Surface Oxidation of Molten Sn(Ag, Ni, In, Cu) Alloys

Y.Y. Lee, H.W. Tseng, Y.H. Hsiao, and C.Y. Liu

The surface oxidations of molten Sn(Ag, Ni, In, Cu) alloys are studied. We conclude that the microstructure (phase and density) of the surface oxide layer is the key factor for the surface oxidation formation. Also, we found that the microstructure (phase and density) of the Sn surface oxide layer is highly influenced by the additives in the solder alloys, which can be roughly anticipated from the additives' electromagnetic field values and Gibbs free energies of oxide formation. The detailed effect (either retarding or enhancing) of the additives on the surface oxidation is discussed in this paper.

INTRODUCTION

PbSn solders have been widely used in solder-joint applications in the integrated circuit (IC) packaging industry. One of most important merits of PbSn solders is their excellent wettability on various metal pads, such as Cu, Ni, and Au. The excellent wettability of PbSn solders comes from the low surface tension and a very limited surface oxidation formation during soldering. Nowadays, due to environmental concerns, PbSn solders have been banned from the IC package industry. Currently, Sn-rich solders have become the major drop-in solution for the replacement of PbSn solders in the IC packaging industry. Yet, the oxidation of Sn-rich solders is more serious than that of PbSn solders. Furthermore, the Sn surface oxide layer is much tougher than that of Pb oxide on the PbSn surface. The tough Sn surface oxide layer of the Pb-free Sn-rich solders would cause serious problems for wave soldering. One of the most critical problems for wave soldering is the surface oxidation on the molten solder pot, which creates a "drossing" problem during the wave soldering process.[1] The surface oxidation of the molten Sn-rich solder is also a concern for the soldering process of flip-chip and ball-grid array (BGA) solder joints. Although flux usually is applied during soldering, any remaining surface oxide on the wetting front of the spreading molten solder would cause poor wettability on the metal bond pad. The current Pb-free Sn-rich solders usually contain metallic additives, such as Cu, Ag, In, and Ni. In this work, we studied how the metallic additives in the Sn-rich solders affect their surface oxidation.

How would you…

…describe the overall significance of this paper?

The overall significance of this paper is that we understand more about the roles of additives in the Pb-free Sn-rich solders play on their surface oxidation formation. The additives would either enhance or retard the surface oxide formation. As two additives are added in Sn with enhancing and retarding effects, respectively, the ultimate Sn surface oxidation depends on the relative concentration ratio between the two additives.

…describe this work to a materials science and engineering professional with no experience in your technical specialty?

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…describe this work to a layperson?

Currently, Sn-rich solders have become the major drop-in solution for the replacement of PbSn solders in the IC packaging industry. Yet, the oxidation of Sn-rich solders is more serious than that of PbSn solders. One of the most critical problems for wave soldering is the surface oxidation on the molten solder pot, which creates a 'drossing' problem during the wave soldering process. The surface oxidation of the molten Sn-rich solder is also a concern for the soldering process of flip-chip and ball grid array solder joints. Here, we studied how the metallic additives in the Sn-rich solders affect their surface oxidation.

EXPERIMENTAL PROCEDURE

The surface oxidations of five Sn-rich solders alloyed with different additives, such as Ni, Ag, In, and Cu, were studied. The content of the additives in the Sn-rich solders ranges from 0.5 wt.% to 10 wt.%. To accelerate the oxidation and obtain accurate measurements of the surface oxidation formation, solder alloys were annealed at a relatively high temperature of 600°C in ambient air. The annealed alloy samples were weighted against the annealing times, then the weight gain was plotted with time. The composition and phase structure of the surface oxide layer were characterized by electron spectroscopy for chemical analysis (ESCA) and x-ray diffraction (XRD).

RESULTS

Oxidation of Binary Sn(M) Alloys

Figure 1a–d plots the weight gain of binary Sn(M) alloys against the annealing time. The curve with the solid markers is the oxidation curve of pure

Sn. We can see that the weight gain of the oxidized pure Sn solder is linear with time. Figure 1a shows the oxidation curves of Sn(Cu) alloys. Clearly, the Cu additive in the Sn(Cu) solder alloys enhances the surface oxidation of the molten Sn(Cu) solder alloys. Unlike the pure Sn, we found that the oxidation curves of Sn(Cu) alloys all have a parabolic relationship with the oxidation time. It suggests that the growth of the surface oxidation of Sn(Cu) alloys could follow the diffusion-controlled process.

