu_3Sn was observed. A pseudo-binary method was proposed and performed to obtain the integrated interdiffusion coefficients and activation energies for diffusion of the intermetallics with limited solubility in one of the elements. The growth of Cu_3Sn in Sn-xAg-yCu/Cu diffusion couples was found to be a little slower than that in binary Sn/Cu diffusion couples. The growth rate of the Cu_6Sn_5 phase in ternary Sn-xAg-yCu/Cu diffusion couples is quite close to

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that in Sn/Cu diffusion couples. The Cu addition in the Sn-based end-member is expected to favor the growth of Cu_6Sn_5 providing instantly available Cu atoms for the formation of Cu_6Sn_5. The Ag addition is suggested to slightly decrease the thermodynamic activity of Sn and further decrease the diffusion of Sn. These interpretations were confirmed by a study of the diffusion behavior in Sn-3.5%Ag/Cu and Sn-1.0%Cu/Cu diffusion couples. The calculated activation energy for interdiffusion in the Cu_3Sn and Cu_6Sn_5 phases in Sn-xAg-yCu/Cu diffusion couples are quite close to those obtained for binary Cu/Sn couples. The obtained conclusions are informative for the Ag-Cu-Sn solder design.

Keywords: intermetallics; Ag-Cu-Sn system; solid state reactions; diffusion.

1 Introduction

Sn-Ag-Cu based alloys are one of the most promising lead-free candidate solders for various applications [1–6]. Many Sn-xAg-yCu solders are already recommended and commercially available, such as Sn-3.0%Ag-0.5%Cu (SAC, JEITA recommended), Sn-3.5%Ag-0.7%Cu (SN96C, iNEMI recommended), Sn-3.8%Ag-0.7%Cu (SN96C, IDEALS recommend), Sn-3.5%Ag (SN96.5, eutectic point of Sn-Ag), Sn-0.7%Cu (Sn99Cu1, US MEMI recommend). The thermo-mechanical properties of solder joints are critical to the design and development of reliable electronic circuit board assemblies. Hence, understanding the microstructure evolution of lead-free soldered assemblies during service time is essential to predict their properties and reliability.

Cu_3Sn and Cu_6Sn_5 are the commonly formed intermetallic compounds (IMCs) between the joined Sn-xAg-yCu alloy and Cu substrate [4–17]. Ag_3Sn only precipitates in the Sn-based end-member and is not involved in the interfacial reactions [5–7,17]. No thermodynamic data on the Ag solubility in Cu_3Sn and Cu_6Sn_5 have been provided in literature, since the solubility of Ag in Cu_3Sn and Cu_6Sn_5 is too small to be measured accurately [18]. The growth rates of the IMCs have been measured experimentally in different types of Sn-xAg-yCu/Cu joints [4,8,10–16] and the values of growth rates obtained in different works are quite scattered. The activation energy for diffusion through the IMCs were estimated in some works [10,14,17], however based on the (incorrect) presumption that the interdiffusion coefficients can be assumed to be equal to the parabolic growth constants. Different, sometimes contradicting, IMCs' growth mechanisms were suggested in previous works. A slower growth of the IMCs in the ternary Sn-xCu-yAg/Cu couples than in the binary Sn/Cu couples has been observed in [6,17,19]. Yang et al [17] attributed the slower growth to the fact that most of the Ag atoms have to diffuse away from the IMC layers, since the solubility of Ag is quite low in the IMC layers. Laurila et al [6,7] suggested that the presence of Ag slightly decreases the activities of the reacting species Sn and thus reduces the driving force for the diffusion of Sn through the Cu_6Sn_5 layer. However, a faster growth of Cu_3Sn in the ternary Sn-xCu-yAg/Cu couples was also observed in some works [12,14]. Lu et al. [20] suggested that the growth of the IMCs in Sn-xCu-yAg/Cu couples can also be faster since the Cu and Ag dissolved in Sn solder may provide more nucleation sites, which make the final effects very complex.

Therefore, the interfacial reactions and growth behavior of IMCs formed in Sn-xAg-yCu/Cu diffusion couples still need more investigation, as a good understanding of their growth behavior is quite important for solder and processing design.

However, diffusion experiments are quite sensitive to material and environmental conditions, like small temperature fluctuations, fine structure of the materials and purity of the

starting metals. The results from different studies are therefore always scattered. To reduce the effects from environmental noise as much as possible, in this work, we prepared Sn-xAg-yCu/Cu diffusion couples and the reference Cu/Sn diffusion couples at the same time, using the same starting metals, and annealed them in the same furnace at the same time to assure the most identical experimental conditions. Two popular Sn-xAg-yCu alloys, namely Sn-3.0%Ag-0.5%Cu and Sn-3.5%Ag-0.7%Cu were selected. Furthermore, the temperature dependence of the diffusion coefficients and activation energy for diffusion cannot be derived from the growth constants [21] and the calculation of the diffusion coefficients for ternary systems is very complicated from a practical point of view, as described in section 3.3. Therefore, in this work, a pseudo-binary method to calculate the interdiffusion coefficients of the IMCs for the special case of a ternary system with IMCs with low solubility in one of the 3 elements is proposed and performed. As shown in this paper, the activation energy for diffusion in the ternary IMCs can then be derived from these diffusion coefficients.

2 Experimental method

Sn (99.9999 wt%) and Cu (99.999 wt%) bars and Ag (99.999%) wires, purchased from ChemPur company, were used as starting materials.

Alloys with compositions Sn-3.0%Ag-0.5%Cu (SAC), Sn-3.5%Ag-0.7%Cu (SN), Sn-1.0%Cu and Sn-3.5%Ag (weight fractions) were synthesized using induction melting. Weighted raw materials were sealed in argon-filled quartz ampoules. Then the quartz ampoules were put in the induction furnace and repeatedly heated to around 1000°C for 1 minute for three times, using an installed far-infrared radiation thermostatic device for controlling the temperature. The composition of the synthesized alloys were analyzed after preparation by chemical analysis using ICP - OES (Inductively Coupled Plasma optical emission spectrometry) analysis method and it was found that the deviation between the intended compositions and the actual composition after alloy preparation was less than 0.5 %.

Cu plates with dimensions of 2*7*5 mm were cut from the raw materials. These plates were polished and cleaned with ethanol in an ultrasonic bath to obtain flat and clean surfaces.

Cu/Sn, Sn-3.0%Ag-0.5%Cu/Cu and Sn-3.5%Ag-0.7%Cu/Cu diffusion couples were assembled by cold pressing of one Cu plate and one Sn or alloy plate together using a hydraulic pressing machine.

These diffusion couples were sealed in argon-filled quartz ampoules and subsequently annealed at 130°C, 150°C, 170°C and 200°C, separately, for a series of times. The same furnace was used for all temperatures. The temperatures were calibrated and controlled with an error range of ±2°C using a K-type thermocouple.

To separately show the effects of addition of Cu and Ag in the Sn-based end-member, Sn-1.0%Cu/Cu and Sn-3.5%Ag/Cu diffusion couples were prepared using the same way and annealed at selected temperatures for a series of periods.

After the annealing heat-treatment, the diffusion couples together with the quartz ampoules were quenched in water. The diffusion couples were taken out of the quartz ampoules and cold-mounted in Epofix resin. The interfaces of the diffusion couples were kept perpendicular to the resin surface with clippers. Mounted samples were grinded, polished and ultrasonically cleaned using standard metallographic techniques.

PHILIPS XL30 FEG Scanning electron microscope (SEM) was used to analyse the phase structure and morphology in the diffusion zones. The composition of the phases in the diffusion layers were analyzed using JXA-8530F field emission electron probe micro-analyzer (EPMA) with wavelength dispersive spectroscopy (WDS) mode. Pure Cu and Sn, remained in the region far away from the interface in the diffusion couples, were employed as the standard materials to calibrate the EPMA results. The quantitative line-scanning module

with step size of 0.25, 0.5 and 1 μm was utilized to obtain the concentration profiles of Cu, Sn and Ag in the diffusion zone.

3 Results and discussion

3.1 Microstructures of interface zones in SN/Cu and SAC/Cu couples

Typical backscattered electron (BSE) images of the diffusion zone formed in SN/Cu and SAC/Cu couples are shown in Fig. 1. Some Ag_3Sn and Cu_6Sn_5 precipitates are distributed in the Sn-based end-member. Cu_3Sn and Cu_6Sn_5 phase layers are formed in the diffusion zone between Sn-xAg-yCu and Cu substrate. Some Ag_3Sn particles are scattered near the interface between the Cu_6Sn_5 layer and the Sn-matrix. A small quantity of Ag_3Sn particles is entrapped in the Cu_6Sn_5 phase layer. The phase boundaries between Cu_3Sn and Cu_6Sn_5 and between Cu_6Sn_5 and the Sn-matrix are wavy, as is also observed in binary Cu/Sn diffusion couples.

It has been suggested in literature that impurities in the Sn-solder cause this scallop-type of Cu_6Sn_5 phase layer [22]. However, Yang et al [17] observed that with the addition of Ag to the solder, the morphology of Cu_6Sn_5 tends to become more planar. In our work, we did not observe a significant difference in the waviness between the ternary and binary couples. A clear effect from the addition of Ag to the Sn-based end-member on the morphology and structure of the diffusion zone is not present.

Fig. 2 shows a typical composition profile measured in the diffusion zone in SN/Cu and SAC/Cu couples. The measured boundary compositions of each phase are listed in Tab. 1.

The EPMA analysis data show that the solubilities of Ag in fcc(Cu), Cu_3Sn, Cu_6Sn_5 and bct(Sn) are quite small, actually much smaller than the systematic error range of 0.5% of EPMA analysis. Basically we can conclude that the solubility of Ag in Cu_3Sn and Cu_6Sn_5 is

below 0.5%. There is no report in literature discussing the solubility of Ag in Cu_3Sn and Cu_6Sn_5.

Unlike reported in literature from previous studies [10,12,23], no obvious Kirkendall voids were observed in the interface between fcc(Cu) and Cu_3Sn or in the Cu_3Sn phase layer. Laurila [6] concluded that the formation of Kirkendall voids strongly depends on the purity of the Cu substrate used in the experiments. Our experimental results are consistent with this conclusion since no Kirkendall voids were observed in the diffusion couples with high purity (99.999%) Cu substrate employed in this work. Moreover, we found that the alloying element Ag present in the Sn-based end-member has no effect on the formation of voids.

As the diffusion behavior of Cu and Sn in Sn-xCu-yAg/Cu diffusion couples appears to be quite similar to that in binary Sn/Cu diffusion couples and the intrinsic diffusion coefficients of Cu and Sn were shown to be different in Sn/Cu diffusion couples [24], it is expected that the intrinsic diffusion coefficients of Cu and Sn in Sn-xCu-yAg/Cu diffusion couples are different too. In principle, Kirkendall voids are therefore expected to exist in the formed interdiffusion layer. It has been suggested that the voids can be annihilated by the atom arrangements during the formation and growth of the IMCs, as described in our previous paper [24]. This mechanism can also explain why we did not observe voids in the ternary Sn-xCu-yAg/Cu diffusion couples.

