Massive spalling of intermetallic compounds in solder-substrate reactions due to limited supply of the active element

S. C. Yang, C. E. Ho, and C. W. Chang
Department of Chemical & Materials Engineering, National Central University, Jhongli City, Taiwan

C. R. Kao[a]
Department of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan

Massive spalling of intermetallic compounds has been reported in the literature for several solder/substrate systems, including SnAgCu soldered on Ni substrate, SnZn on Cu, high-Pb PbSn on Cu, and high-Pb PbSn on Ni. In this work, a unified thermodynamic argument is proposed to explain this rather unusual phenomenon. According to this argument, two necessary conditions must be met. The number one condition is that at least one of the reactive constituents of the solder must be present in a limited amount, and the second condition is that the soldering reaction has to be very sensitive to its concentration. With the growth of intermetallic, more and more atoms of this constituent are extracted out of the solder and incorporated into the intermetallic. As the concentration of this constituent decreases, the original intermetallic at the interface becomes a nonequilibrium phase, and the spalling of the original intermetallic occurs. © *2007 American Institute of Physics.*
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I. INTRODUCTION

Solder joints play at least two important roles in electronic packages: they serve as electrical interconnections between components and as mechanical support for the devices. Unfortunately, solder joints have long been recognized as the weak links of an electronic package, and the reliability of each individual joint determines the overall lifespan of an electronic product. One important factor influencing the solder joint reliability is the interfacial reaction between the solder and the substrate during soldering and the subsequent aging. Consequently, knowledge of solder/substrate reactions is necessary in order to improve the reliability of electronic products.

One interesting issue in solder/substrate reactions is the spalling of intermetallic compounds from the solder/substrate interface. Here, spalling refers to the detachment of the intermetallic compound, the reaction product, from the interface during the reaction. A classical example is the spalling of Cu_6Sn_5 during the reaction between the PbSn solder and the Cu/Cu-Cr thin-film metallization.[1,2] Spalling here was caused by the exhaustion of the Cu film, which had a good wetting with Cu_6Sn_5, and the subsequent direct contact between Cu_6Sn_5 and the remaining Cu-Cr layer, which had a relatively poor wetting with Cu_6Sn_5. This poor wetting between Cu-Cr and Cu_6Sn_5 caused the molten solder to penetrate into the roots of the Cu_6Sn_5 grains, leading to the spalling of Cu_6Sn_5 grains into the molten solder.

Recently, another type of spalling was observed in several solder/substrate systems, including SnAgCu soldered on Ni substrate,[3–5] SnZn on Cu,[6] high-Pb PbSn on Cu,[7,8] and high-Pb PbSn on Ni.[9] In these solder/substrate systems, the intermetallics detached themselves in a massive scale during reflow, even though the wetting layer had not been depleted. Such a phenomenon was referred to as massive spalling.[3,4] In short, the massive spalling differs from the regular spalling in two ways: the apparent difference in the scale of spalling and the fact that massive spalling can occur even when the wettable layer is intact. Despite the fact that massive spalling has been observed across several solder/substrate systems, a unified explanation to rationalize this behavior is still lacking. The major objective of this article is to propose a thermodynamic argument to explain this rather peculiar phenomenon.

II. MASSIVE SPALLING DUE TO THE SHIFTING OF THE EQUILIBRIUM PHASE

In the following, the proposed argument and the supporting thermodynamic evidence for the massive spalling in SnAgCu/Ni will be presented in detail. The same argument will then be applied to the other three systems: SnZn/Cu, high-Pb PbSn/Cu, and high-Pb PbSn/Ni.

A. Massive spalling in SnAgCu/Ni

A typical example of the massive spalling is shown in Figs. 1(a)–1(c) for a 760 μm diam Sn3Ag0.5Cu (wt. %, same below) solder ball soldered over a Au/Ni substrate with a 600 μm diam opening. During reflow, the peak reflow temperature was 235 °C and the time during which the solder was molten was 5 min. The outer $(Cu_{1-x}Ni_x)_6Sn_5$ layer had detached itself from the interface. The intermetallic compound that was still attached to the Ni layer was $(Ni_{1-y}Cu_y)_3Sn_4$. The gap between these two layers was originally occupied by the solder, but the solder there was etched away during sample preparation. It is clear from Figs. 1(a)