As Sn is alloyed with Ag, Ni, and In additives, shown in Figure 1b–d, the surface oxidation is retarded. As shown in Figure 1b, Ag additive apparently slows down the surface oxidation. Also, as the Ag alloying concentration increases, the surface oxidation decreases. Figure 1c shows the oxidation curves of Sn(Ni) alloys. Ni additive also reduces the surface oxidation of the molten Sn(Ni) alloys. But the effect of the oxidation retarding by the Ni additive is smaller than that of the Ag additive. For Sn(In) alloys, as shown in Figure 1d, we find that the weight gain is very little against the oxidation time, compared with Sn alloyed with Ag and Ni additives. This means that In addition can significantly reduce the surface oxidation of molten Sn(In) alloys. Yet, we notice that the oxidation retarding effect by the In additive also depends on the concentration of In additive. For the low-In Sn0.7In alloy, like other Sn(In) alloys, the weight gain of the Sn0.7In is very little in the initial 20-hours annealing. However, the weight gain of the Sn0.7In alloy starts to greatly increase after 20 hours annealing. We believe that the increase jump of the oxidation is due to the substantial depletion in the In additive after 20-hours annealing. Once the In additive is depleted in the Sn(In) alloy, the oxidation behavior of the Sn0.7In alloy is back to being dominated by the pure Sn oxidation.

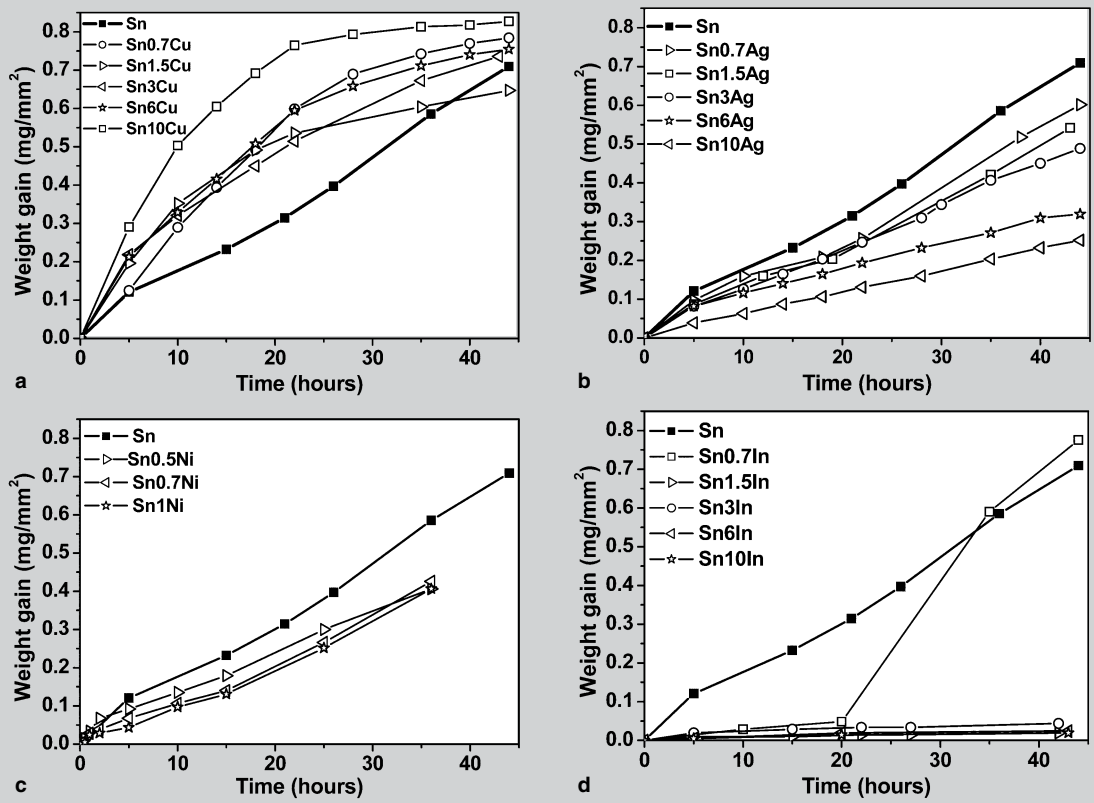

Figure 1. Weight gain of binary Sn(M) alloys against the oxidation time. (a) Sn(Ag) alloys, (b) Sn(In) alloys, (c) Sn(Ni) alloys, and (d) Sn(Cu) alloys.