3.2 Determination of the parabolic growth constants of the Cu_3Sn and Cu_6Sn_5 phase layers in Sn-xCu-yAg/Cu diffusion couples

At steady-state diffusion controlled growth, the thickness of each phase layer has a relation with time, as shown in equation (1) [24,25],

$$k^{(j)} = \left[\frac{(\Delta x^{(j)})^2}{2(t - t_0)}\right] \quad (1)$$

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where j denotes the corresponding phase, $\Delta x^{(j)}$ is the thickness of phase layer j in the diffusion zone after annealing for a time t. $k^{(j)}$ is the parabolic growth constant of formation of phase j.

Because of the wavy boundaries of the IMC phase layers, the average thickness of the phase layer was used to derive the parabolic growth constants of Cu_3Sn and Cu_6Sn_5 in Sn-xCu-yAg/Cu couples. Firstly, the area of each phase layer was obtained from the 2D BSE images of the microstructures using a digitization based on the grayscale values. Then, the thickness of the IMC layer was calculated using the measured area of the IMC layer divided by the cross length of the diffusion zone. For each sample, several BSE images at different locations in the sample were analyzed. The average value of the thickness of each IMC layer was used to be $\Delta x^{(j)}$ in equation (1).

As shown in Fig.3, for both the Cu_3Sn and Cu_6Sn_5 phases, the square of the layer thickness shows a linear relationship with time. To determine the growth constants for the Cu_3Sn and Cu_6Sn_5 phase, a linear interpolation of the data based on equation (1) was performed. The resulting parabolic growth constants for the 2 IMC phases are listed in Tab. 2 and plotted in Fig. 3 and Fig. 4. Literature data from previous measurements of the growth rate coefficient are added for comparison. Since the empirical equation, $\Delta x^{(j)} = kt^{1/2}$ is commonly employed in experimental literature, the literature data were squared and divided by 2 when listed in Tab. 2 to allow for comparison with the current data obtained based on equation (1). Similar as for the binary Cu/Sn couples [24], an initial reaction-controlled transient stage was found for the growth behavior of Cu_3Sn formed at the interface in Sn-xAg-yCu/Cu diffusion couples. Such a reaction-controlled growth stage of Cu_3Sn was also observed at the early stage for Sn-3.5Ag/Cu joints by Abdelhadi et al [11]. The growth data for the IMCs formed in Sn-1.0%Cu/Cu and Sn-3.5%Ag/Cu diffusion couples are also listed in Tab. 2 for comparison and will be discussed further in section 3.4.

3.3 Determination of the integrated diffusion coefficients of Cu_3Sn and Cu_6Sn_5 in Sn-xCu-yAg/Cu diffusion couples using a pseudo-binary method

As it is noted in [21,26], $k^{(j)}$ does not have an Arrhenius temperature dependence, and is a function, not only of the phase (j) itself, but also of its neighboring phases. A true physical activation energy for diffusion should be a property of only the investigated phase itself, and should thus be derived from the diffusion coefficients of the different phases.

However, to obtain the four diffusion coefficients as shown in equation (5) for a ternary system, two diffusion couples with intersection of the composition profiles on the interested point are needed [27,28], which is actually quite difficult to be designed in experiments. Firstly the intersection point has to be in the interested phase. Secondly, only one point can be obtained from two diffusion couples and thus a massive amount of experiments will be needed to characterize the diffusion properties of one phase in a ternary system. Furthermore, due to the narrow homogeneity range of the IMCs formed in the diffusion zone in the considered couples, it is hard to really fix the intersection point. As shown in Fig. 5, for the special case studied in this work, the diffusion paths for the different Sn-xAg-yCu/Cu couples and the binary Cu/Sn couples are almost the same along the Cu_3Sn and Cu_6Sn_5 segments. Therefore, from a practical point of view, the diffusion coefficients of Cu_3Sn and Cu_6Sn_5 in ternary Ag-Cu-Sn systems cannot be derived experimentally using the standard method since, practically, it is not possible to obtain the different $\partial C_i/\partial x$.

Paul developed a pseudo-binary method for multi-component joints for the case that only two of the elements diffuse and the composition of the other elements is the same in both end members and constant throughout the diffusion couple [29,30]. In our case, the concentration of Ag is, however, not the same in the two end-members and, since the difference is 3.5at% , it cannot be ignored. Moreover, the Ag concentration in the diffusion layer is extremely (negligibly) small. Hence we suggest another pseudo binary method based on the small

solubility of the third element in the diffusion layer to deal efficiently with the diffusion couples considered in this work.

According to the equation derived by Dayananda [31], the interdiffusion fluxes of all components can be determined directly from their concentration profiles using the following equation:

$$J_i = \frac{1}{2t} \int_{C_i^- \text{ or } C_i^+}^{C_i(x)} (x - x_0)\, dC_i \qquad (2)$$

where J_i is the flux of the corresponding component i at position x, t is the diffusion time, C_i^- and C_i^+ are the terminal concentrations, and x_0 refers to the location of the Matano plane.

In this case, it is practically impossible to determine the Matano plane if the volume change is considered. Hence, we did not derive the real position of the Matano plane and this information is also not needed in our following analysis. However, to facilitate the error approximation, we initially assumed a location of the Matano plane and neglected the volume change. According to the literature on Cu-Sn diffusion couples [32], the Matano plane is typically located in the Cu_6Sn_5 phase layer. Since the morphology of the diffusion layer in the Sn-xAg-yCu/Cu diffusion couples is quite similar to that in Sn/Cu diffusion couple, we assumed that the Matano plane is located in the Cu_6Sn_5 phase layer as well in Sn-xAg-yCu/Cu diffusion couples for the following explanation, which aims to illustrate the advantages and accuracy of the proposed pseudo-binary method. It will be shown, that, in fact, the position of the Matano plane does not play a role.

Let's choose a point x_* on the right side of the Matano plane in the Cu_6Sn_5 phase layer, as shown in Fig. 6.

According to our measurements, the concentrations of Ag, Cu and Sn in the Cu_3Sn and Cu_6Sn_5 phase layers can be assumed as constants. As an upper bound, we assume a maximum concentration of Ag of 1 at% in the two IMCs.

Then we can calculate the fluxes of Ag and Sn at the point x_* according to equation (2), giving equations (3) and (4):

$$J_{Ag} = \frac{1}{2t} \int_{C_{Ag}^{+}}^{C_{Ag}(x_*)} (x - x_0)\, dC_{Ag} \approx \frac{1}{2t}(x_* - x_+)C_{Ag} \qquad \textbf{(3)}$$

$$J_{Sn} = \frac{1}{2t} \int_{C_{Sn}^{+}}^{C_{Sn}(x_*)} (x - x_0)\, dC_{Sn} \approx \frac{1}{2t}(x_* - x_+)C_{Sn} \qquad \textbf{(4)}$$

According to the concentrations in the related diffusion layer, we have $\frac{J_{Ag}}{J_{Sn}} = \frac{C_{Ag}}{C_{Sn}} = \frac{0.01}{0.455} < 5\%$. In the same way, we also have $\frac{J_{Ag}}{J_{Cu}} = \frac{C_{Ag}}{C_{Cu}} = \frac{0.01}{0.545} < 5\%$, and we can make a similar derivation for the ratio of the fluxes in a point on the left side of the Matano plane according to the ratio of concentrations of elements in the Cu_3Sn phase (hence the position of the Matano plane will not affect our conclusion on the accuracy of the method).

This analysis shows that in both the Cu_3Sn and Cu_6Sn_5 phases, the flux of Ag will not exceed 5% of the flux of Cu or the flux of Sn. Since this 5% is of the similar order as the experimental error, it is therefore acceptable to neglect the flux of Ag and treat this system as a pseudo binary system. Then, the related diffusion parameters can be derived using the same analysis techniques as for binary diffusion couples and a meaningful comparison of the diffusion in the binary and ternary systems can be conducted with good accuracy.

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Alternatively, since the concentration of Ag in the diffusion layer is quite small, big errors would probably be obtained when calculating the gradient of the concentration of Ag. Hence, we suggest that the method proposed by Dayananda [31] should not be directly applied in this case. Therefore, we propose here a pseudo binary method derived as given below.

In a ternary diffusion system,

$$J_i = -(D_{i1}\frac{\partial C_1}{\partial x} + D_{i2}\frac{\partial C_2}{\partial x}) \quad (5)$$

where subscripts $i = 1, 2\ or\ 3$, denote the composed components, D denotes the interdiffusion coefficients and C_i denotes the concentration of the corresponding component i.

If the solubility of component 3 in the investigated phase is quite small and the variation of concentration of component 3 along the diffusion layer is also small, the gradients of component 1 and component 2 are almost equal to each other in absolute value, but opposite. We thus have

$$\frac{\partial C_1}{\partial x} \cong -\frac{\partial C_2}{\partial x} \quad (6)$$

Then equation (5) can be simplified to

$$J_1 \cong -(D_{11} - D_{12})\frac{\partial C_1}{\partial x} = D_1'\frac{\partial C_1}{\partial x} = D_1'\frac{\partial C_2}{\partial x} \quad (7)$$

$$J_2 \cong -(D_{21} - D_{22})\frac{\partial C_2}{\partial x} = -D_2'\frac{\partial C_2}{\partial x} \quad (8)$$

where D' also includes the contribution from the third component.

J_1 and J_2 can then be interpreted as an approximation of the fluxes of component 1 and component 2 (which has an error of maximum 5% for the considered systems as we derived above). If the flux of the third element is negligible, similar as definition (9) for binary systems, we can define equation (10) for a pseudo-binary system

$$\widetilde{D} = \frac{V_m(N_2J_1 - N_1J_2)}{\partial N_2/\partial x} = N_2D_1 \ + N_1D_2 \qquad (9)$$

$$\widetilde{D'} = \frac{V_m(N_2J_1 - N_1J_2)}{\partial N_2/\partial x} = N_2D_1' + N_1D_2' \qquad (10)$$

where V_m is the molar volume and N_i is the mole fraction of component i.

Thus $\widetilde{D'}$ in the ternary system can be calculated using the same procedures as for the calculation of the interdiffusion coefficient in a binary system [24]. Further, if the intermetallic compound(s) in a ternary system ha(s)(ve) a narrow homogeneity range, the integrated calculation method for phases with narrow homogeneity range [24,25,33], often applied to binary diffusion couples, can be applied too, in this case, to calculated $\widetilde{D'}^{int}$. This $\widetilde{D'}^{int}$ depends only on the property of the investigated phase. The activation energy for diffusion can be determined from the $\widetilde{D'}^{int}$ values at different temperatures, accordingly. It is shown that the obtained activation energy for diffusion according to this method represents the property of the investigated phase, excluding the effects from other phases.

The detailed method to calculate the interdiffusion coefficient from the concentration profile across the diffusion zone was described in [24].

Here we suggested this pseudo binary method, where the concentrations of the third element in the end members are small and the solubility of the third element in the diffusion layer is negligible. We should note our method is an approximate method since there is always a little solubility of one element in another. If the solution of the third element is quite small, the approximated values can be acceptable and insightful. They facilitate the comparison between the diffusion behavior in binary and ternary diffusion couples.