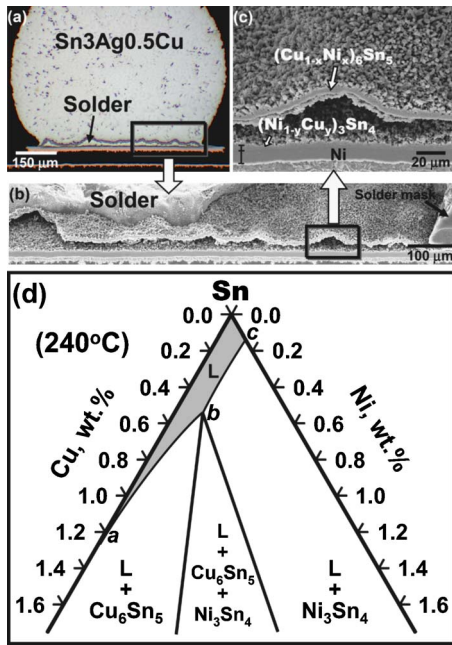
a)Electronic mail: crkao@ntu.edu.tw

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FIG. 1. (a) Micrograph showing the massive spalling in a Sn3Ag0.5Cu/Au/Ni solder joint after a reflow that had a 235 °C peak reflow temperature. The duration when the solder was molten was 5 min. The spalled layer was $(Cu_{1-x}Ni_x)_6Sn_5$. The joint was formed by reflowing a 760 μm diam Sn3Ag0.5Cu ball over a Ni substrate with a 600 μm diam opening. (b) Micrograph showing the same joint in (a) after etching. Most of the solder had been etched away. Some solder residue was left near the upper-left corner. (c) Zoom-in micrograph of (b). (d) Sn-rich corner of the Sn-Cu-Ni isotherm at 240 °C (Ref. 4).

and 1(c) that the spalling occurred across the entire joint. More intriguing micrographs showing the massive spalling can be found in the articles by Ho *et al.*[3,4]

To understand the occurrence of massive spalling even in the presence of an intact wettable Ni layer, one has to start from the phase equilibrium of the relevant elements. The Sn-rich corner of the Sn-Cu-Ni isotherm at 240 °C is shown in Fig. 1(d).[4] The constituent Ag is inert as far as the interfacial reaction is concerned and can be ignored in the present analysis.[10,11] This isotherm shows that solders with different Cu concentration are in equilibrium with different phases. When the Cu concentration is high (between *a* and *b*), the molten solder is in equilibrium with $(Cu_{1-x}Ni_x)_6Sn_5$, and when the Cu concentration is low (between *b* and *c*), the molten solder is in equilibrium with $(Ni_{1-y}Cu_y)_3Sn_4$. At point *b*, the molten solder, $(Ni_{1-y}Cu_y)_3Sn_4$, and $(Ni_{1-y}Cu_y)_3Sn_4$ are in three-phase equilibrium. According to this isotherm, one might anticipate that the reaction between Ni and the molten solder with different Cu concentrations would produce different compounds at the interface. This strong Cu concentration dependency indeed had been observed experimentally in the reaction between SnCu solder and Ni,[12] as well as between SnAgCu and Ni.[10,11] It was found that, upon increasing the Cu concentration, the reaction product changed from single-phase $(Ni_{1-y}Cu_y)_3Sn_4$, to two-phase $(Ni_{1-y}Cu_y)_3Sn_4 + (Cu_{1-x}Ni_x)_6Sn_5$, and then to single-phase $(Cu_{1-x}Ni_x)_6Sn_5$.[10–12] As $(Cu_{1-x}Ni_x)_6Sn_5$ or $(Ni_{1-y}Cu_y)_3Sn_4$ grew thicker, more and more Cu atoms in the solder were extracted out of the solder and became incorporated into