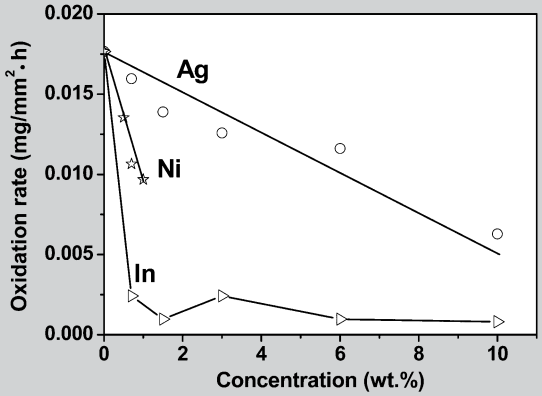

Figure 2. Oxidation rate against the concentration of additives (Ag, In, and Ni).

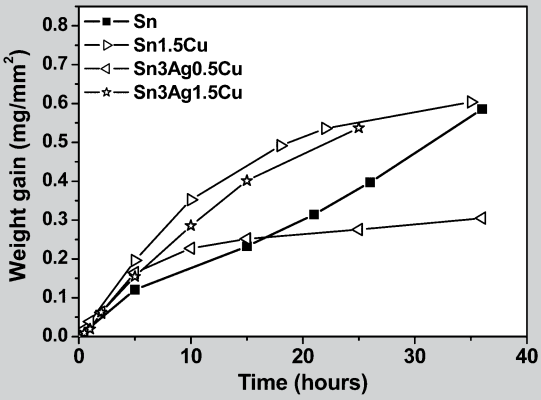

Figure 3. Oxidation curves of ternary Sn-Ag-Cu alloys.

For the above oxidation results of the Ag, Ni, and In additives, we notice that all the oxidation curves have a linear relationship with the oxidation time, which is different from the parabolic curves of the Sn(Cu) alloys. The weight gain of the oxidized Sn(M) alloys is attributed to the oxide formation on the surface of Sn(M) solders. So, the slopes of the linear curves of the molten Sn(M) alloys (in Figure 1) represent the oxidation rates. Figure 2 plots the oxidation rates of Sn(Ag), Sn(Ni) and Sn(In) alloys against the additive concentration. We find that the oxidation rates of Sn(Ag) and Sn(Ni) alloys decrease linearly with the additive concentration.

Oxidation of Ternary Sn(A, B) Alloys

From the oxidation results of the binary Sn(M) alloys, we can categorize the additive elements into two groups: the oxidation-retarding group (Ag, Ni, and In) and the oxidation-enhancing group (Cu). Nowadays, the implementation of Pb-free solders has become a trend for the IC packaging industries. Many promising Pb-free solder alloys have been intensively studied and developed. Currently, most of the promising Pb-free solder candidates often contain two additives such as Sn-Ag-Cu, Sn-Cu-Ni, Sn-Cu-In, Sn-Ag-In, and so on. We realize that many Pb-free ternary solders, for example, Sn-Ag-Cu, Sn-Cu-Ni, and Sn-Cu-In, simultaneously contain the additives belonging to the oxidation-retarding group and the oxidation-enhancing group, respectively. So, it is of interest to study how the surface oxidation of those ternary alloys would behave. In other words, which additive in the ternary solder alloys would dominate the surface oxidation behavior? In the following, the same surface oxidation study is performed on two ternary alloys (Sn-Cu-Ag and Sn-Cu-In) containing the oxidation-enhancing additive (Cu) and the oxidation-retarding additive (either In or Ag). The weight gain of the oxidized ternary alloys is measured against the annealing time.

Figure 3 shows the oxidation curves of ternary Sn-Cu-Ag alloys. Note that the Cu additive has an opposite effect of the Ag additive on the surface oxidation. From the results shown in Figure 3, we can find that the Sn3Ag1.5Cu alloy has a similar oxidation curve with that of the Sn1.5Cu. It implies that the Ag additive shows no effect on the oxidation of Sn3Ag1.5Cu alloy. In other words, the Cu additive dominates the oxidation behavior of the ternary Sn3Ag1.5Cu alloy. For the lower Cu-containing Sn3Ag0.5Cu ternary alloy, the oxidation rate is larger than that of the pure Sn in the initial 10-hour annealing time. Again, it indicates that the Cu additive dominates the surface oxidation in the initial 10-hours annealing. After 10 hours annealing, the oxidation of the Sn3Ag0.5Cu alloy greatly decreased and became lower than the oxidation of pure Sn. This could be because the 0.5 wt.% of Cu content might be greatly consumed after 10-hours annealing. After Cu content is substantially depleted, the 3.0 wt.% Ag additive content takes over and slows down the surface oxidation. From the above discussion, we can conclude that the oxidation-enhancing effect of the Cu additive dominates the surface oxidation behavior over the retarding effect from the Ag additive. Yet, we should note that the above statement is valid only when there is a sufficient Cu additive (over 0.5 wt.%) in the ternary solder alloys.

