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REVIEW

Early stages of wetting of copper by Sn–Zn eutectic alloy

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Abstract

The manuscript presents studies of the interaction of Sn–Zn eutectic solder alloy with a solid copper substrate, in the early times of the wetting process. The wetting tests were performed using the sessile drop method, with flux, in air, at 230 °C, 250 °C and 280 °C and reflow time of 2 s, 5 s, 10 s, 20 s, 40 s, 90 s and 180 s. The wetting time was measured from the moment of contact of the liquid solder with copper. It was noted, that during the reaction of copper with the liquid solder, an IMC (intermetallic compound) layer formed in the interface. Solidified solder/substrate couples were studied using scanning electron microscopy (SEM) and synchrotron measurements. The intermetallic phases of Cu–Zn system that formed at the solder/substrate interface were identified as epsilon and gamma. The kinetics of the formation and growth of the intermetallic layer were determined. The model describing the sequence of events in the early time of wetting was proposed. The earliest stage of wetting the copper substrate by liquid solder Sn–Zn included: adsorption of Zn atoms on the Cu surface, surface diffusion of Zn atoms on the copper surface, dissolution of the copper pad by the liquid solder and diffusion of Cu atoms into the liquid. In the liquid solder, the copper atoms combined with zinc atoms to create clusters of the epsilon phase. Those clusters coagulated and a short-range ordered (SRO) Cu–Zn structure formed in the liquid. After short heating and cooling, the liquid solidified and the $CuZn_5$ border-layer appeared in the interface. Further heating caused the saturation of the reaction zone with Cu atoms and the crystallization of two intermetallic phases Cu_5Zn_8 from the solid support side and $CuZn_4$ one from the solder side occurred.

1 Introduction

The continuous development of microelectronics in respect to miniaturization and efficiency improvement motivates the search for new materials and technologies capable of allowing, for the cost reduction, the increase of the density of connections and efficiency as well as for improving their reliability.

The European Parliament's and the Council of Europe's directives issued in 2003 prohibited the use of solders containing health hazardous metals such as Pb and Cd [1–3]. Similar steps have been taken by USA [4], China [5] and Japan [6]. Those then urged manufactures and research institutes to look for and devise new, environmentally friendly alloys. Concerning the solders employed in electronics the research has been focused mainly on Sn–Ag, Sn–Ag–Cu systems with eutectic composition and with various alloying dopants [7, 8]. The properties of these alloys have been widely studied and revealed a number of drawbacks, one of which is the high melting point [9–11].

Low-melting solders are used to connect elements thermally prone to decomposition, such as circuit board laminates, integrated circuit (IC) package encapsulates and other heat sensitive devices [12]. Soldering alloys based on the Sn–Zn eutectic are competitive to Sn–Ag, Sn–Ag–Cu based alloys with eutectic composition (SAC) due to lower melting temperatures, better physical, chemical and mechanical properties as well as lower manufacturing costs [13]. Presently, flip-chip technologies are commonly used in electronics for surface-mounting (SMT) and also in BGA systems. BGA (Ball Grid Array) is a type of IC characterized by mounting to the ground with the help of solder bumps. The disadvantages of solder (Sn–Ag, Sn–Ag–Cu) that are currently used in the BGA technology are low resistance to shocks, impacts [14, 15] and to multiple thermal cycles [16]. New solders, based on Sn–Zn eutectic should eliminate these defects [17, 18]. The possibility of electrolytic deposition from non-toxic citrate baths is an important advantage of Sn–Zn alloys [19, 20]. In the case of Sn–Ag alloys, obtaining the stable baths requires the use of

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toxic complex components [21]. Furthermore, many publications related to the technologies in electronics, indicate a shift from photolithographic technology to electrolytic deposition [22, 23].

The main principle of soldering is the interaction between the liquid solder and the surface of joined metals. The effect of this interaction is the appearance of intermetallic phases or solid solutions at the interface of joined surfaces. The IMC formation promotes bonding between the solder and the substrate, while the excessive growth of IMC, worsens the mechanical properties of the joint [24–26] and also hinders miniaturization [27–29]. For the Cu–Zn and related systems, the typical morphology reported for the intermetallic layer is a relatively planar, two phase structure: γ phase near the Cu substrate and ε phase near the solder. The paper [30] describes the wetting process in the Sn8.8Zn / Cu system. Based on thermodynamic calculations, the authors found that gamma was the phase that should be formed before the epsilon phase appeared.

However, the results of the research presented in this publication do not confirm this, the first to occur is the epsilon phase and later the gamma phase appears. Similar results were obtained by Fima at al. [31], who investigated the wettability of copper by liquid solders of Sn–Zn + xCu. Initially, in 15 and 30 s, only single layer was present with the composition close to $CuZn_4$. After a longer time (60 and 180 s) two interlayers could be distinguished at the interface. One was gamma adjacent to the substrate, and another was epsilon close to the Sn–Zn–Cu alloy. In addition, they assumed that the γ arose as a result of the diffusion of copper from the solid substrate to the epsilon phase, followed by the nucleation and crystallization in ε . The mechanism of reactive wetting of metals with liquid metals, due to, for instance, the lack of complex theory of interphase boundary, is rather speculative and further research is required to better understand its nature.

Generally it is believed, that the interface reaction products between substrates and solder alloys have a great effect on mechanical properties of the substrate/solder joint. Thus, it seems that the earliest wetting step is of great importance, since the sequence of the IMCs formed has a significant effect on the morphology and evolution of the IMC layers, which consequently affects the reliability of the joints.

This paper is focused on the description of the wetting process and modeling the intermetallic phases growth in the first moments of wetting, when the copper substrate is in contact with the Sn–Zn molten solder.

2 Experimental section

The alloys for tests were prepared by melting pure metals (Sn—99.999%, Zn—99.95%) in graphite crucibles, in a glovebox filled with Ar (99.9992%) protective atmosphere (oxygen and water vapour pressure below 1 ppm) to avoid oxidation. Wetting tests were performed using ALU33® flux applied to the solder sample and surrounding part of the substrate. The flux components are aminoethylethanolamine ($C_4H_{12}N_2O$) and ammonium fluoroborate (NH_4BF_4). According to ISO 9454-1, this is the 2.1.2-type flux, i.e., organic, water-soluble, and activated with halides. The masses of samples used for wetting tests were 0.5 g and the dimensions of copper and aluminum pads were 40×40×0.5 mm. Copper pads (99.5%) were prepared in accordance with EN ISO 9455-10:2000. The wetting tests were conducted using the method of sessile drop (SD) described in [32].

The setup consisted of two zones: cold zone in which initially the sample was placed and hot zone in which measurements were performed. Covered with a thin layer of flux the copper substrate was delivered to the hot zone. After heating the cooper to the appropriate temperature, 0.5 g of solder covered with flux was transported to the hot zone using a separate dispenser. After several seconds, the molten solder fell on the copper substrate and a stopwatch measuring the wetting time was turned on. After the experiment time is run off, the sample was quickly transported to the cold zone and cooled in water at ambient temperature. In order to determine the activation energy of the growth of the gamma and epsilon phases, wetting test were performed at 230, 250 and 280 °C for different annealing times: 2, 5, 10, 20, 40, 60 and 180 s. The wetting tests were carried out with the use of the Alu-33® flux produced by Amasan and without a protective atmosphere. For each set of the temperature and time five independent wetting tests were performed. The wetting angle data were the average of individual measurements for all samples. The contact angles were determined from photographs using the application ImageJ [33, 34]. The contact angles were measured on the solidified drops, at the end of the tests and after the remaining flux was dissolved by water. After wetting tests, the selected solidified solder/substrate couples were cut perpendicular to the plane of the interface, mounted in conductive resin and polished for microstructural characterization. Microstructural and energy dispersive spectroscopy (EDS) analyses were performed via scanning electron microscopy (SEM) using a Quanta 3D FEG system, at 20 kV, with the standardless analysis EDAX system based on the Genesis 4000 software. Phase identification was carried out using diffraction of high-energy synchrotron radiation (87.1 keV, λ = 0.142342 nm) with beam line P07 at DESY (Hamburg, Germany).