$(Cu_{1-x}Ni_x)_6Sn_5$, or $(Ni_{1-y}Cu_y)_3Sn_4$. Consequently, if the Cu concentration of the solder is not maintained at a constant level by certain means, the Cu concentration of solder will decrease with the growth of the reaction product(s). In the studies reporting the Cu concentration effect,[10–12] the amount of solders used was quite large, and therefore the Cu concentration of the solders could be regarded as constant. However, real solder joints are quite small. For example, current ball-grid-array solder joints can be as small as 300 μm in diameter, and flip-chip solder joints are in the 100 μm range. The small joint size, compounded by the fact that the Cu concentration in solders is usually very low (typically <1 wt. %), leads to the fact that the total amount of Cu in real solder joints is very limited. As a result, the Cu concentration in solder can markedly decrease as the reaction product(s) at the interface grow. Ignoring those Cu atoms in $(Ni_{1-y}Cu_y)_3Sn_4$ on the grounds that the thickness of this compound is relatively thin and that its Cu concentration is low compared to that of $(Cu_{1-x}Ni_x)_6Sn_5$, one can obtain the following equation, relating the drop of the Cu concentration to the thickness of $(Cu_{1-x}Ni_x)_6Sn_5$ at the interface:[3]

$$w_{Cu} - w_{Cu}^0 [\text{wt. } \%] \approx -40 \left(\frac{d_{pad}^2}{d_{joint}^3} \right) \ell_{(Cu_{0.60}Ni_{0.40})_6Sn_5}, \quad (1)$$

where w_{Cu}^0 and w_{Cu} represent the Cu concentrations (wt. %) in solder before and after the soldering, respectively. The symbols d_{joint} and d_{pad} represent the diameters of the solder joint and the diameter of soldering pad's opening in microns, respectively. The symbol $\ell_{(Cu_{0.60}Ni_{0.40})_6Sn_5}$ is the thickness (in microns) of $(Cu_{0.60}Ni_{0.40})_6Sn_5$ at the interface. This specific $(Cu_{0.60}Ni_{0.40})_6Sn_5$ composition is used because it is the composition observed by many researchers under similar situations.

After a typical reflow, the thickness of $(Cu_{0.60}Ni_{0.40})_6Sn_5$ becomes about 1−2 μm.[4] The drop in Cu concentration for smaller solder joints can be quite substantial according to Eq. (1). For example, if 2 μm of $(Cu_{0.60}Ni_{0.40})_6Sn_5$ forms in the 100 μm/85 μm ball/pad combination, the Cu concentration will drop by as large as 0.58 wt. %. Under such a condition, the remaining Cu concentration in the solder will approach zero because most of the popular commercial SnAgCu solders have Cu concentration less than 0.7 wt. %. Consequently, the phase equilibrium at the interface changes from the $(Cu_{1-x}Ni_x)_6Sn_5 + L$ two-phase region to the $(Ni_{1-y}Cu_y)_3Sn_4 + L$ two-phase region, and there will be a driving force for $(Cu_{1-x}Ni_x)_6Sn_5$ to leave the interface in order to form a more stable $(Ni_{1-y}Cu_y)_3Sn_4$.

To test this theory, three different sizes of Sn3Ag0.6Cu solder balls, 760, 500, and 300 μm, were planted onto 375 μm Ni soldering pads, and reflowed at 235 °C for 20 min. As shown in Fig. 2, the $(Cu_{1-x}Ni_x)_6Sn_5$ thickness after reflow was 2.3, 1.7, and 1.6 μm for 760, 500, and 300 μm balls, respectively. The corresponding drop of Cu concentration according to Eq. (1) was 0.03, 0.08, and 0.33 wt. %, respectively. In other words, the remaining Cu concentration in the solder was 0.57, 0.52, and 0.27 wt. %, respectively. Therefore, for the cases of 760 and 500 μm balls, the equilibrium at the interface remained in the $(Cu_{1-x}Ni_x)_6Sn_5 + L$
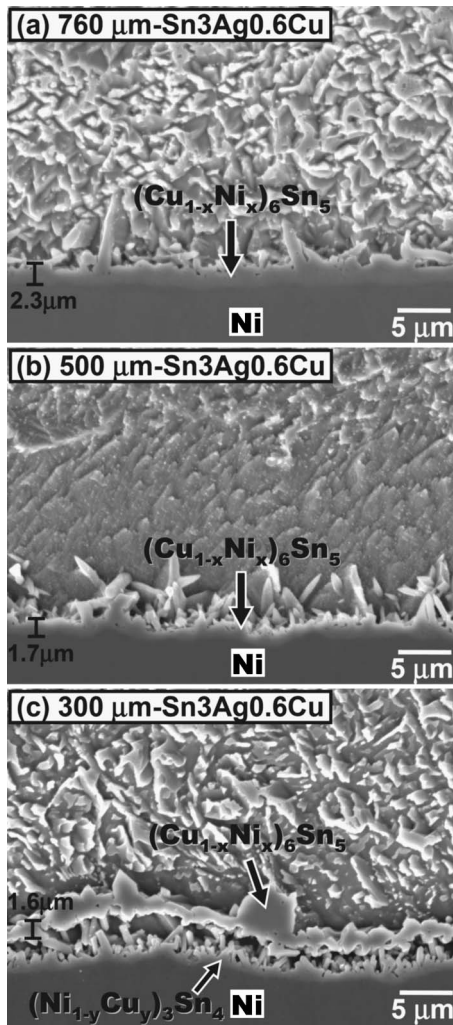
FIG. 2. (a) Micrograph showing the interface of a solder joint by reflowing a 760 μm Sn3Ag0.6Cu solder ball on a 375 μm opening Ni pad. The reaction conditions were 235 °C for 20 min. No spalling had occurred as the residual Cu concentration was 0.57 wt. % according to Eq. (1). (b) Same as (a) but the ball diameter was 500 μm. No spalling occurred as the residual Cu concentration was 0.52 wt. %. (c) Same as (a) but the ball diameter was 300 μm. Spalling had occurred because the residue Cu concentration was only 0.27 wt. %.