For Sn-Cu-In ternary alloys, as shown in Figure 4a–c, their oxidation

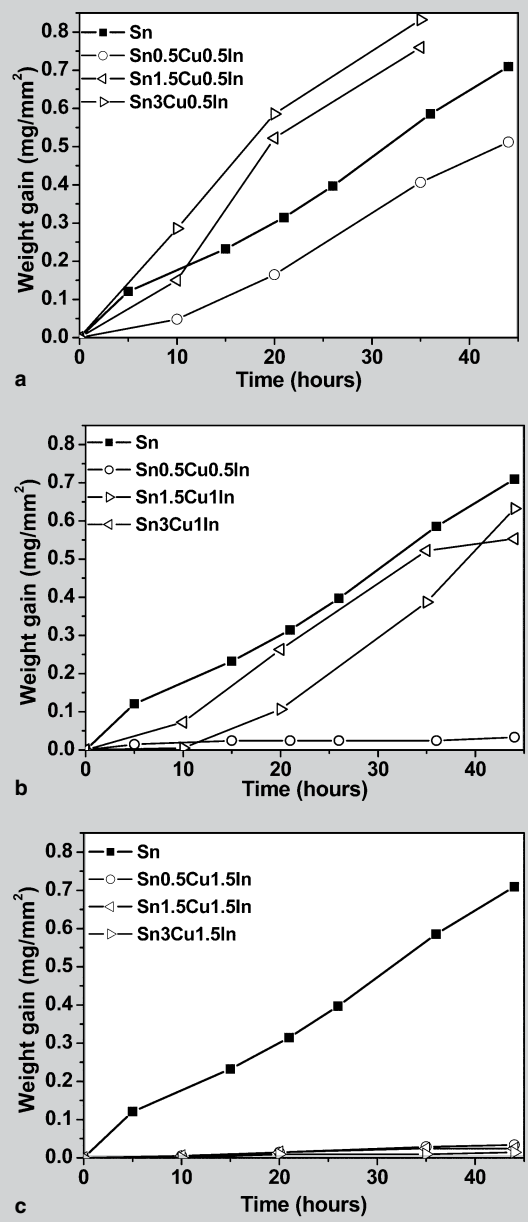

Figure 4. Oxidation curves of Sn-Cu-In alloy system, (a) SnCu0.5In, (b) SnCu1.0In, and (c) SnCu1.5In.

behaviors are divided into three groups for discussion. First, we consider low In-content (0.5 wt.%) alloys. As the content of the Cu additive is larger than 0.5 wt.%, the oxidation-enhancing effect from the Cu additive would dominate the surface oxidation over the oxidation retarding effect from the In additive. Thus, the surface oxidation of low-In Sn-Cu-In alloys (Sn1.5Cu0.5In and Sn3Cu0.5In) is larger than that of pure Sn. On the other hand, if the content of the Cu additive is below 0.5 wt.%, the oxidation retarding effect from the In additive would suppress the oxidation enhancing effect from the Cu additive.

Next we consider medium In-content (around 1 wt.%) alloys. According to the results of binary Sn(In) alloys, we know that if the In additive is over 0.7 wt.%, the surface oxidation would be sufficiently suppressed. So we can expect that the weight gain of the oxidized Sn1.0In should be very little against time. As the Cu additive (over 0.5 wt.%) is added in the Sn1.0In alloy, the oxidation-retarding effect by the In additive is compensated by the oxidation-enhancing effect by the Cu additive. Therefore, as seen in Figure 4b, the oxidation of Sn1.5Cu1In and Sn3Cu1In alloys is only slightly smaller than that of the pure Sn. Yet, if the content of the Cu additive is below 0.5 wt.%, then the compensation effect and the oxidation-enhancing effect by the Cu additive are very limited. The 1.0 wt.% In additive can suppress the surface oxidation, thus, the Sn0.5Cu1In alloy shows very little oxidation weight gain against time. We conclude that the retarding effect from In (1 wt.%) additives would totally dominate the oxidation of Sn-Cu-In alloy, when the content of the Cu additive is smaller than 0.5 wt.%.