3 Results and discussion

The interaction of liquid Sn–Zn solder with solid Cu substrate was analyzed in the work. However, the heating profile was different from that commonly reported in

literature [15–17, 30–32, 35, 36], where the solid solder in the form of a cylinder, lying on a solid substrate, was heated to measurement temperature T (Fig. 1a). When the T temperature was reached, the solder melted and the wetting process started. The diffusion in the solid state took place during heating at the interphase (Fig. 1b) resulting in a continuous layer of intermetallic phases formed at the surface of the Cu substrate. The melted solder wetted the intermetallic phase instead of copper (Fig. 1c), according to the interaction of liquid solder/ IMC—layer. Such an occurrence of IMC layer (gamma and epsilon) without the contribution of liquid phase was observed, among others, in "cold" Sn–Zn electrolytic coatings deposited on the Cu substrate [19].

The heating profile used in the present work is shown in Fig. 2a. The liquid solder of T temperature fell at the Cu substrate covered with flux of the same temperature giving start to the wetting process liquid solder/Cu substrate (Fig. 2b). In that case, the layer of intermetallic phases formed as a result of the reaction of liquid solder material with the solid Cu substrate (Fig. 2c).

3.1 Wetting tests

The results of wetting tests on copper substrate are shown in Fig. 3. According to authors of works [10, 37], the value of angle φ in range $0 < φ < 30°$ proves very good wetting, $30° < φ < 40°$ means good wetting, $40° < φ < 55°$ sufficient wetting, $55° < φ < 70°$ is typical for weak wetting, while $φ > 70°$ suggests very weak wetting. The measured φ values of the copper substrate with the eutectic Sn–Zn alloy were contained within range 41–55°, which could be described as sufficient. As it can be seen from Fig. 3, the wetting angle changed in a very small range together with the increase of temperature. Moreover, it can be observed, that the longer time of annealing the higher was the wetting angle value, which suggested, that the wettability worsened. However, the change of the angle was within the limits of the measurement error, which reached 8%.

Soldering is a process consisting in joining metal objects using an additional, melted metal called solder, whose melting temperature is significantly lower than the melting temperature of joined metals. The durability of soldered joint depends to some extent on adhesion of the solder to the metals upon bonding, which is connected with the ability of liquid alloy to spreading during the

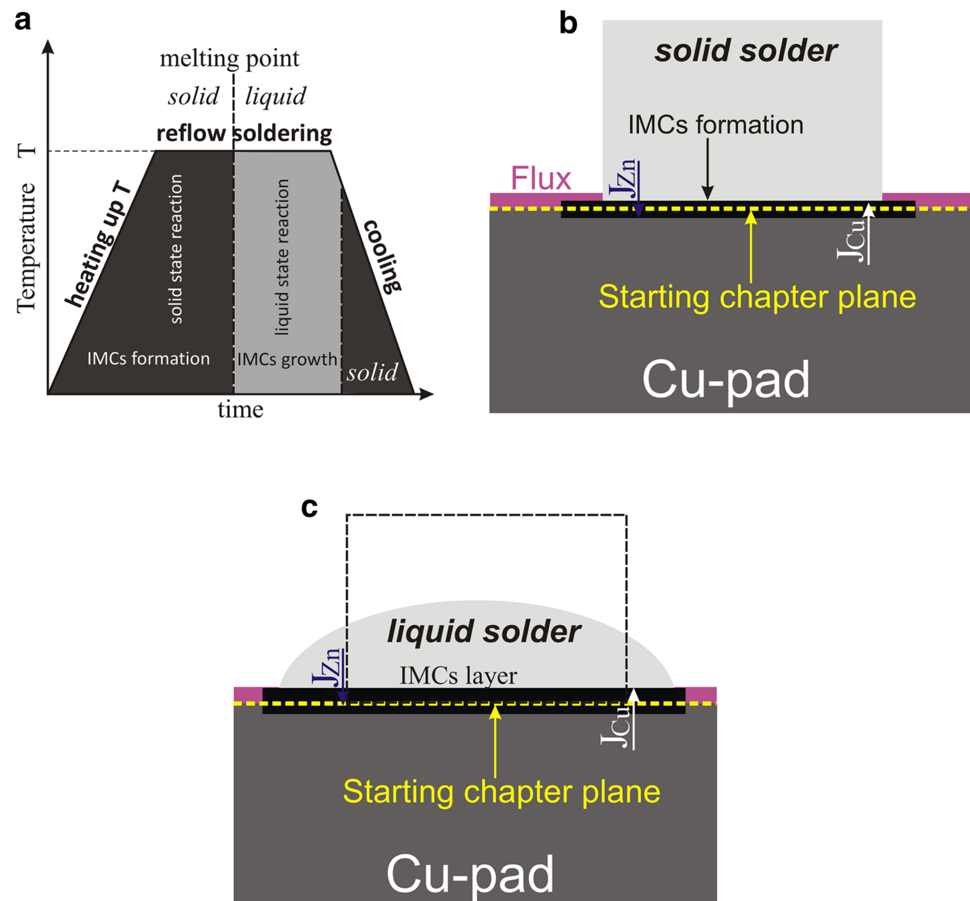

Fig. 1 Schematic representation of wetting process according to literature [15–17, 30–34]. **a** heating profile, **b** before solder melting **c** during wetting, "starting chapter plane"—original copper substrate surface before wetting processes

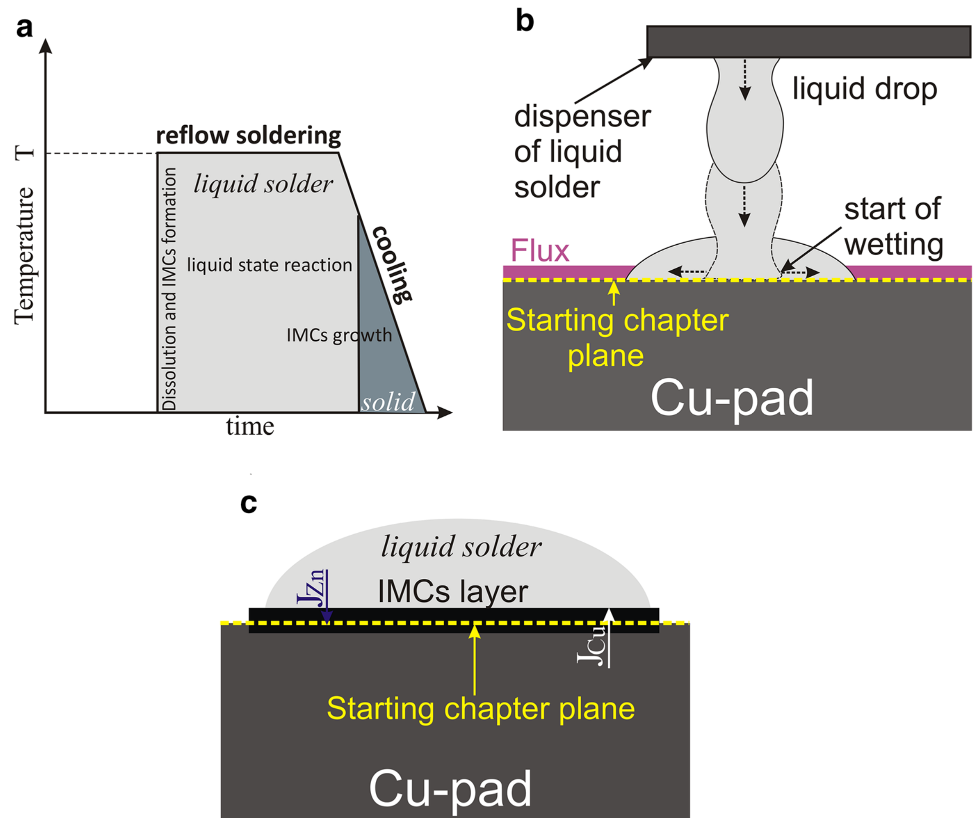

Fig. 2 Schematic representation of wetting process used in this study. **a** heating profile, **b** the first contact of liquid solder with substrate, **c** wetting, "starting chapter plane"—original copper substrate surface before wetting processes