FIG. 3. (a) Micrograph showing the massive spalling in a SnZn/Cu solder joint after reaction at 250 °C for 10 min. The spalled layer was CuZn. (b) Sn-rich corner of the Sn-Zn-Cu isotherm at 250 °C. This isotherm was redrawn based on the information determined by Chou *et al.* (Ref. 13).

two-phase region, and there was no spalling as shown in Figs. 2(a) and 2(b). Nevertheless, for the case of 300 μm ball, the equilibrium at the interface shifted from the $(Cu_{1-x}Ni_x)_6Sn_5 + L$ two-phase region to the $(Ni_{1-y}Cu_y)_3Sn_4 + L$ two-phase region, and $(Cu_{1-x}Ni_x)_6Sn_5$ indeed left the interface, as shown in Fig. 2(c). A layer of $(Ni_{1-y}Cu_y)_3Sn_4$ formed between Ni and solder at the interface.

In summary, two conditions are necessary for the occurrence of the massive spalling. The number one condition is that at least one of the reactive constituents of the solder (Cu in the present case) must be present in a limited amount so that during reaction its concentration can have a substantial change. The second condition is that the soldering reaction must be very sensitive to the concentration of this constituent so that the concentration change during reaction can induce a change in the local equilibrium phase at the interface. Such a change in the equilibrium phase causes the spalling of the phase that is no longer in local thermodynamic equilibrium.
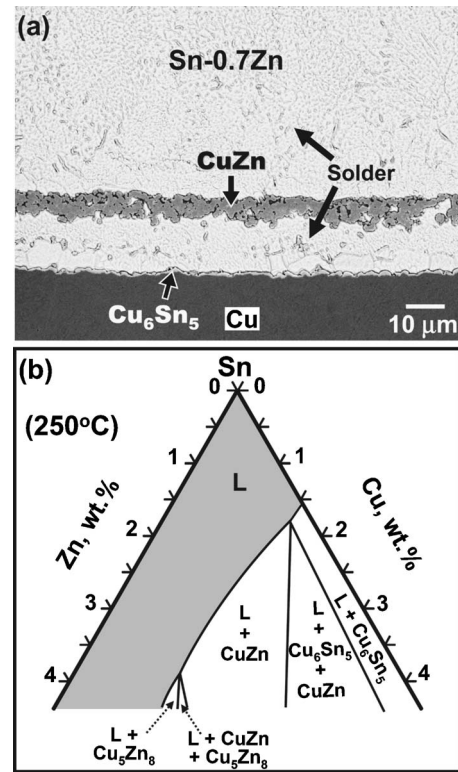
B. Massive spalling in SnZn/Cu

The thermodynamic rationalization presented in the previous section can be extended to explain the massive spalling observed recently in SnZn/Cu.[6] Similar to the SnAgCu/Ni system, the SnZn/Cu reaction depends strongly on the Zn concentration. According to our previous study,[6] when the Sn concentration was greater than 2 wt. %, only Cu_5Zn_8 formed at the interface. When the Zn concentration was less than 0.5 wt. %, only Cu_6Sn_5 formed. Additionally, Zn is a minor, but the most reactive, constituent in SnZn. Accordingly, the SnZn/Cu systems meet the two necessary conditions for mass spalling presented in the previous section. The massive spalling indeed occurs in the reaction between Sn0.7Zn and Cu, as shown in Fig. 3(a). A thin layer of Cu_6Sn_5 formed between the solder/Cu interface, causing the spalling of the CuZn from the interface.