As we illustrated above, the flux of Ag in these Sn-xAg-yCu/Cu diffusion couples is neglectable and the homogeneity range of Cu_6Sn_5 and Cu_3Sn are quite narrow in Ag-Cu-Sn ternary systems. Hence a defined $\widetilde{D'}^{int}$ and activation energy for diffusion for the Cu_6Sn_5 and

Cu_3Sn phases in Sn-xAg-yCu/Cu diffusion couples can be calculated using the pseudo-binary method described above. The calculated results can then be compared, in a meaningful way, with values of the integrated interdiffusion parameters of the Sn/Cu binary diffusion couple. An instructive comparison of the diffusion in the binary and ternary system can then be conducted. The calculated results are listed in Tab. 3 and Fig. 7 and will be discussed in the next sections.

3.4 Comparison of the IMC growth in ternary Sn-xAg-yCu/Cu couples and binary Sn/Cu couples

As shown in Tab. 2, the obtained parabolic growth constants for the Cu_3Sn and Cu_6Sn_5 phases in diffusion couples from different studies are quite scattered. Hence we focused on the comparison among the SAC/Cu, SN/Cu and Sn/Cu couples analysed in the current study, where we guaranteed the most identical experimental conditions.

It is seen from Fig. 4 that, although the global composition of the initial Sn-based end-member is different in the different couples, the growth behavior of IMCs (Cu_3Sn and Cu_6Sn_5) in SAC/Cu and SN/Cu couples are quite similar. The morphology and phase structure in the diffusion zones of the 2 kinds of couples are identical and the growth rates of the Cu_3Sn and Cu_6Sn_5 phase layers are quite close to each other.

According to the phase diagram of the Ag-Cu-Sn ternary system as well as the SEM analysis on the Sn-based end-member, the solidified structures of SAC alloy and SN alloy (after synthesis and before being adjoined with Cu substrate) are quite similar, where small Cu_6Sn_5 grains and Ag_3Sn grains are distributed in the Sn-based end-member. The only difference is the size and quantity of the Cu_6Sn_5 grains and Ag_3Sn grains in the Sn-based end-member. The composition of the Sn-matrix (Sn primary phase) in solidified SAC alloy and

SN alloy should also be the same according to the phase diagram, which was also confirmed by the EPMA analysis of the composition of the Sn-matrix in this work. Since the diffusion of Cu and Sn in the Sn primary phase are much faster compared to the diffusion of Cu and Sn in the Cu_3Sn and Cu_6Sn_5 phase [34] and Ag atoms were rarely involved in the formation of IMCs, the composition of the Sn-matrix can be treated as constant and saturated during the interfacial reactions between the Sn-matrix and Cu substrate. Therefore, our finding that the growth behavior and growth rates of the IMCs is identical in SAC/Cu and SN/Cu couples is quite reasonable, since the compositions of the Sn-matrices in both couples are the same.

As shown in Tab. 1, the Cu and Sn content of the Cu_3Sn and Cu_6Sn_5 phases in binary Sn/Cu couples and in ternary Sn-xAg-yCu/Cu couples are almost the same and the Ag solubilities in fcc(Cu), Cu_3Sn, Cu_6Sn_5 and bct(Sn) are quite small. It is expected that additions of Ag and Cu in the Sn-based end-member have only very little effect on the growth behavior of Cu_3Sn and Cu_6Sn_5. Our results show this feature. It is observed that the growth rates of Cu_6Sn_5 in SAC/Cu, SN/Cu and Cu/Sn couples are almost equal to each other within the experimental error range. The growths of Cu_3Sn in SAC/Cu and SN/Cu ternary couples are a little slower than those in Cu/Sn binary diffusion couples. Nevertheless, taking the experimental error range in consideration, this difference may not be significant. The activation energies for diffusion through Cu_3Sn and Cu_6Sn_5 do not change much with the addition of Ag and Cu in the Sn-based end-member.

It has been suggested that the Ag flux through the IMC layers generally decreases the growth rates of the Cu_3Sn and Cu_6Sn_5 phases [6,7]. The Cu addition in the Sn-based end-member can be expected to favor the formation of the Cu_6Sn_5 layer since the Cu atoms solved in the Sn-matrix can immediately be involved in the formation of Cu_6Sn_5. The retarding effect due to the Ag addition and the accelerating effect due to the Cu addition on the growth of Cu_6Sn_5 counterweights each other. Hence the growth rate of Cu_6Sn_5 is not obviously affected

by the simultaneous addition of Cu and Ag in the Sn-based end-member, as we observed. However, we found that farther away from the Sn-end, the growth of Cu_3Sn appeared to be slightly slowed down by the presence of Ag. It has been suggested that the presence of a small quantity of Ag in the Sn-based end-member changes the activity of Sn and decreases the driving force for diffusion of Sn [6,7] through the IMC layers. Since the Ag solubility in Cu_3Sn and Cu_6Sn_5 are quite small, the exact influence on the activities of Cu and Sn coming from the Ag solution is hard to be determined quantitatively.

To verify these effects from Cu and Ag separately, two more series of diffusion couples were prepared, where only one component Ag or Cu was added to the Sn-based end-member. The observed growth behavior of the IMCs in Sn-1.0%Cu/Cu and Sn-3.5%Ag/Cu diffusion couples indeed proved these assumed effects of Ag and Cu addition in the Sn-based end-member. As seen in Tab. 2, it is observed that the growth rates of the Cu_3Sn and Cu_6Sn_5 phases in Sn-3.5%Ag/Cu diffusion couples annealed at 170°C and 200°C were a little smaller than those in the Cu/Sn couples, which shows that the Ag addition in the Sn-based end-member slows down the growth of Cu_3Sn and Cu_6Sn_5. Analysis of the Sn-1.0%Cu/Cu diffusion couples showed that the addition of Cu in the Sn-based end-member has no obvious effect on the growth of Cu_3Sn, but slightly favors the growth of Cu_6Sn_5, where the parabolic growth constant of Cu_6Sn_5 was $2.06 \times 10^{-17}\ m^2 \cdot s^{-1}$, which is higher than that in the binary Cu/Sn couple and that in the SAC/Cu and SN/Cu couples. This accelerated growth due to Cu addition can also be seen by comparing the growth of the IMCs in the SAC/Cu, SN/Cu and Sn-3.5%Ag/Cu diffusion couples. Cu_6Sn_5 grows slower in the Sn-3.5%Ag/Cu diffusion couples, where there is no Cu addition to the Sn-based end-member. It should be noted that these effects were found to be quite small and that more delicate experiments are needed for a solid conclusion.

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3.5 The activation energy for diffusion of Cu and Sn in Cu_3Sn and Cu_6Sn_5

Based on the obtained pseudo-binary integrated interdiffusion coefficients for interdiffusion of Cu and Sn in the Cu_3Sn and Cu_6Sn_5 phases formed in Sn-xAg-yCu/Cu diffusion couples, the activation energy for diffusion of these two phases were calculated and listed in Tab. 3. This method excludes the effects of adjacent phases.

As shown in Tab. 3 and Fig. 7, although the integrated interdiffusion coefficients of the Cu_3Sn and Cu_6Sn_5 phases are different for Su/Cu diffusion couples and Sn-xAg-yCu/Cu diffusion couples, the calculated activation energies for diffusion of the IMCs are quite close to each other for the different sets of diffusion couples, considering the experimental error range. This result is reasonable since the growth behavior of these two phases is quite similar in binary Sn/Cu diffusion couples and in ternary Sn-xAg-yCu/Cu diffusion couples. Since the crystal structures and composition ranges of the Cu_3Sn and Cu_6Sn_5 phases remain almost constant within the investigated temperate range in the binary and ternary systems, it can be expected that the temperature dependence of diffusion is very similar.

The values obtained for the activation energy for diffusion in other studies [10,14,17,35] are also listed in Tab. 3 for comparison. In these works [10,14,17], however, the activation energies for diffusion were calculated based on the assumption that the diffusion coefficient of phase is equal to the parabolic growth constant measured for that phase. In this way, they obtained quite different values for the ternary Sn-xAg-yCu/Cu diffusion couples compared to those obtained for the binary Sn/Cu diffusion couples. As clarified in [21,26], these values do, however, not show the real property of the investigated phase.

4 Conclusions

The interfacial reactions and growth behavior of the Cu_3Sn and Cu_6Sn_5 phases in Sn-xAg-yCu/Cu diffusion couples were investigated at several temperatures starting from solid state

bonding. The results are compared with those in binary Cu/Sn couples with the guarantee of the most identical experimental conditions. The Ag solubility in the IMC phases Cu_3Sn and Cu_6Sn_5 formed at the interface is quite small. The parabolic growth constants of the Cu_3Sn and Cu_6Sn_5 phases were calculated. A transient stage for the growth of Cu_3Sn was observed and the growth of Cu_6Sn_5 is observed to be diffusion-controlled from the beginning, as was also found for binary diffusion couples assembled by solid state bonding.

The pseudo-binary integrated interdiffusion coefficients of the Cu_3Sn and Cu_6Sn_5 phases were calculated using a pseudo-binary method and the activation energies for diffusion of the 2 IMC phases were derived based on the values obtained at different temperatures for these pseudo-binary integrated interdiffusion coefficients.

The growth of Cu_3Sn in Sn-xAg-yCu/Cu diffusion couples was observed to be slightly slower than that in Sn/Cu diffusion couples. The growth rate of the Cu_6Sn_5 phase in Sn-xAg-yCu/Cu diffusion couples is similar to that in Sn/Cu diffusion couples. It was verified by a study of the diffusion behavior in Sn-xAg/Cu and Sn-xCu/Cu diffusion couples that these phenomena can be attributed to two combined effects. On the one hand, the Ag addition in the Sn-based end-member slightly slows down the growth of both the Cu_3Sn and Cu_6Sn_5 phases. On the other hand, the Cu addition in the Sn-based end-member favors the growth of Cu_6Sn_5, since more Cu atoms are directly available for the formation of Cu_6Sn_5.

The obtained activation energies for diffusion for the Cu_3Sn and Cu_6Sn_5 phases in ternary Sn-xAg-yCu/Cu diffusion couples have been determined and turn out to be quite similar to those in binary Sn/Cu diffusion couples, considering the experimental error range.

The proposed pseudo-binary method can be applied in other ternary systems where the solubility of one of the third element is limited in the diffusion layer. The obtained conclusions about the diffusion features in Sn-xAg-yCu/Cu diffusion couples are instructive

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for the Ag-Cu-Sn solder design since the composition of Ag-Cu-Sn solder is always in the Sn rich side.

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Captions:

Tables:

Tab. 1 Interface concentrations of the phases present in SN/Cu couples obtained by EPMA analysis.

Tab. 2 The parabolic growth constants of the Cu_3Sn and Cu_6Sn_5 phases in Sn-xAg-yCu/Cu couples.

Tab. 3 The calculated pseudo-binary integrated interdiffusion coefficient $\widetilde{D'^{int}}$ of the Cu_3Sn and Cu_6Sn_5 phases in Sn-xAg-yCu/Cu couples and comparison with the integrated interdiffusion data obtained for the Cu_3Sn and Cu_6Sn_5 phases in Sn/Cu couples.

Figures:

Fig. 1 Typical BES images of the annealed SAC/Cu and SN/Cu diffusion couples.

(a) SAC/Cu couple annealed at 150°C for 672 hours

(b) SN/Cu couple annealed at 170°C for 672 hours

Fig. 2 Composition profile of the diffusion zone in SN/Cu diffusion couple annealed at 150°C for 1008 hours, obtained using EPMA analysis with quantitative line scanning mode.

Fig. 3 Square of the layer thickness as function of time of the Cu_3Sn and Cu_6Sn_5 layers formed in SAC/Cu and SN/Cu diffusion couples at different temperatures.