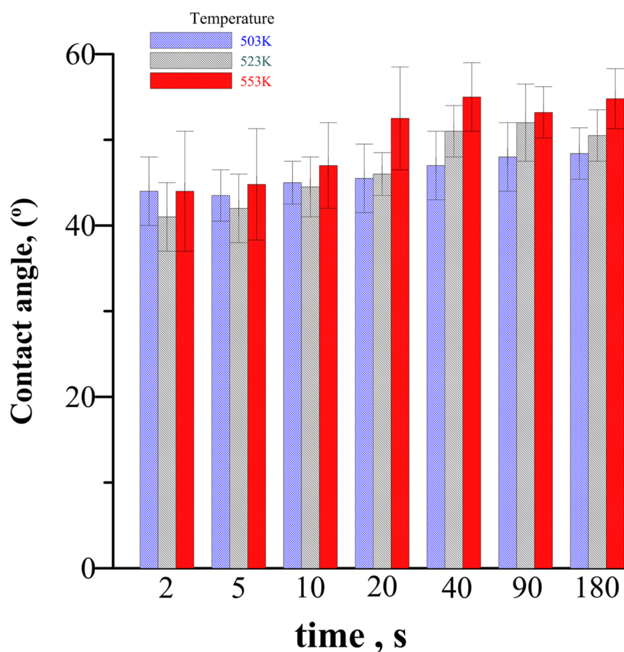

Fig. 3 Contact angles of Sn–Zn on copper after 2, 5, 10, 20, 40, 90 and 180 s at 503, 523 and 553 K

process of soldering i.e. wettability and the formation of a new interphase between the liquid and the solid. Generally, the wettability improves together with the increase of temperature due to the decrease of surface tension and following cohesion work. Taking into consideration the kind of interaction, the wettability can be divided into non-reactive and reactive one [38–40]. The first one covers weak interactions like in non-reacting liquid metal-ceramic systems or strong ones for the case of liquid metal–metal. The wettability in the non-reactive liquid/solid system is a result of the interaction of two concurring forces of cohesion and adhesion [41].

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \quad (1)$$

$$W_{ad} = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} = \gamma_{LV}(1 + \cos\theta) \quad (2)$$

$$W_{coh} = 2\gamma_{LV} \quad (3)$$

where: γ_{LV}, γ_{SV}, γ_{SL}—liquid–vapour surface tension, solid–vapour surface tension, solid–liquid interfacial tension, θ equilibrium contact angle, W_{ad}, W_{coh}—work of adhesion and work of cohesion.

The work of adhesion is characterized as the work indispensable to detach the liquid from an elementary solid surface with the simultaneous formation of two new surfaces of the same size: liquid–gas and solid–gas. The work of cohesion is connected with the coherence of the liquid,

i.e. the higher surface tension the bigger coherence, but, at the same time, the wettability becomes more difficult.

The Young's Eq. (1) is the most basic starting point for understanding the complex process of wetting. The wetting angle θ , size and rate of spreading are the main parameters describing wettability of solids with liquid.

The description of the soldering process becomes more complicated in the case of reactive wetting, because the reaction zone formed in the interface changes the parameters of the process (e.g. surface tension of the liquid and the surface energy of the solid substrate). The surface tension for the Sn–Zn alloy of eutectic composition reported in [42] was 0.555 N/m at T = 523K. Such a value proved high integrity of the liquid alloy and in the case of wetting also the great work of adhesion amounting to about 0.9 J/m^2. Such a high value of the adhesion work indicates a strong interfacial bond interphase binding (chemical or metallic bond) [41]. Thin IMC layer between the melted solder and the substrate was observed to form during welding copper with the eutectic Sn–Zn alloy. It testified to a strong chemical binding between them. The layer consisted of two intermetallic phases: epsilon from the solder side and gamma adjacent to the copper substrate. Instead of the expected Cu–Sn IMCs, Cu–Zn IMCs were formed in the Sn–9Zn/Cu couple, because the value of ΔG_f (Gibbs energy of formation) of Cu–Zn IMC was more negative than that of Cu–Sn IMC at 230–280 °C [43, 44] and so was its activation energy of growth [45]. The layer of intermetallic phases appearing in the interphase is the reason for the change of the wetting system from liquid solder/Cu-pad into liquid solder/ IMC layer one (Fig. 2). Moreover, the composition of liquid phase changes during the dissolution of copper matrix together with time of the process. As the concentration of Cu in liquid solder increases, its surface tension increases. These facts may explain the deterioration of the wettability with the duration of annealing (Fig. 3).

3.2 Effect of time and temperature on chemical reaction at interface during spreading

The wetting tests were carried out at 230 °C, 250 °C and 280 °C. At each temperature seven reflow times were applied: 2 s, 5 s, 10 s, 20 s, 40 s, 90 s and 180 s. All experiments were performed without protective atmosphere. During the reaction of copper with liquid solder the IMC layer was formed in the interphase.

3.2.1 Temperature 230 °C

Figure 4 illustrates the interfacial microstructure of Sn–Zn/Cu couples after 2, 40 and 90 s of wetting, respectively. It was established, that a layer of intermetallic epsilon phase appeared in the interphase as a result of the reaction of liquid solder with the solid Cu substrate after short reflow times up to 40 s (Fig. 4a, b). Next, after 90 s of annealing, the gamma phase formed apart from the ε phase (Fig. 4c), which were both confirmed by the chemical composition analysis EDS (Fig. 4), synchrotron radiation diffraction shown in Fig. 4d and also by literature analysis [15, 17, 19, 25, 31, 32, 43, 45] as well as thermodynamic one [46]. The EDS analysis, performed in place marked in Fig. 4, is presented in Table 1.

3.2.2 Temperature 250 °C

Figure 5, the SnZn eutectics reacted with the copper substrate during soldering (5, 20 and 40 s) by forming intermetallic compounds of gamma and epsilon, based on the EDS analysis and SR-XRD result. During the reaction of liquid solder with the Cu substrate, only epsilon phase appeared in the early stage, similarly as it happened at the lower temperature of 230 °C (Fig. 5a, b). The phase proved to be non-uniform in regard to the Zn content; it consisted of ε-$CuZn_5$ and ε-$CuZn_4$ compounds, which were established based on the synchrotron radiation diffraction shown in Fig. 5d, followed by the gamma phase formed after 40 s of annealing (Fig. 5c). Further annealing up to 3 min resulted in the increase of layer thicknesses of both intermetallic phases. The EDS analysis, performed in the place marked in Fig. 5, is presented in Table 2.