The Sn-rich corner of the Sn-Zn-Cu isotherm at 250 °C, redrawn according to the study of Chou and Chen,[13] is shown in Fig. 3(b). Notice that the molten Sn phase can be in two-phase equilibrium with Cu_6Sn_5, CuZn, or Cu_5Zn_8, which depend mainly on the Zn concentration. Similar to the mechanism proposed for the SnAgCu/Ni system, such CuZn massive spalling is attributed to the depletion of the most reactive element (Zn) in the solder. During the reaction, CuZn initially formed at the interface. As this compound grew thicker, more and more Zn atoms became incorporated into CuZn, and the Zn concentration in the solder decreased. When the Zn concentration decreased to such a level that CuZn was no longer in equilibrium with the solder, the equi-

librium phase now became Cu_6Sn_5 and this phase nucleated between CuZn and Cu, and the spalling of CuZn occurred.

The analysis in this section can be extended to Zn-doped SnAg, SnCu, and SnAgCu solders, because Zn is the most reactive constituent in these solders. If the Zn doping is high enough, say, higher than about 0.7 wt. %, the initial compound at the interface will be Sn-Zn based compounds. Nevertheless, if the Zn concentration is very low, Cu-based intermetallic compounds (Cu_6Sn_5 and Cu_3Sn) would be the dominant phases at the interface. Recently, it was reported that, in the SnAgCu/Cu reaction, minor Zn addition into the solder was an effective method for reducing the growth rate of Cu_3Sn, which was responsible for the formation of detrimental Kirkendall's voids.[14] When doping Zn to these solders to avoid the formation of excessive Kirkendall's voids, one must be careful not to exceed a certain maximum level, or massive spalling might occur. We estimate that this maximum level is about 0.7 wt. % Zn. However, more studies are needed to obtain a more precise value.

C. Massive spalling in Pb5Sn/Cu

High Pb solders, such as Pb5Sn, are exempt from the EU RoHS requirements for flip-chip applications, and are expected to be used in this area for an extended period of time in the future. Recently, it was reported that massive spalling could also occur in the Pb5Sn/Cu system.[7,8] As will be shown below, the Pb5Sn/Cu system indeed exhibits the two necessary conditions for massive spalling pointed out in Sec. II A. One apparent difference is that, unlike SnAgCu/Ni and SnZn/Cu, where spalling occurred in the reflow stage when the solder were molten, spalling in Pb5Sn/Cu occurred in the aging stage when the solder was in the solid state. The reason for the occurrence of massive spalling in the solid state will be given below.