Fig. 4 The parabolic growth constants obtained for the growth of the Cu_3Sn and Cu_6Sn_5 layers in the SN/Cu and SAC/Cu diffusion couples obtained in this work compared with the data obtained for binary Sn/Cu diffusion couples [24] for which the experimental conditions were identical.

Fig. 5 Schematic picture of the diffusion paths observed in SAC/Cu and SN/Cu diffusion couples. The lines do not represent the real experimental data. However, a common characteristic is that they coincide over the Cu_6Sn_5-Cu_3Sn and Cu_3Sn and Cu segments.

Fig. 6 The scheme of diffusion layers formed in Sn-xAg-yCu/Cu couples, where x_0 shows the location of Matano plane.

Fig. 7 The integrated interdiffusion coefficients for interdiffusion of Cu and Sn in the Cu_3Sn and Cu_6Sn_5 phase layers in SN/Cu and SAC/Cu diffusion couples compared with data obtained from binary Cu/Sn couples.

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Tab. 1 Interface concentrations of the phases present in SN/Cu couples obtained by EPMA analysis

	SN/Cu						
Temp.	Composition (atom percent, Cu remaining)						
(°C)	FCC(Cu)	Cu_3Sn (left)	Cu_3Sn (right)	Cu_6Sn_5 (left)	Cu_6Sn_5 (right)	BCT(Sn)	Ref.
130	0.02 at% Ag 0.2 at% Sn	0.03 at% Ag 24.3 at% Sn	0.02 at% Ag 25.2 at% Sn	0.01 at%Ag 45.1 at% Sn	0.1 at% Ag 47.6 at% Sn	0.2 at% Ag 98.8 at% Sn	
150	0.02 at% Ag 0.2 at% Sn	0.02 at% Ag 24.5 at% Sn	0.03 at% Ag 25.6 at% Sn	0.02 at% Ag 44.5 at% Sn	0.07 at% Ag 47.2 at% Sn	0.02 at% Ag 99.1 at% Sn	This work
170	0.02 at% Ag 0.2 at% Sn	0.00 at% Ag 24.7 at% Sn	0.00 at% Ag 25.9 at% Sn	0.00 at% Ag 44.2 at% Sn	0.00 at% Ag 47.6 at% Sn	0.00 at% Ag 98.8 at% Sn	
200	0.03 at% Ag 0.13 at% Sn	0.02 at% Ag 0.250 at% Sn	0.10 at% Ag 25.5 at% Sn	0.17 at% Ag 45.2 at% Sn	0.23 at% Ag 48.0 at% Sn	0.03 at% Ag 99.2 at% Sn	

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Tab. 2 The parabolic growth constants of the Cu_3Sn and Cu_6Sn_5 phases in Sn-xAg-yCu/Cu couples

Diffusion couples	Temp. (°C)	k_{Cu_3Sn} $(m^2 \cdot s^{-1})$ $\times 10^{-17}$	$k_{Cu_6Sn_5}$ $(m^2 \cdot s^{-1})$ $\times 10^{-17}$	Ref.
Sn-3.0%Ag-0.5%Cu/Cu (99.999%)	130	0.07	0.27	This work
	150	0.15	0.56	
	170	0.48	1.84	
	200	1.36	5.59	
Sn-3.5%Ag-0.7%Cu /Cu(99.999%)	130	0.07	0.26	
	150	0.14	0.62	
	170	0.44	1.82	
	200	1.57	7.24	
Sn-1.0%Cu/Cu(99.999%)	170	0.61	2.06	
Sn-3.5%Ag/Cu(99.999%)	170	0.29	1.10	
	200	1.25	4.10	
Sn(99.9999%)/Cu(99.999%)	130	0.11	0.17	[24]
	150	0.20	0.50	
	170	0.68	1.61	
	200	2.62	8.00	
Sn-0.3%Ag-0.7%Cu/Cu(99.99%)	100		0.05	[10]
	135	0.005	0.02	
	170	0.8	0.8	
Cu/Sn/Cu, film couple Bonding at 250°C for 1 min	120	0.08	0.01	[17]
	150	0.27	0.023	
	180	0.64	0.35	
	200	1.5	1.4	
Cu/Sn-3.5%Ag/Cu, film couple Bonding at 250°C for 1 min	120	0.015	0.010	
	150	0.16	0.061	
	180	0.57	0.52	
	200	0.74	0.95	
CSP and PWM, liquid bonding	100	0.002		[12]
	125	0.033		
	150	0.16		
Sn-3.0%Ag-0.5%Cu/Cu, reflowed at 270°C for 120s	100	0.001	0.01	[14]
	120	0.002	0.03	
	140	0.10	0.09	
	170	0.22	0.22	

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Tab. 3 The calculated pseudo-binary integrated interdiffusion coefficient $\widetilde{D'^{int}}$ of the Cu_3Sn and Cu_6Sn_5 phases in Sn-xAg-yCu/Cu couples and comparison with the integrated interdiffusion data obtained for the Cu_3Sn and Cu_6Sn_5 phases in Sn/Cu couples

Diffusion couples	Temp. (°C)	$\widetilde{D'^{int}_{Cu_3Sn}}$ $(m^2 \cdot s^{-1})$ $\times 10^{-17}$	Q_{Cu_3Sn} (kJ)	$\widetilde{D'^{int}_{Cu_6Sn_5}}$ $(m^2 \cdot s^{-1})$ $\times 10^{-17}$	$Q_{Cu_6Sn_5}$ (kJ)	
SAC/Cu	130	0.03	70.3	0.09	70.6	This work
	150	0.06		0.19		
	170	0.20		0.61		
	200	0.56		1.85		
SN/Cu	130	0.03	73.3	0.09	75.5	This work
	150	0.06		0.02		
	170	0.18		0.60		
	200	0.67		2.36		
Sn/Cu	130	0.03	77.6	0.06	85.4	[24]
	150	0.07		0.18		
	170	0.24		0.57		
	200	1.00		2.75		
Sn-3.8%Ag-0.7%Cu/Cu	170	0.08		0.098		[35]
Sn-0.3%Ag-0.7%Cu/Cu(99.99%)	97-170		119.04		51.59	[10][a]
Sn-3.0%Ag-0.5%Cu/Cu	100-170		114.7		58.6	[14][a]
Cu/Sn/Cu	120-200		59		93	[17][a]
Cu/Sn-3.5%Ag/Cu			84		91	

[a] calculated based on the approximation that the interdiffusion coefficient is equal to the parabolic growth constant

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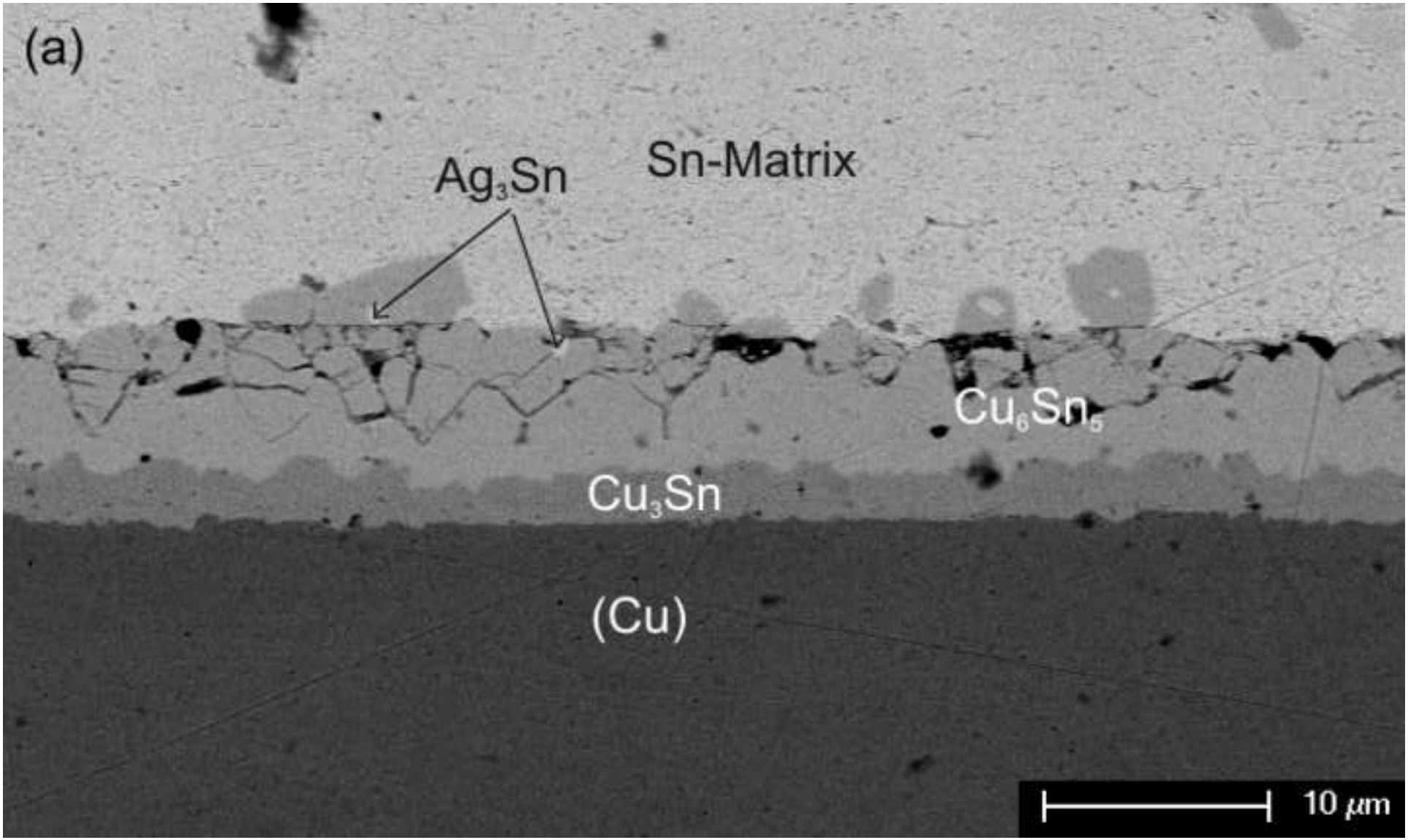
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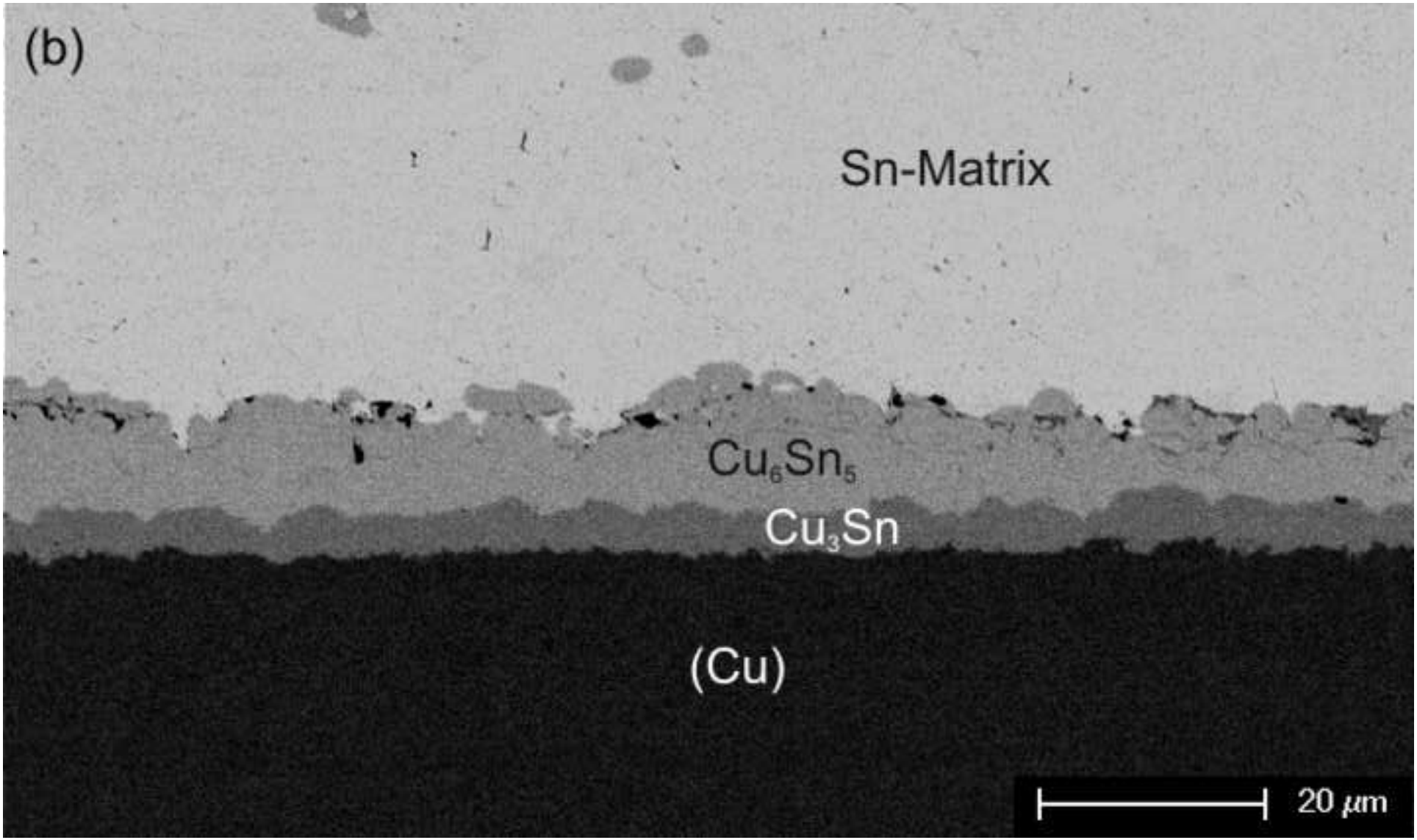
Cu_6Sn_5
Cu_3Sn
(Cu)
10 μm