3.2.3 Temperature 280 °C

Figure 6 shows the microstructure of a cross-section of liquid solder Sn–Zn on the Cu substrate for times of (a) 5 s, (b) 20 and (c) 90 s at temperature of 280 °C and (d) SR-XRD result. The EDS analysis, performed in the place marked in Fig. 6, is presented in Table 3. It was observed that the IMC layer formed and broadened faster than at lower temperatures (Fig. 6). The appeared epsilon phase was at first quite differentiated in composition (Fig. 6d). The gamma phase followed after already 20-sec-annealing, which happened quicker than at T = 250 °C (after 40 s, Fig. 6b) and at T = 230 °C (after 90 s Fig. 6c). The epsilon phase occurred in the form of "scallops" of variable size, which grew on the expense of the smaller ones (Figs. 4, 5, 6). Therefore, one can assume that one of the mechanisms for the formation of epsilon intermetallic layer was Ostwald ripening mechanism [47]. It was also observed that, like at lower wetting temperatures, the thickness of both intermetallic layers grew together with time of annealing. Obviously, the microstructure of the interfacial layers in the Sn–Zn/Cu joint is in correlation with the reaction time and reaction temperature which may also affect the properties of solder joints.

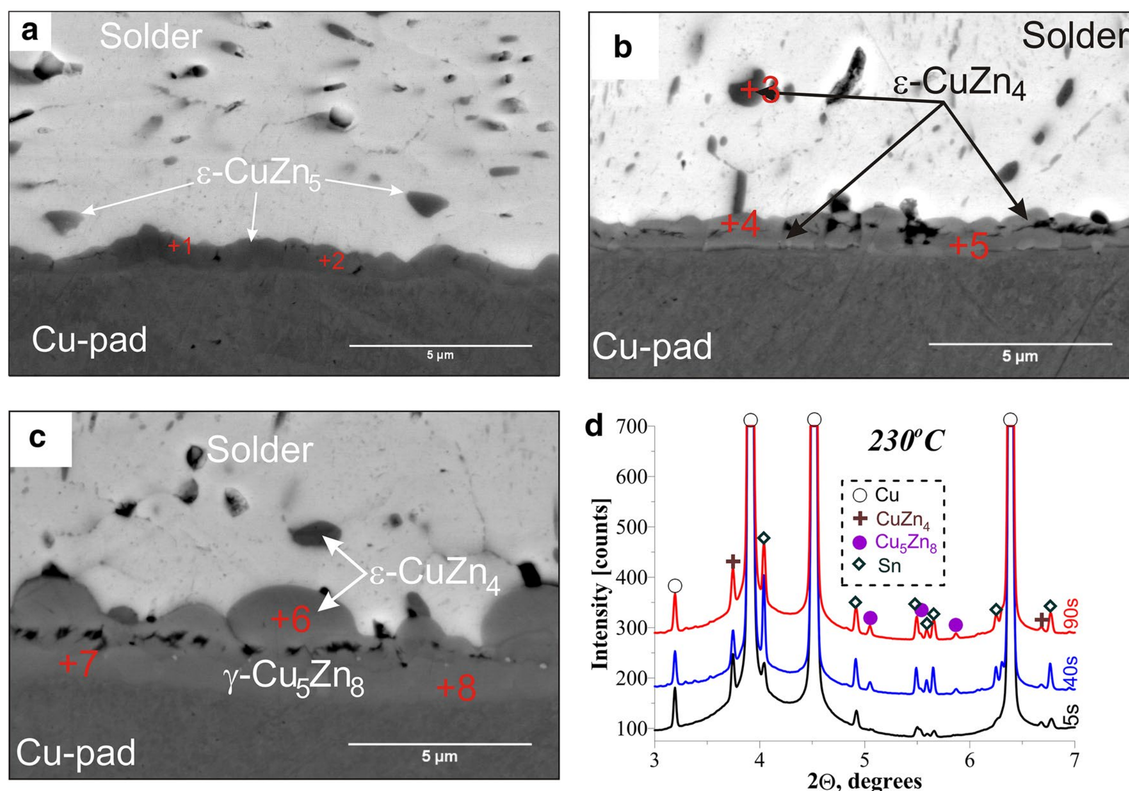

Fig. 4 Interfacial microstructure of Sn–Zn/Cu couples, temperature 230 °C, time: **a** 5 s, **b** 40 s, **c** 90 s, **d** SR-XRD result and EDS analysis at the points marked

Table 1 SEM EDS analysis marked in Fig. 4, T = 230 °C

No of marked points (time, s)	At.%		
	Zn^K	Cu^K	Sn^K
1 (5)	78	15	7
2 (5)	78.5	16	5.5
3 (40)	77.5	20	2.5
4 (40)	79	20	1
5 (40)	78.5	20	1.5
6 (90)	79	20,5	0.5
7 (90)	68	32	0
8 (90)	65	35	0

3.3 Analysis of intermetallic compound thickness

Figure 7 presents the growth kinetics of IMC layer on the Cu substrates after three annealing times. The growth rate can be described with Eq. (4).

$$\delta = k * t^n \tag{4}$$

It yields from Fig. 7 that the higher annealing temperature the higher the growth rate of IMC layer. After 3 min of annealing at different temperatures, the growth of IMC layer reached 5.4 µm for T = 280 °C, 3.6 µm for T = 250 °C and 3.3 µm at T = 230 °C. The n and k values computed from the curves of Fig. 8 were as follows: n = 0.52, 0.53 and 0.56 and k = 0.21, 0.23 and 0.3 µm /s^n for T = 230, 250 and 280 °C, respectively. Moreover, it can be noticed that the value of the exponential factor n amounts to about 0.5. Therefore it can be assumed, that the growth of intermetallic layer does obey a parabolic growth law of interdiffusion. It suggests that the volume diffusion is the main mechanism of mass transport [48].

Figure 8 illustrates the comparison of growth kinetics of layer thickness for the γ and ε phases after different annealing temperatures: 230 °C (Fig. 8a), 250 °C (Fig. 8b) and 280 °C (Fig. 8c). What is more, the growth kinetics of epsilon phase was divided into two parts; before the appearance of the gamma phase and after its crystallization. In general, the thickness of intermetallic layer increased with time at all temperatures. The gamma phase grew adjacent to copper substrate, while the epsilon one to the liquid solder. Such a two-sided growth confirms that gamma phase was permeable for the Cu atoms and the epsilon phase for the Zn atoms.

It results from Figs. 4, 5, 6 and 8 that the epsilon phase exists only in the initial stage of wetting. The gamma appears after some time depending on annealing temperature; the lower temperature the longer time is required for its creation. It is probably connected with the fact that the