It is well known that only Cu_3Sn forms when high-lead PbSn solder is reacted with Cu.[15,16] In the study of Jang *et al.*,[7] the Cu_3Sn layer formed during reflow, and adhered well to the interface after reflow. Spalling of Cu_3Sn was not observed after 200 h of solid-state aging at 170 °C, and only after 500 h of aging could spalling of Cu_3Sn be observed.[7] Shown in Fig. 4(a) is the microstructure of spalling after solid-state reaction at 170 °C for 1000 h.[7] Jang *et al.* pointed out that spalling occurred because Sn near the interface had been consumed locally, and the diffusion of Sn in the solder was so slow that those Sn atoms far away from the interface could not diffuse back to the interface fast enough to keep the Sn concentration up. According to the Pb-Sn-Cu isotherm shown in Fig. 4(b), the local equilibrium at the interface changes from the $Cu_6Sn_5+(Pb)$ two-phase field, to the $Cu_3Sn+(Pb)$ two-phase field, then to the $(Cu)+(Pb)$ two-phase field with decreasing Sn concentration. Therefore, spalling was again caused by the depletion of the most reactive constituent (Sn in the present case) in the solder, although here the depletion occurred only locally near the interface. In fact, it had been shown in a follow-up study[8] that spalling would not occur in Pb10Sn/Cu diffusion couples subjected to the same treatment because the supply of Sn was more abundant.
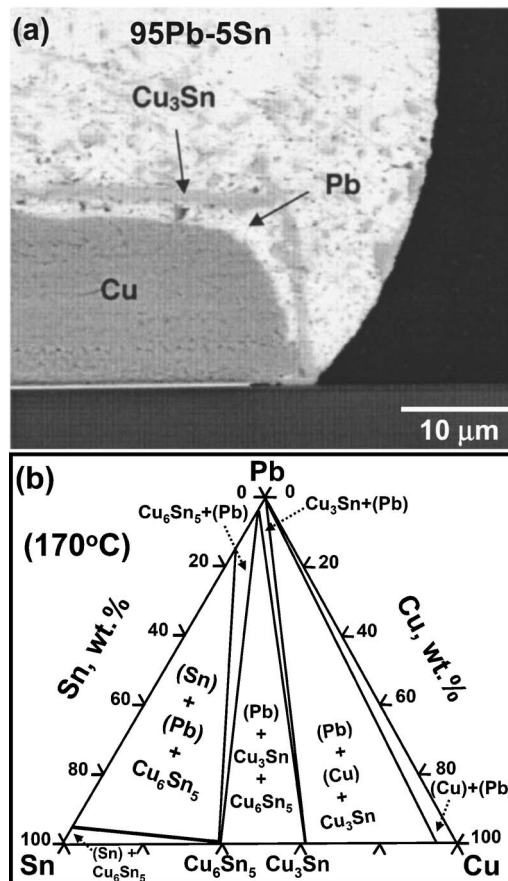

FIG. 4. (a) Micrograph showing the massive spalling in a Pb5Sn/Cu solder joint after aging at 170 °C for 1000 h observed by Jang *et al.* (Ref. 7). The spalled layer was Cu_3Sn. (b) The Pb-Sn-Cu isotherm at 170 °C. The phase relations in this isotherm are from the study of Tu and Zeng (Ref. 1).

The reason that spalling did not occur in the reflow stage was twofold. The number one reason was that the formation of Cu_3Sn consumed relatively less Sn because the Cu/Sn atomic ratio in Cu_3Sn is 3:1. The formation of the Cu_3Sn layer did not significantly reduce the total amount of the available Sn atoms in Pb5Sn. The second reason is that Sn diffusion in the molten solder was much faster so that the Sn concentration near the interface never dropped below the level where Cu_3Sn was no longer in equilibrium with the molten solder. Only in the solid state could the local Sn concentration near the interface drop below the level leading to mass spalling.

D. Massive spalling in Pb5Sn/Ni

The Pb5Sn/Ni also exhibits the two necessary conditions for massive spalling, and massive spalling was indeed observed in this system.[9] Figure 5(a) shows the massive spalling of Ni_3Sn_4 after reaction at 350 °C for 90 min,[9] and Fig. 5(b) shows the 250 °C Pb-Sn-Ni isotherm calculated by Ghosh.[17] The Pb-Sn-Ni isotherm at 350 °C is not available, but the 250 °C isotherm should give a reasonable approximation of the geometry of the phase relationships. Figure 5(b) shows that the equilibrium phase with (Pb) changes from Ni_3Sn_4 to Ni_3Sn_2, and then to Ni_3Sn, upon decreasing the Sn concentration. Therefore, as more and more Sn atoms were incorporated into the growing Ni_3Sn_4, the Sn concen-
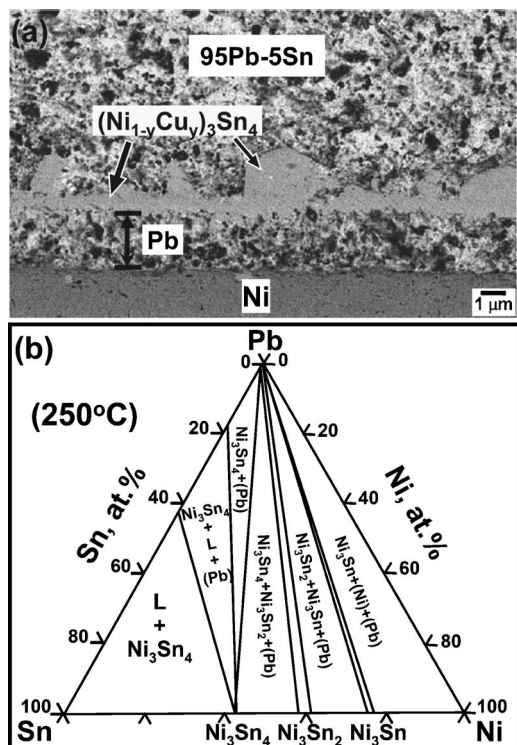
FIG. 5. (a) Micrograph showing the massive spalling in a Pb5Sn/Ni solder joint after reaction at 350 °C for 90 min observed by Wang and Chen (Ref. 9). The spalled layer was $(Ni_{1-y}Cu_y)_3Sn_4$. (b) Pb-Sn-Ni isotherm at 250 °C. The phase relations in this isotherm are from the study of Ghosh (Ref. 17).