(b)
Sn-Matrix
Cu_6Sn_5
Cu_3Sn
(Cu)
20 μm

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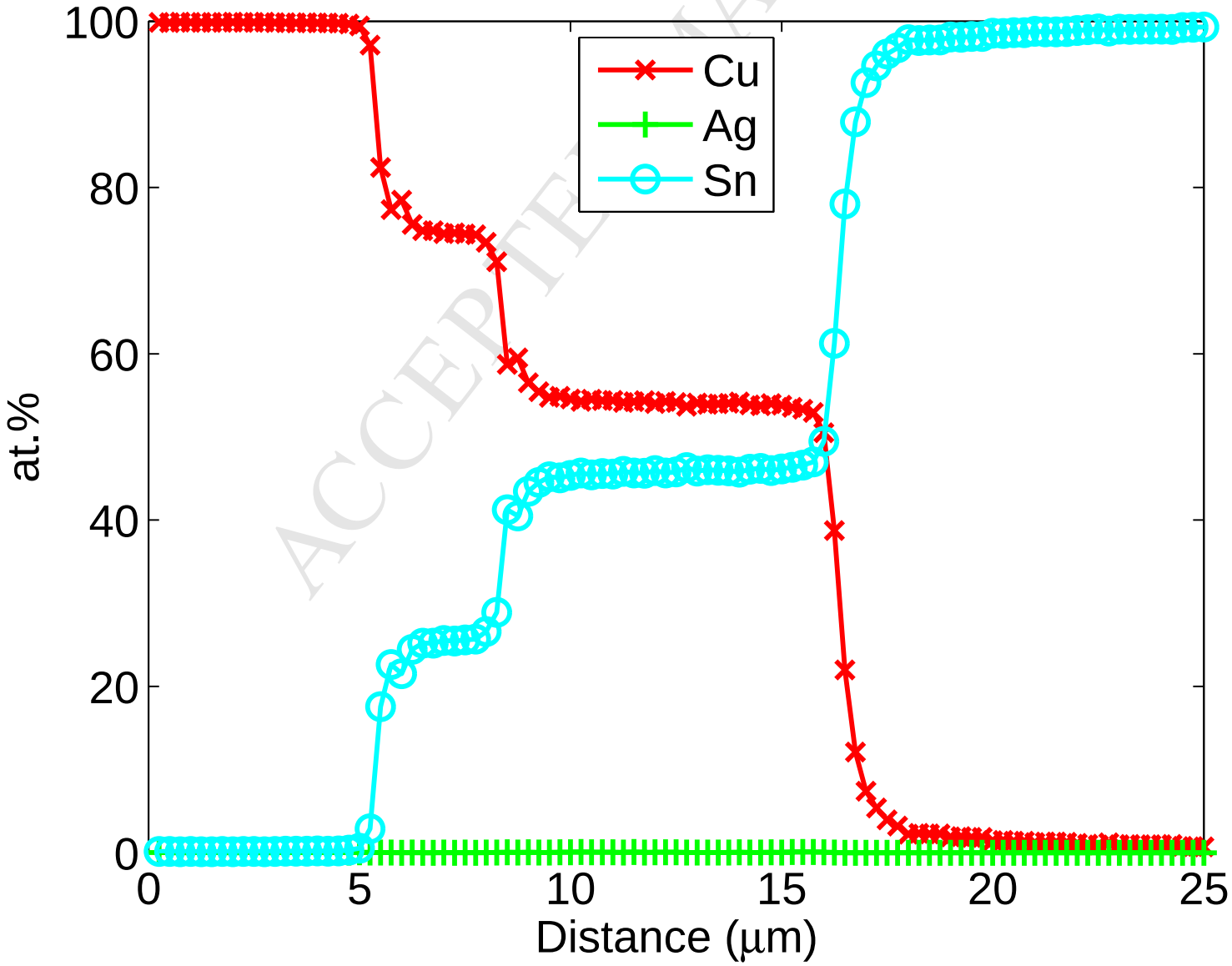

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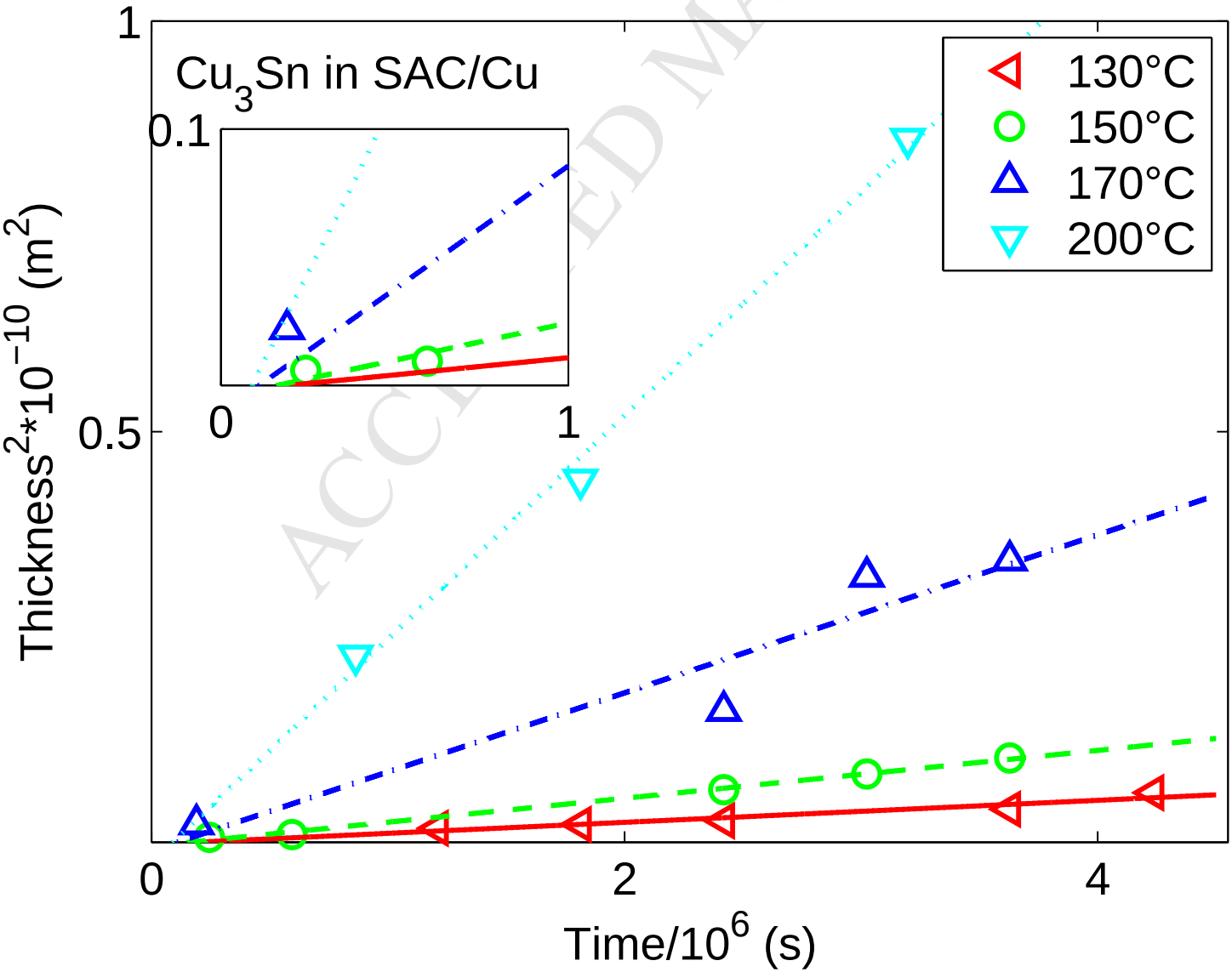