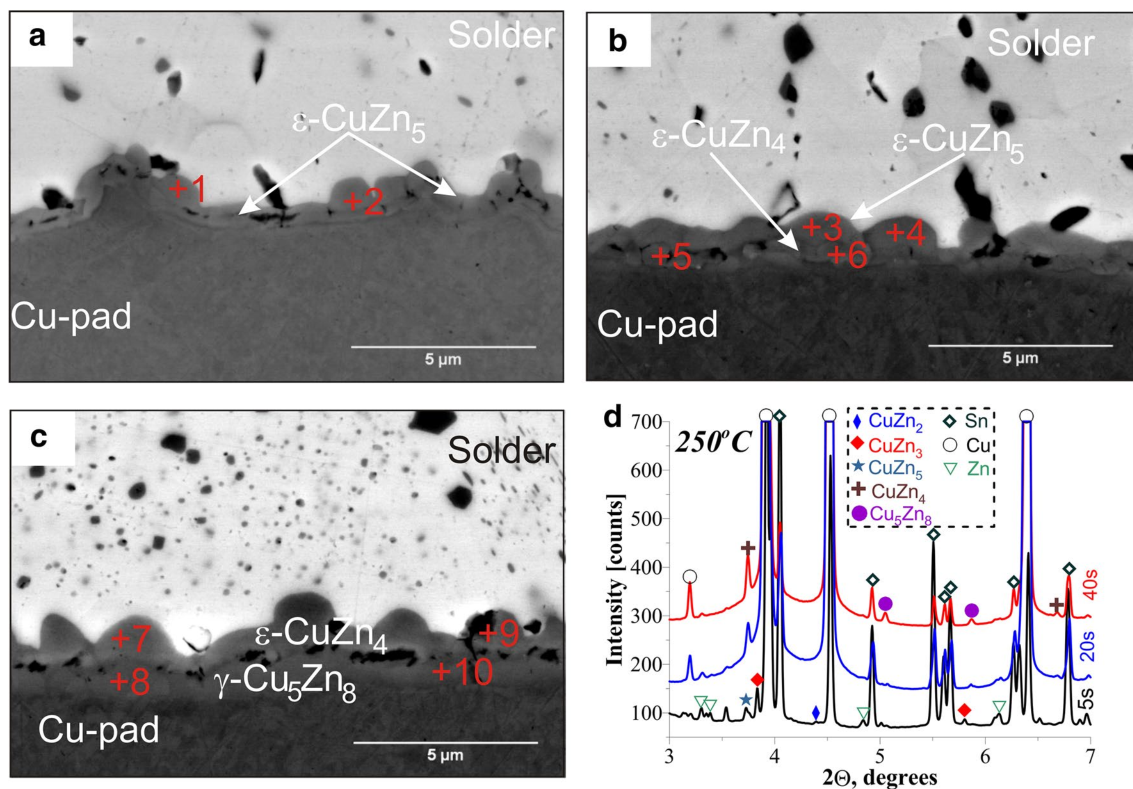

Fig. 5 Interfacial microstructure of Sn–Zn/Cu couples, temperature 250 °C, time: **a** 5 s, **b** 20 s, **c** 40 s, **d** SR-XRD result and EDS analysis in the points marked

Table 2 SEM EDS analysis marked in Fig. 5, T = 250 °C

No of marked points (time, s)	At.%		
	Zn^K	Cu^K	Sn^K
1 (5)	82	16.5	1.5
2 (5)	81.5	16	2.5
3 (20)	80	15.5	4.5
4 (20)	82	16,5	2.5
5 (20)	80	20	0
6 (20)	81	19	0
7 (40)	81.5	16.5	2
8 (40)	65.5	34.5	0
9 (40)	77	19	4
10 (40)	67.5	32.5	0

saturation of liquid alloy with the Cu atoms increases with temperature. The authors of work [31] claim, that at the beginning, the liquid Zn of the solder reacts with dissolved Cu atoms from the solid substrate giving start to a thin layer of epsilon phase. They also report that the reason of ε phase formation instead of γ one is the fact, that the supply of Zn to the substrate exceeds the dissolution rate of copper. Therefore each Cu atom is used up immediately, since new fresh Zn atoms are supplied from the whole substrate. Next, Zn diffuses through epsilon towards the substrate, while at the same time, Cu moves in the opposite direction and the gamma forms in the vicinity of the substrate. Because the Zn atoms diffuse from the solder, γ-Cu_5Zn_8 continuously grows and its width gets greater than that of epsilon, since the gamma phase is more thermodynamically stable.

The growth kinetics of individual phases was described with Eq. (4). It resulted from their analysis that there were different mechanisms of formation and growth of two above mentioned phases. The exponential factor n for the epsilon phase in the initial stage of wetting oscillated around the value of 0.5, but when the gamma phase appeared, the values n and k changed to 0.3, which indicated the decrease of the ε phase growth rate ε (Fig. 8). It can be also assumed that the formation and growth of epsilon phase was a compilation of some mechanisms, among others, surface diffusion. However, its growth depended first of all on the dissolution rate of the copper substrate.

It is commonly assumed, that the growth of intermetallic compound layer is controlled by the volume diffusion of reagents to the boundary of reaction phases. The parabolic decrease of growth rate in time illustrates the increase of diffusion path, because already formed intermetallic layers hinder the transport of additional reagents. Exponential factor n in the equations of growth kinetics of γ phase in this work is higher

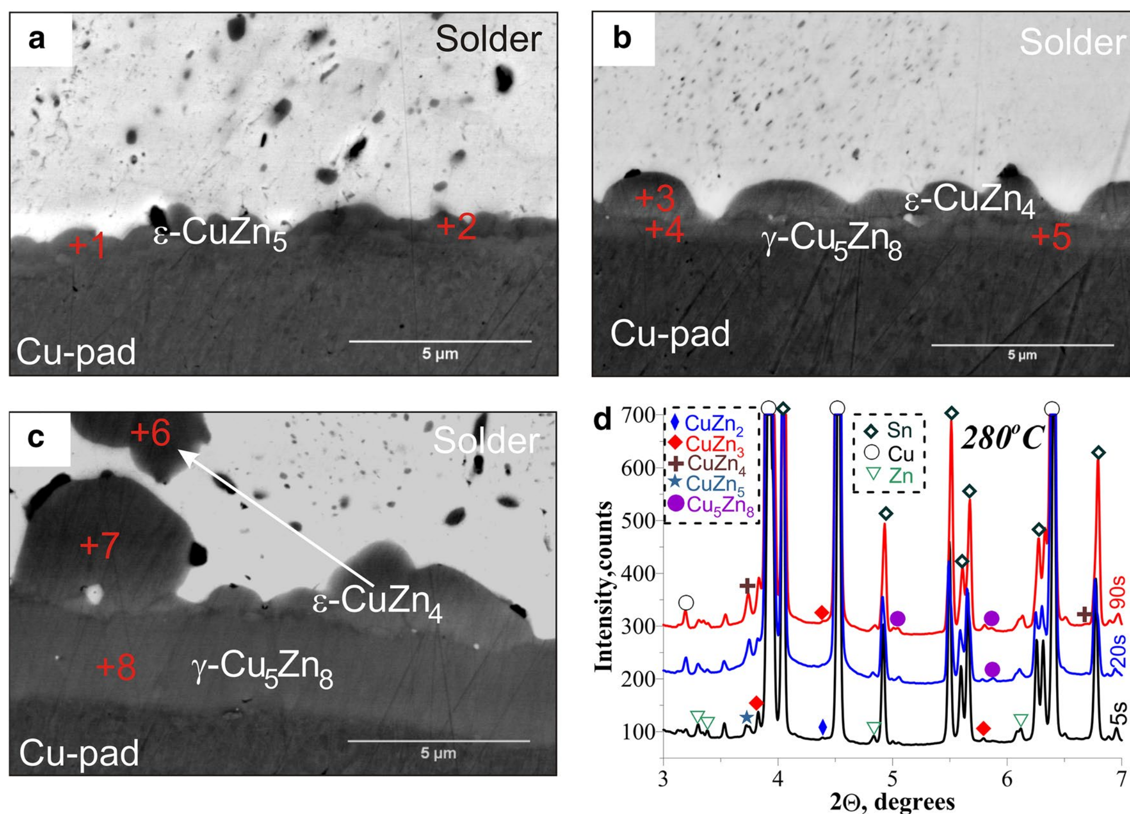

Fig. 6 Interfacial microstructure of Sn–Zn/Cu couples, temperature 280 °C, time: **a** 5 s, **b** 20 s, **c** 90 s, **d** SR-XRD result and EDS analysis in the points marked