tration decreased. Eventually the Sn concentration dropped to a level where Ni_3Sn_4 was no longer stable at the interface, and the spalling of this compound occurred.

In contrast to the Pb5Sn/Cu reaction, mass spalling could occur during the reflow stage in the Pb5Sn/Ni reaction. The reason was that the growth of the reaction product Ni_3Sn_4 required a larger amount of Sn. The atomic ratio of Ni/Sn was now 3:4. Even with this higher amount of Sn consumption, the reaction time had to be as long as 90 min to consume enough Sn to bring the Sn concentration down to the level required for massive spalling.

III. DISCUSSION

Despite several differences between the regular spalling and the massive spalling discussed in the previous sections, these two types of behavior do share one common feature in that they are all due to the exhaustion of a limiting constituent. In regular spalling, it occurs after the exhaustion of the reaction layer of the substrate,[1,2] and in massive spalling, it occurs when the reactive constituent in the solder falls below a certain level.

According to the arguments presented in Sec. II, several factors tend to favor the occurrence of mass spalling. The number one factor is the original composition of the reactive constituent of the solder [w^0 in Eq. (1)]. If this composition is much greater than the threshold concentration required to change the equilibrium phase at the interface, then the mass spalling is less likely or will take a longer time to appear. This was indeed the case for the Pb5Sn/Cu reaction. In this case, the formation of Cu_3Sn during reflow simply could not

lower the Sn concentration to the required level. The massive spalling could only occur during the aging stage when the diffusion of Sn in solid solder was slow.

The second factor that can influence massive spalling is the reflow time. The thickness of the compound at the interface grows with the reflow time, and according to Eq. (1), the thicker the compound is at the interface, the larger is the drop in the concentration of the most reactive component. Therefore, the longer the reflow time is, the greater will be the chance for occurring massive spalling.

The third factor is the solder joint size. For industrial applications, it is typically $d_{joint} \sim 1.2 d_{pad}$. As a result, the concentration drop is proportional to $1/d_{joint}$, and will be large for smaller d_{joint}. In other words, smaller joints tend to favor the occurrence of massive spalling.

The last factor is the existence of certain other coating layer on the substrate. For example, in the SnAgCu/Ni case, our preliminary study shows that a thin layer of Au over the Ni substrate tends to favor the occurrence of massive spalling. The reason for this Au effect is not clear at this moment, and a detailed study is underway to uncover this phenomenon.

It should be emphasized that the arguments presented here are purely thermodynamic in nature. Nothing is said about dynamically how massive spalling occurs. In other words, we only identify the driving force for the massive spalling. The step-by-step mechanism is an important and extremely interesting area worthy of more studies. Without question, the interfacial energy must play an important role in "peeling" the intermetallic layer away from the interface.

IV. SUMMARY

A unified thermodynamic argument is presented to rationalize the occurrence of the massive spalling in four different solder/substrate systems, including SnAgCu/Ni, SnZn/Cu, PbSn/Cu, and PbSn/Ni. The massive spalling occurs because, during reaction, the original reaction product at the interface is no longer in local thermodynamic equilibrium with the solder, and this compound is driving away to make room for the nucleation and growth of the equilibrium phase. Two necessary conditions for the occurrence of massive spalling are identified. The number one condition is that the reactive constituent must be present in a limited amount, and the second is that the soldering reaction must be very sensitive to the concentration of this element. Four factors are identified to favor the occurrence of the mass spalling: smaller initial concentration of the reactive constituent, longer reaction time, smaller joint size, and the presence of certain coating layer over the substrate.

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