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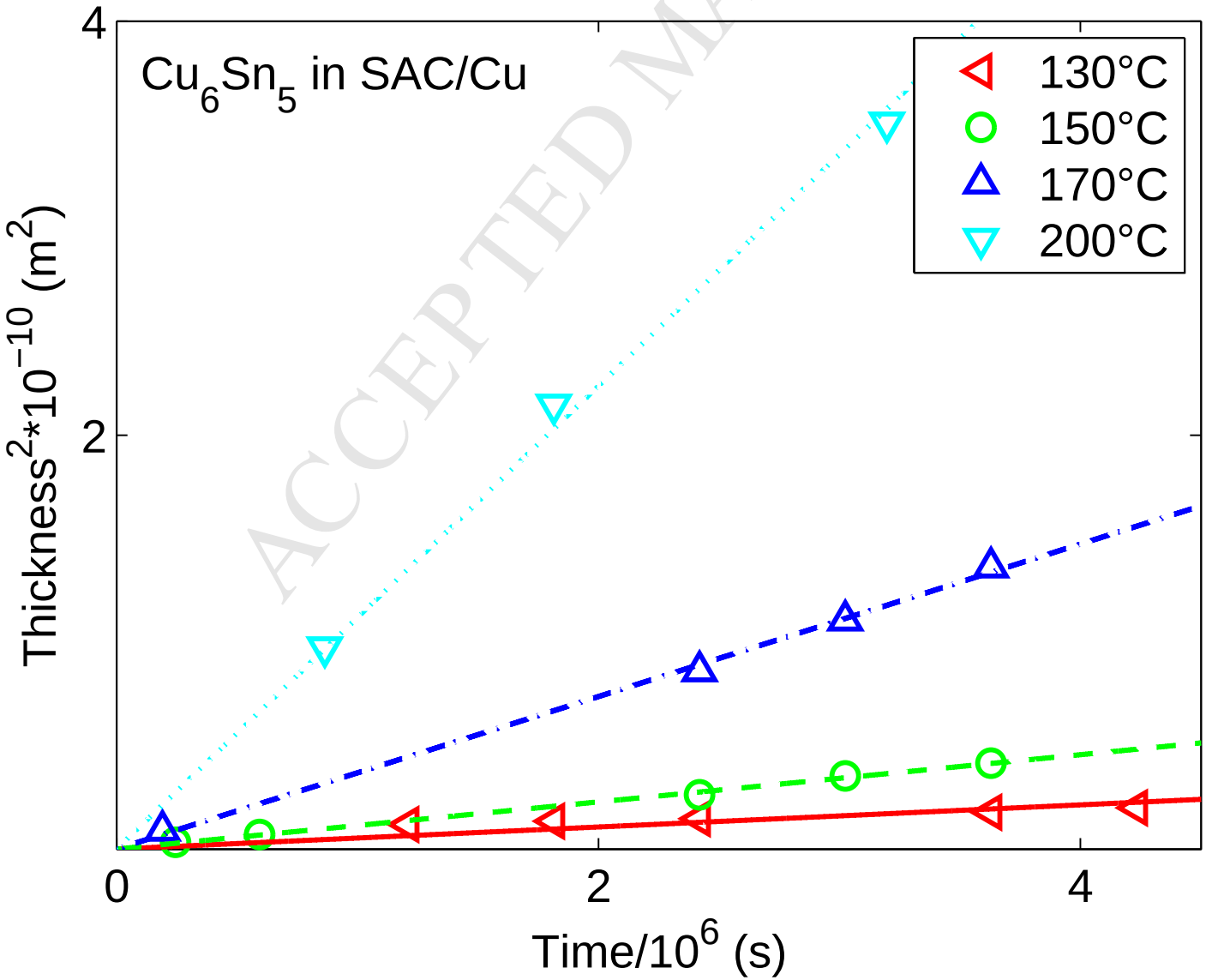

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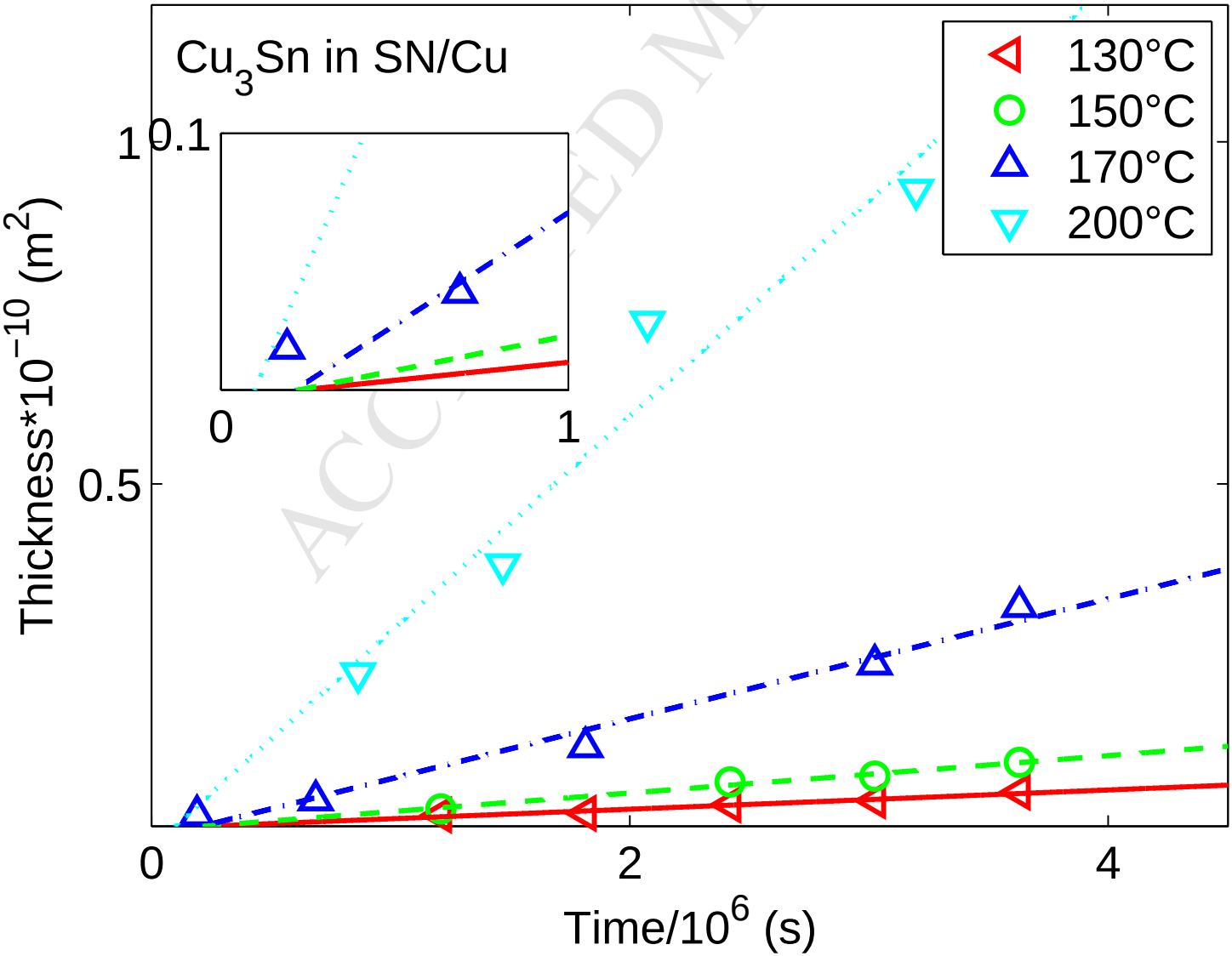

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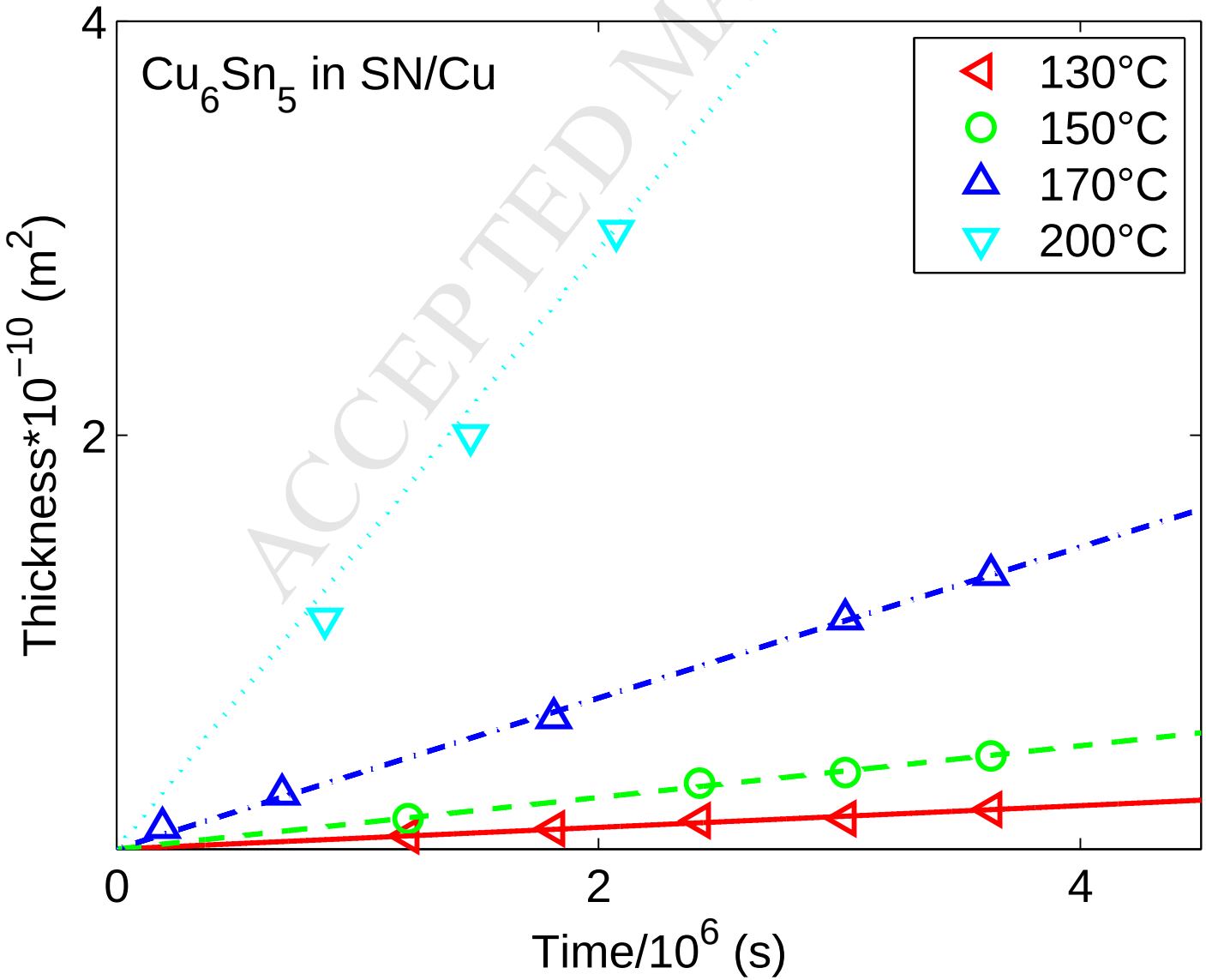