Table 3 SEM EDS analysis marked in Fig. 7, T = 280 °C

No of marked points (time, s)	At.%		
	Zn^K	Cu^K	Sn^K
1 (5)	81.5	17	1.5
2 (5)	80	16.5	3.5
3 (20)	78.5	19	2.5
4 (20)	66.5	33.5	0
5 (20)	67	33	0
6 (90)	79	19.5	1.5
7 (90)	80	19.5	0.5
8 (90)	67	33	0

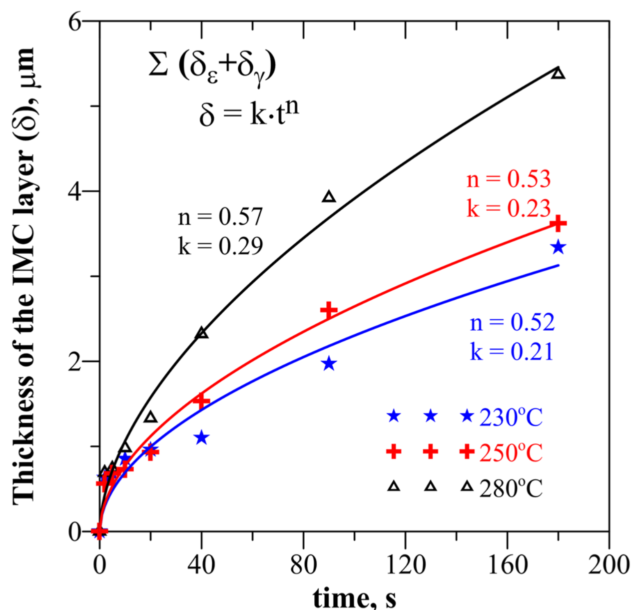

Fig. 7 Thickness of the IMC layer for different temperatures: 230 °C, 250 °C, 280 °C

than 0.5 and attains about 0.7. One of factors affecting deviations from the growth kinetics of IMC layer from the parabolic course is diffusional dissolution of Cu in the liquid solder. Also, the gamma phase partially forming from the consumption of the epsilon phase according to the chemical reaction (5) adds to the deviation. The precipitation of γ phase out of ε one requires a simultaneous course of the change of chemical composition and the type of crystallographic lattice. The change of chemical composition is connected with greater diffusion of Cu atoms than that of Zn ones. The change of lattice can take place, among others, thanks to the thermally activated movement of Cu atoms. At higher temperatures, the consumption accelerates because of higher Cu diffusion, therefore after

Fig. 8 Thickness of IMCs on Cu substrate vs time for different temperatures: **a** 230 °C, **b** 250 °C, **c** 280 °C

3 min of annealing at T = 280 °C the "negative" activation energy was obtained (Fig. 9a).

$$5CuZn_4 \rightarrow Cu_5Zn_8 + 12Zn \quad (5)$$

The hypothetical increase of ε-$CuZn_4$ phase thickness, as if the γ-Cu_5Zn_8 never appeared and the growth mechanism did not change with time, was marked with dotted line in Fig. 8. The difference between the measured and the hypothetical thickness of epsilon phase, when the gamma phase appeared, was denoted with symbol Δδε. If it was assumed that the difference resulted from the consumption of the ε phase, the precise duration of the γ phase could be determined. Hence, Δδε was 0.21 μm and the thickness of γ phase was 0.69 μm for T = 250 °C. In this case, it can be noted, that the δ phase thickness in the moment of crystallization was 0.48 μm. Inserting it into Eq. (4) together with factors of Fig. 8, the exact time of the emergence of the gamma compound at T = 250 °C, could be obtained as t = 23.5 s. Similar analysis was carried out for T = 280 °C and the time of gamma phase appearance was determined to be 12 s.

Figure 9 illustrates the relation between the growth rate and reciprocal soldering temperature, according to Eq. (6).

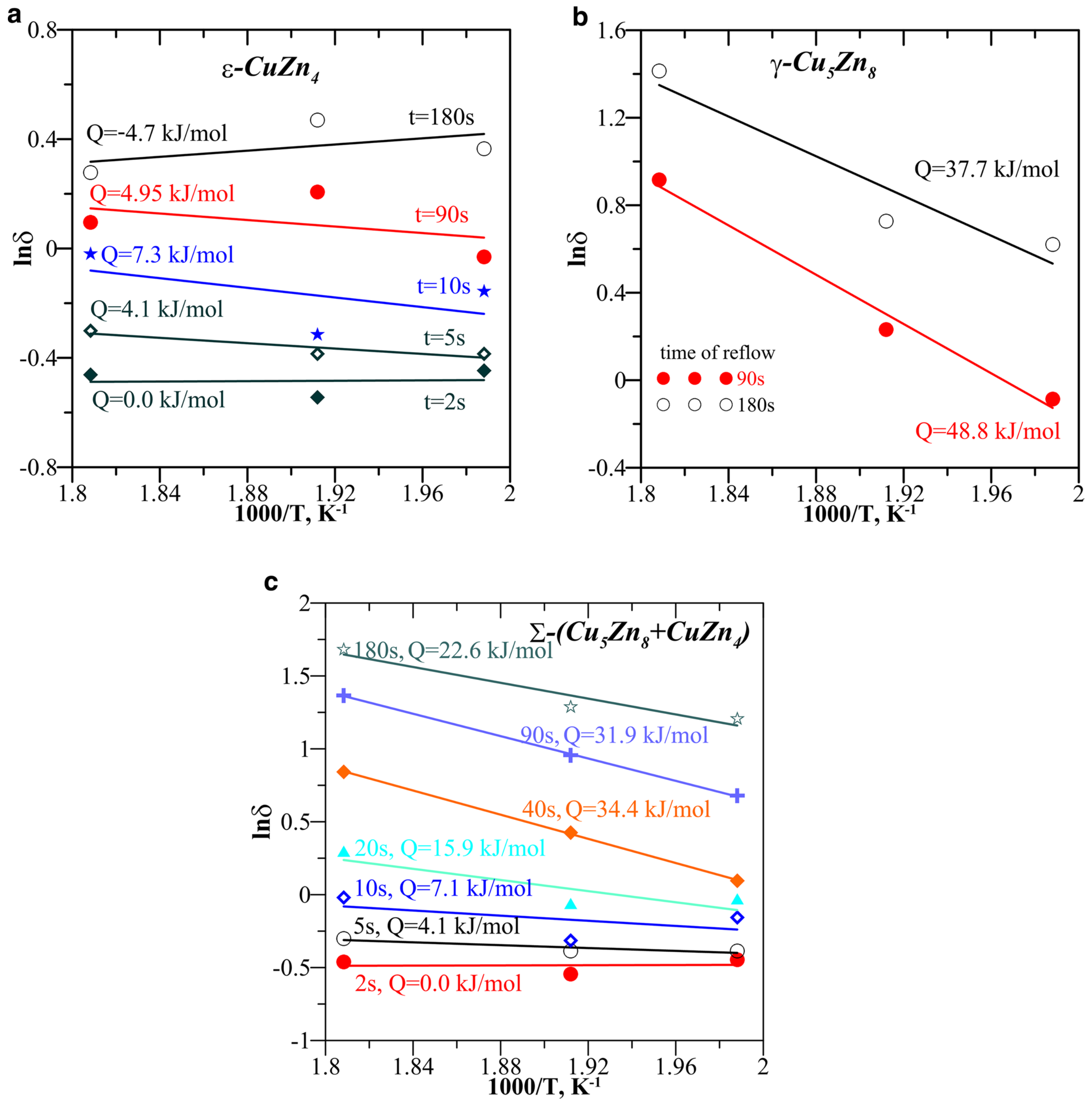

Fig. 9 Arhenius plot for the activation energy of **a** epsilon, **b** gamma and **c** (epsilon + gamma) phase layer at the interface between molten $(Sn–Zn)_{eut}$ and Cu substrate

$$\ln\delta = \ln k + n \ln t - Q/RT \quad (6)$$

In order to determine the activation energy of the growth of the ε (Fig. 9a), γ (Fig. 9b) and sum ε+γ phases (Fig. 9c).

When summing up, it can be stated, that the epsilon phase crystallizes in the first stage of wetting in which the IMC layer thickness practically does not depend on temperature. The activation energy of ε-$CuZn_4$ phase formation is equal to 0 kJ/mol (Fig. 10a) and its thickness about 0.6 µm after 2 s (Fig. 9). It appears spontaneously. This indicates that its formation is not controlled by diffusion but by other processes like adsorption or dissolution. The rate of the reaction depends on the number of active centers formed on the Cu substrate. Together with the increase of wetting time the activation energy rises and reaches 7.3 kJ/mol after 10 s. After 20 s annealing (12 s

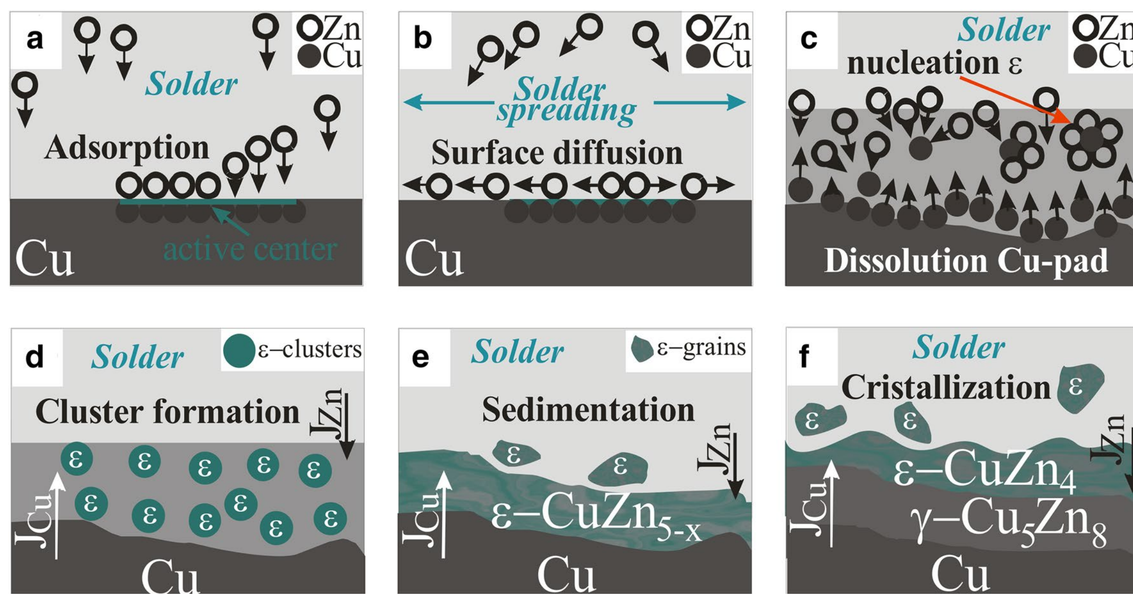

Fig. 10 A schematic model of the early stage of liquid solder-solid Cu interaction. **a** adsorption of zinc atoms on the copper surface, **b** the surface diffusion of Zn atoms, **c** dissolution of copper substrate, diffusion of Cu atoms into liquid solder, creation of stable nuclei of the epsilon phase, **d** growth and coagulation of the epsilon phase, **e** solidification of ε-$CuZn_{5-x}$, **f** crystallization of ε-$CuZn_4$ and γ-Cu_5Zn_8

according to calculations) at T = 280 °C the gamma phase occurs. At lower temperatures, it forms after 40 (calculated time 23.5) and 90 s at T = 250 °C and T = 230 °C, respectively. The activation energies of growth of the γ-Cu_5Zn_8 phase is 48.8 kJ/mol for 90 s and 37.7 kJ/mol for 180 s reflow times. The decrease in the values of the activation energy of gamma-phase growth may be related to the consumption of epsilon phase in accordance with the chemical reaction (5).

The activation energy is higher than these reported in literature: 26 kJ/mol in [45] and 29.5 kJ/mol in [49], which is connected with the fact that in the cited works another annealing profile of the samples was applied (Figs. 1, 2). In general, the activation energy of growth of the epsilon is much lower than the energy of the gamma phase. Therefore, it could be anticipated, that the first compound to appear at the boundary between the Sn–Zn solder and the Cu substrate would the ε phase, which is in accordance with the experiment. Similar results were obtained in works [30, 45, 50].

Moreover, the epsilon phase slowly decays after 180 s of annealing and transforms in the gamma phase according to reaction (5). That was confirmed by studies contained in paper [31], in which the authors observed the nucleation of γ-Cu_5Zn_8 phase within the ε-$CuZn_4$ grains. Accordingly, Lee et al. [51] reported, that the intermetallic ε–$CuZn_5$ phase was consumed by the γ-Cu_5Zn_8 one during ageing.

3.4 Model of interfacial reactions during wetting

Let us consider such a situation, that the liquid solder with flux of T temperature falls onto copper substrate of the same temperature also covered with flux (Fig. 2b). The contact of the liquid solder alloy with the Cu substrate takes place and the liquid spreads over the solid surface giving start to wetting. The earliest stage of wetting consists of some stages. During spreading of the liquid soldering material, the flux is removed from the copper surface and the new interface is created.

In the first stage, places called active centers by Langmuir, appear on the surface of copper pad (absorbent) due to the action of the flux [50]. The Zn atoms are adsorbed in these places creating mono-atomic adsorption cakes (Fig. 10a). Another stage encloses the surface diffusion of the adsorbed Zn atoms on the Cu surface (Fig. 10b). As a result of surface diffusion of Zn atoms, spreading of the liquid solder begins. As it was earlier mentioned, rapid lowering of the system energy causes spreading of the liquid solder on the copper surface. Such lowering of the energy is a result of formation of new interface. Therefore it can be assumed, that wetting can take place only when the appropriate number of Zn atoms is adsorbed in the active centers. The third stage of wetting consists in dissolving copper substrate by the liquid solder and the diffusion of Cu atoms into the liquid (Fig. 10c). Diffusing copper atoms collide with atoms of zinc to form stable nuclei of epsilon phase. Between the Cu-substrate and liquid solder "reaction zone" is created. Since

this moment copper is being dissolved by the liquid layer of "reaction zone" and not by solder. In the next stage, the appearance of stable nuclei is followed by their growth. As a result of this process, other atoms attach to the surface of the resulting nuclei and form clusters (Fig. 10d). These clusters might coagulate and create structure of short range ordered (SRO) Cu–Zn in the liquid. A similar effect was observed by Yu et al. [52], who studied the microstructure of brazing Sn–Zn and Sn–Zn–Cu eutectic alloys. They noted that atoms Sn and Zn in the Sn–Zn solder were randomly distributed, while in the Sn–Zn–xCu-alloy the structure of SRO (short range ordered) Cu Zn was established. With the increase in content of Cu, the SRO structure became greater, and the activity of Zn decreased. That reduced the surface tension of the solder, which contributed to a better wettability. So it can be assumed that, ordered structures form even in the very early stages of wetting. This is caused by the presence of Cu atoms in the liquid solder [52] or the action of solid copper substrate on liquid [53]. The authors of [53] noted that the presence of solid substrate brought about a degree of ordering in the liquid near the interface and the formation of a layered area. Besides, they claimed that ordering of atoms in the solid–liquid phase boundary in liquid metals controlled the transport phenomena, such as spreading or diffusion. It was assumed in the present work, that all the copper dissolved in the liquid solder was concentrated in the coagulated clusters of the ε phase (Fig. 10d). If the clusters are large, the buoyancy force loses with the force of gravity and the next stage begins: the sedimentation on the Cu substrate. After rapid cooling, the boundary layer of ε-$CuZn_5$ phase formed in the interface between the liquid solder and Cu substrate. Grains of this phase that have not fallen, also solidify in the solder. (Fig. 10e). Probably the epsilon phase (with the $CuZn_5$ composition) is less stable than epsilon (with the $CuZn_4$ composition) and has therefore transformed into a more stable ε-$CuZn_4$ compound during the reaction with the Cu atoms in the reaction post pad (7).