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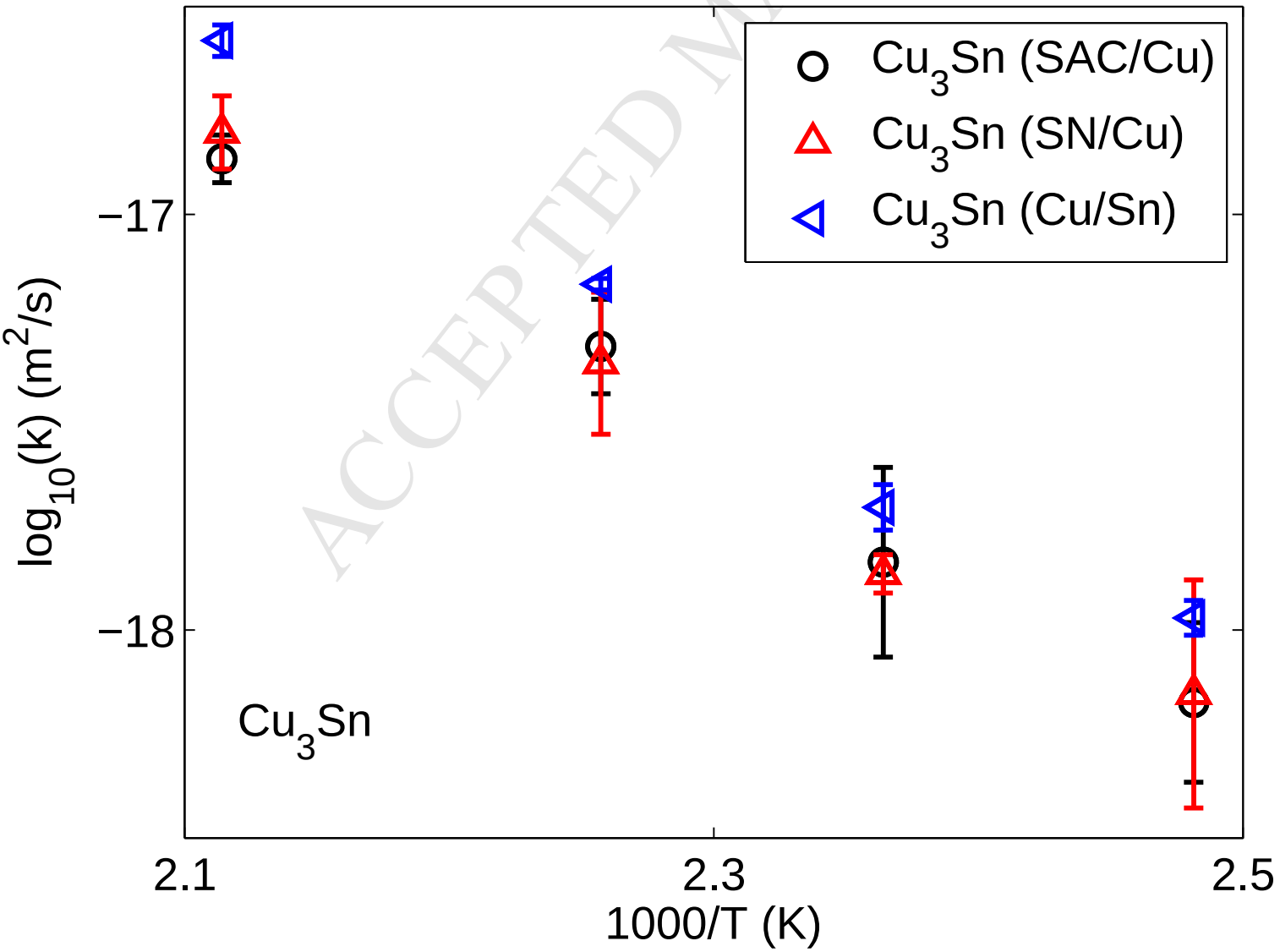

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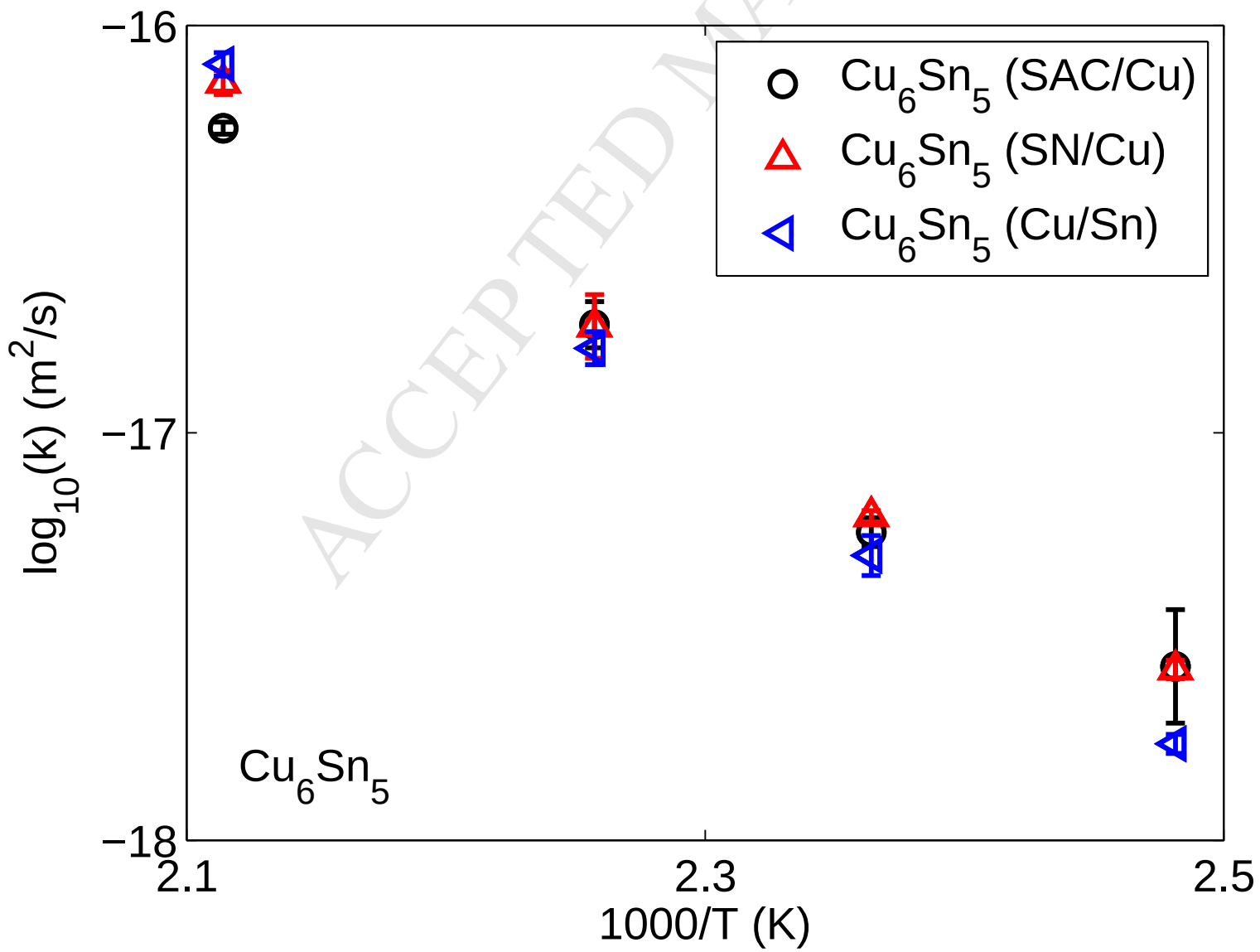