$$4CuZn_5 + Cu \rightarrow 5CuZn_4 \quad (7)$$

The Cu content in the "reaction zone" increased after longer annealing times. It yielded from the mass balance, that if the content of Cu exceeded 25 at%, the crystallization of two intermetallic phases gamma from the side of solid substrate and epsilon from the side of solder occurred (Fig. 10f). If annealing went on, zinc diffused through the epsilon towards the substrate, while copper moved in the opposite direction throughout the Cu_5Zn_8.

The layer of intermetallic phases grew continuously due to the Zn diffusion from the solder and Cu from the substrate but the growth of γ-Cu_5Zn_8 was faster than epsilon. Quicker widening of the gamma phase had two reasons:

1. The volume diffusion was responsible for the transport of copper atoms from the Cu substrate across the gamma, while the diffusion along grain boundaries controlled the transportation of Zn atoms from the solder through epsilon [54, 55].
2. Since the gamma phase was more stable, the epsilon phase transformed in the gamma phase following the heterogeneous mechanism according to Eq. (7) [31]. Last reason was responsible for decaying the ε-$CuZn_4$ phase after longer annealing times and ageing [56].

Figure 11 illustrates how the concentration of elements changes in the "reaction zone" together with time of wetting at 250 °C and, which follows, how the microstructure of the soldered joint changes.

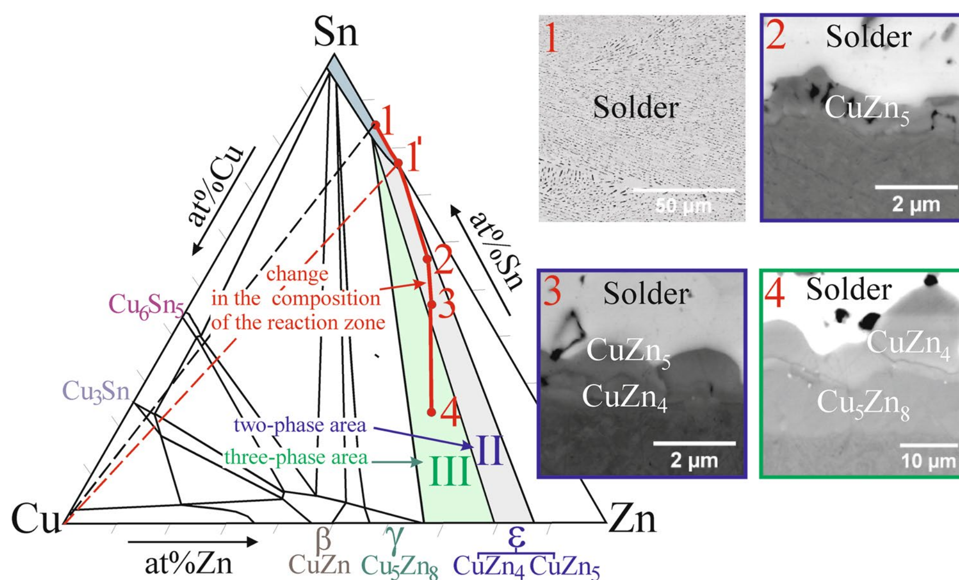

Fig. 11 Change in the composition of the reaction zone. Isothermal section of the Sn–Zn–Cu ternary system at 250 °C taken from [46]

Point 1 presents the composition and microstructure of the Sn-Zn soldering alloy of eutectic composition, which falls onto the Cu pad. The wetting process starts and a "reaction zone" appears in the interface. As shown in Fig. 10a, the first wetting moment (liquid solder is enriched in zinc locally) is the adsorption of zinc atoms on the copper surface. As a result, the zinc content in the "reaction zone" (liquid solder close to copper substrate) increases with the expiration of the heating time. The content of zinc grows along the line connecting points 1 and 1′ in Fig. 11. If the Zn content in the "reaction zone" were the same as in the eutectic alloy (point 1), the dissolution of the copper would run along the black dashed line connecting point 1 to Cu (Fig. 11). And in the interface, it would be the first to crystallize the gamma phase. Which is not true. If the Zn content is the same as at 1′, dissolution of Cu runs along the red dashed line connecting point 1′ with Cu and the first phase crystallized is epsilon. This is consistent with the experiment.

During annealing the content of Cu and Zn rises in the reaction zone. When the process is interrupted after 2–10 s, then the reaction zone will have the composition of point 2 and the layer of epsilon phase (with the $CuZn_5$ composition) appears in the interface. When the process is interrupted after 20 s, the reaction zone will have composition of point 3. The solidified epsilon phase in the interface will not only increase its thickness but also it will consist of two layers different by means of morphology and composition. Based on the EDS analysis, it was established that from the substrate side there is epsilon phase (with the $CuZn_4$ composition), while from the side of the solder the epsilon phase (with the $CuZn_4$ composition). After 24 s of annealing the content of Cu in the zone exceeds 25 at.% (in point 4 after 40 s) and a jump of conode from the two-phase to triple-phase area (Fig. 8b) can be visible. In consequence, two intermetallic phases ε and newly formed γ-Cu_5Zn_8 one apart from the liquid, coexist in the interface.

4 Conclusions

- The paper describes the earliest stages of wetting of copper substrate with the liquid Sn–Zn solder of eutectic composition. The wettability studies of Sn–Zn eutectic on the Cu substrate were performed in the presence of flux over the temperature range of 230–280 °C for wetting times in the of range 2–180 s.
- It was established, that the first contact of liquid with Cu brought a layer of intermetallic epsilon phase created in the interphase. The phase proved to be non-uniform in regard to the Zn content; it consisted of $CuZn_5$ and $CuZn_4$ compounds.
- Further annealing led to the saturation of the reaction zone with Cu atoms above 25 at.% and to the crystallization of two intermetallic phases γ-Cu_5Zn_8 from the solid substrate and ε-$CuZn_4$ from the solder side.
- The process implies two things: the change of wetting system from liquid solder/Cu-substrate into liquid solder/IMC-substrate resulting in worsening of wetting (increase of wetting angle) and the change of mass transport mechanism from the dissolution of copper substrate and liquid state processes into diffusion mechanisms in the solid state.
- *Model* The earliest stage of wetting the copper substrate by liquid solder Sn–Zn included: adsorption and surface diffusion of Zn atoms, dissolution of the copper pad and diffusion of Cu atoms into the liquid, nucleation and create clusters of the epsilon phase, clusters coagulated, sedimentation and solidification [57, 58].

It seems that the initial stage of wetting with the formation of clusters of ε-$CuZn_{5-x}$ phase had a key meaning for the properties of soldered joints. The appropriate selection of wetting time would allow the determination of the proper thickness of the epsilon phase in the solder, while small clusters of that phase would contribute to strengthening the connection.

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