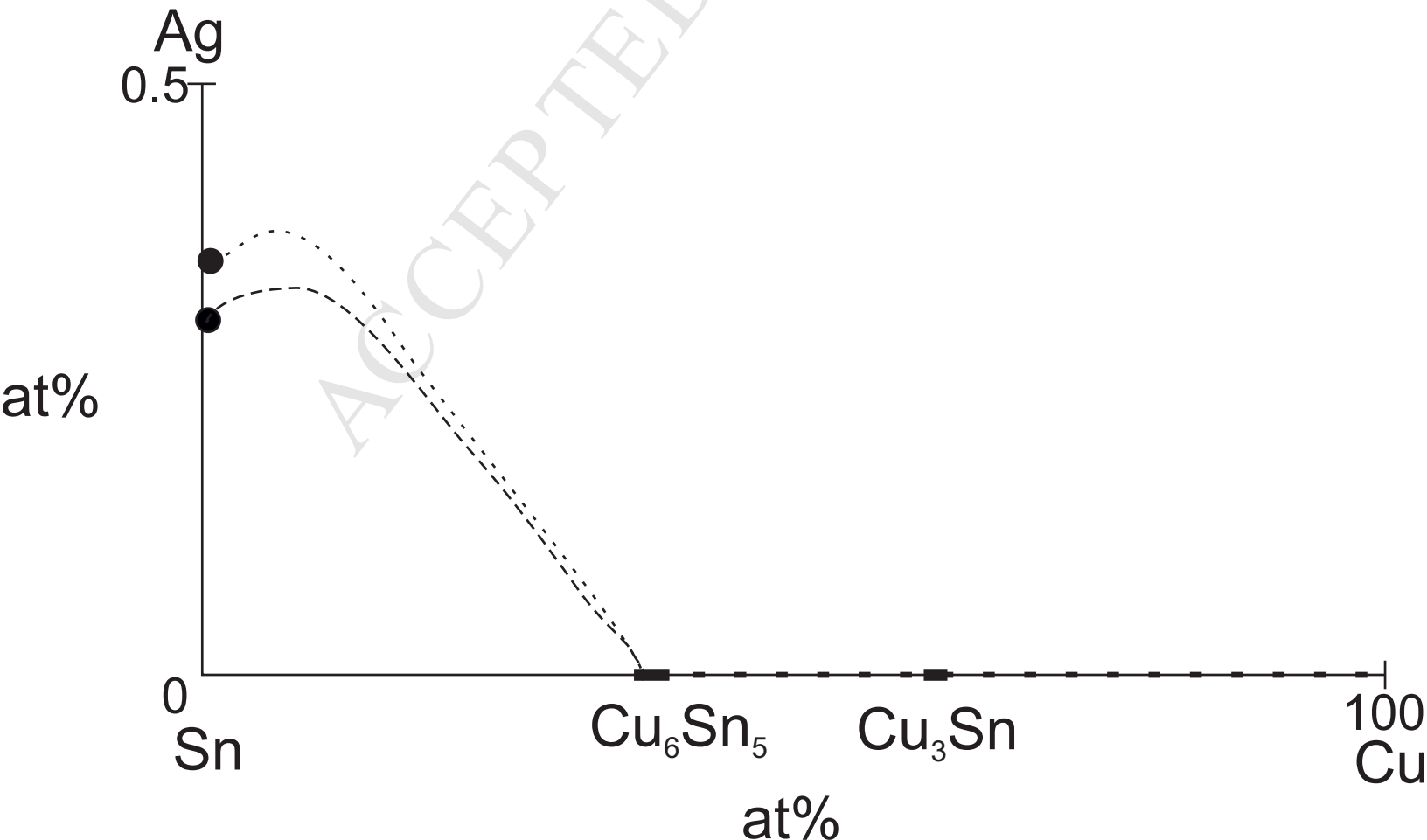

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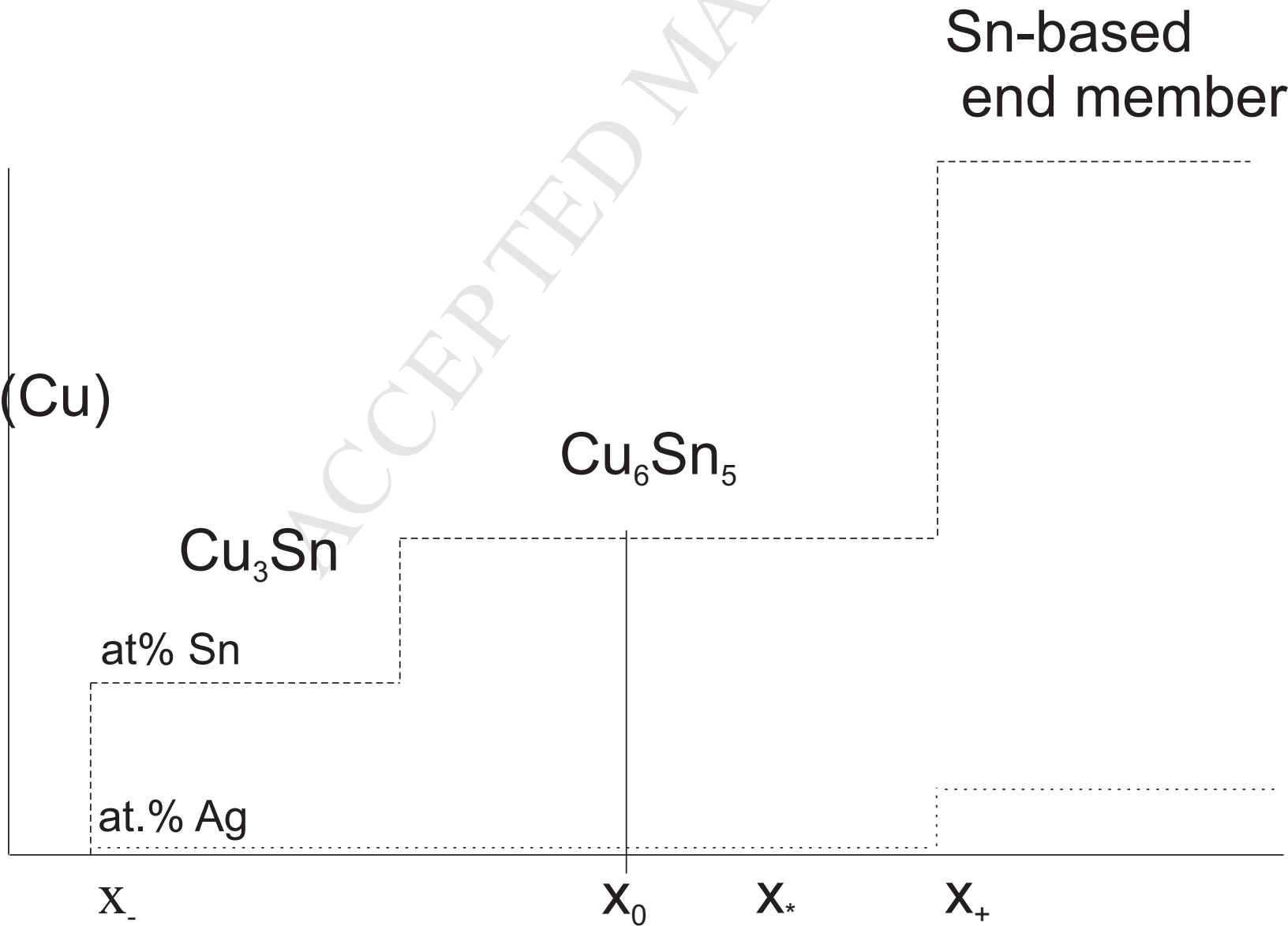

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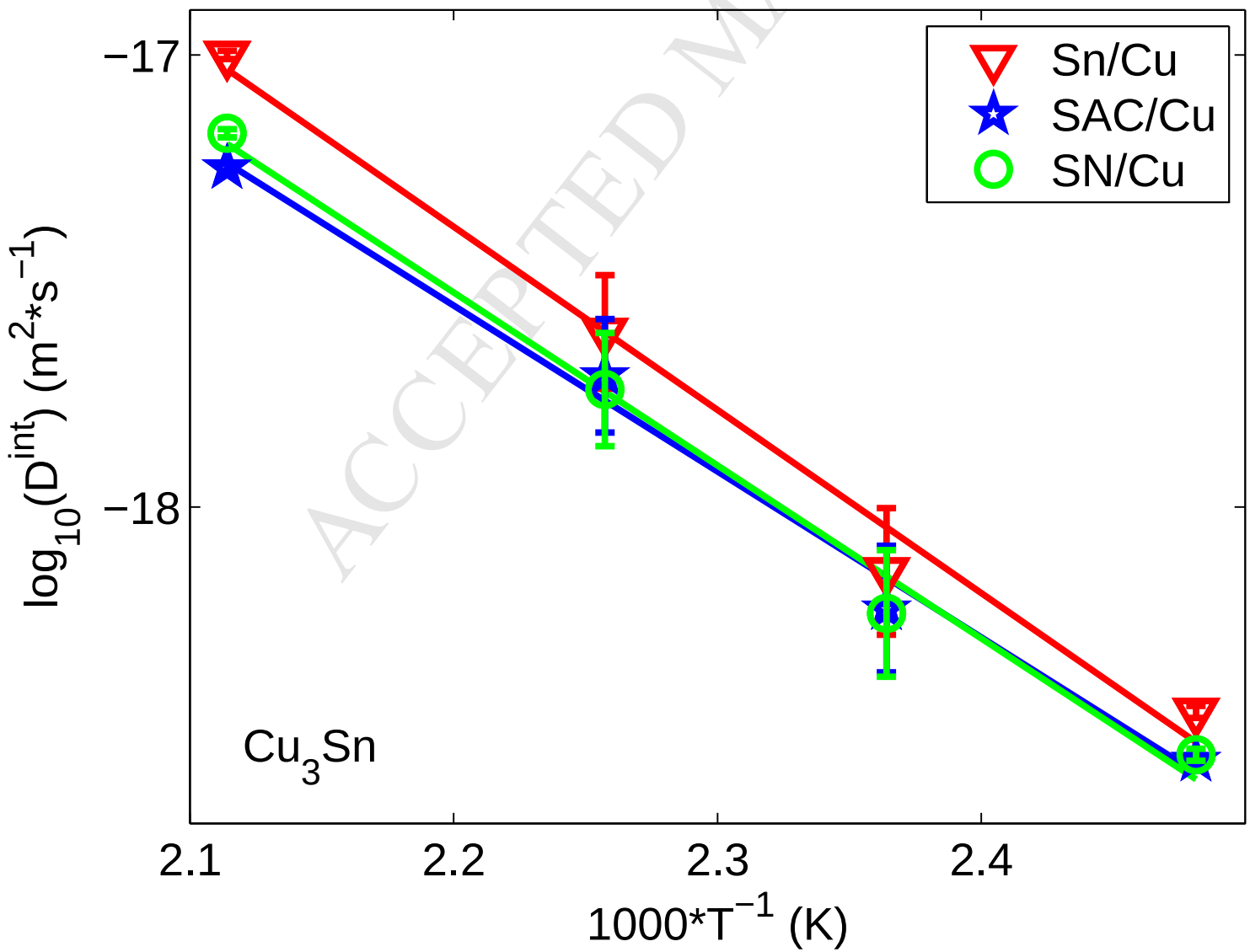

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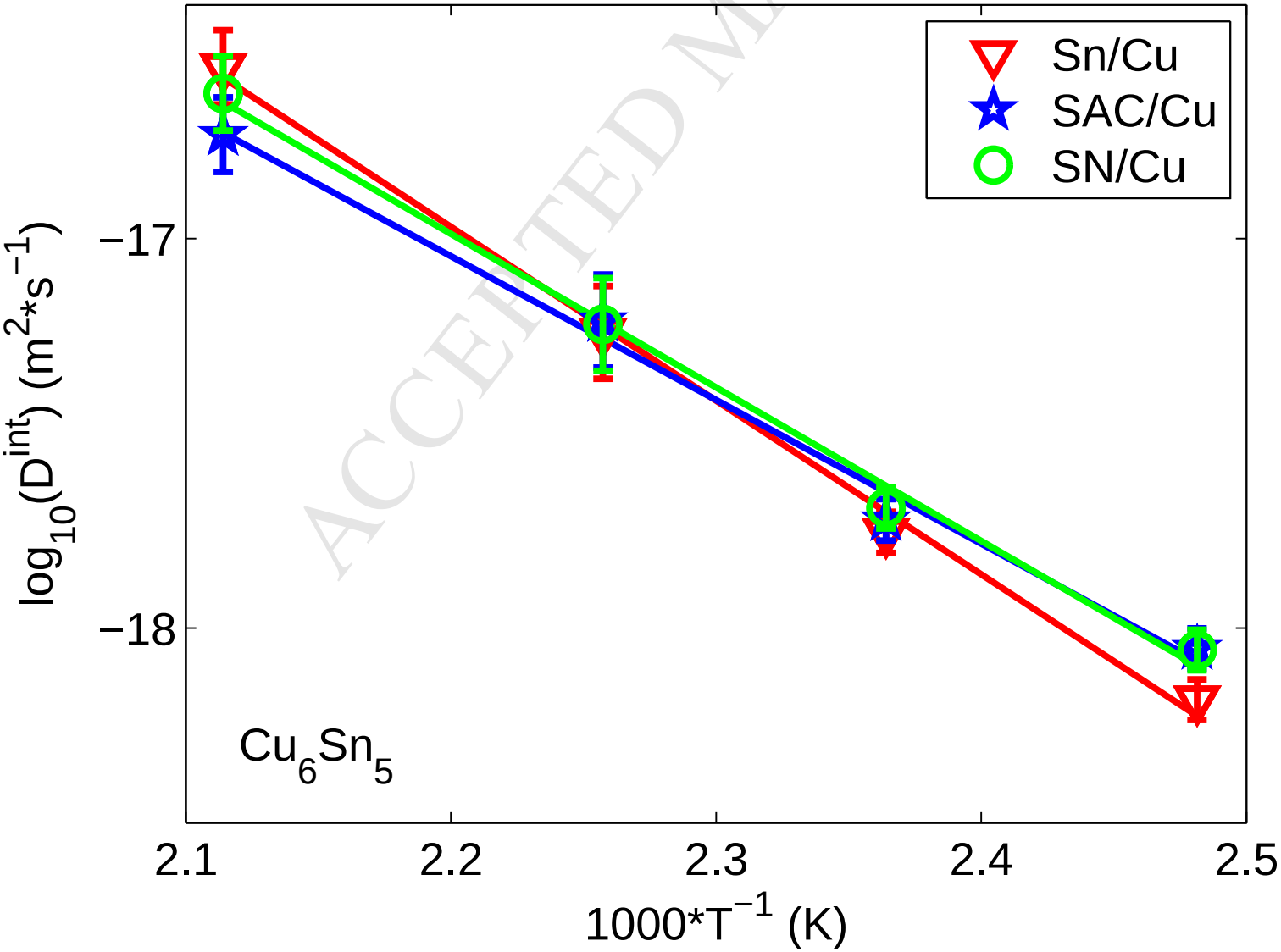

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Highlights:

1, Diffusion behavior in Sn-xAg-yCu/Cu studied under identical experimental conditions.

2, The $Q^{diffusion}$ were derived excluding effects from adjacent phases.

3, A pseudo-binary method is proposed to calculate D^{int} for narrow ternary IMCs.

4, Effects of additions of Ag and Cu in the Sn-matrix were interpreted and verified.

5, The results are instructive for Sn-Ag-Cu solder design

ACCEPTED MANUSCRIPT