Third are high In-content (1.5 wt.%) alloys. In these, the oxidation-retarding effect from the In additive (over 1.5 wt.%) completely overwhelms the oxidation-enhancing effect from the Cu additive. So, as shown in Figure 4c, the surface oxidation of Sn-Cu-In alloys with 1.5 wt.% In content is very little against time.

Figure 5a is a three-dimensional (3-D) diagram showing the oxidation rate against In additive content and Cu additive content. The horizontal section is plotted at the constant oxidation rate of pure Sn, called the Sn-oxidation-rate section. The portion above the Sn-oxidation-rate section defines the composition of the ternary Sn-Cu-In alloys having a higher surface oxidation rate than that of pure Sn surface oxidation. The portion below the Sn-oxidation-rate plane defines the composition of the ternary Sn-Cu-In alloys having a lower surface oxidation rate than that of pure Sn surface oxidation. Figure 5b shows the projection of the curve on the surface of the oxidation rate of ternary Sn-Cu-In alloys intersecting with the Sn-oxidation-rate plane. The projection curve, shown in the In vs. Cu content plot, defines the region of oxidation enhancing and oxidation retarding. With plots of Figure 5a and b, one can predict the oxidation rate of the certain composition of the ternary Sn-Cu-In alloys.

In the above, we have discussed the surface oxidation of the Sn-based ternary solders alloying with two additives having an opposite effect on the

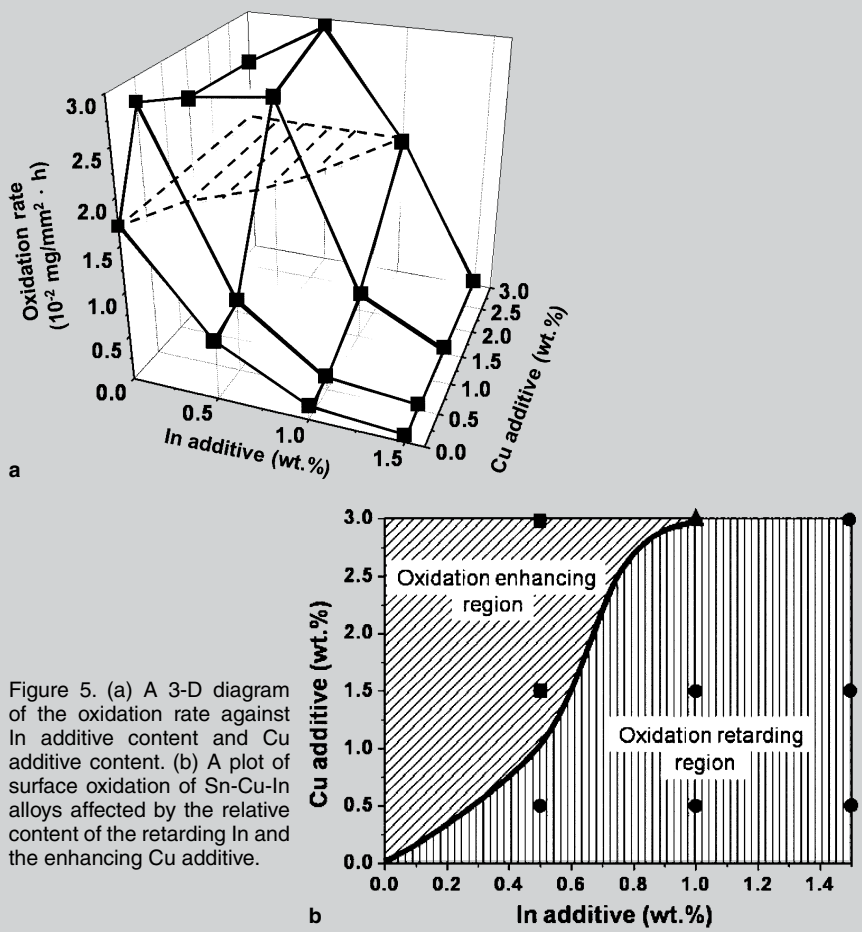

Figure 5. (a) A 3-D diagram of the oxidation rate against In additive content and Cu additive content. (b) A plot of surface oxidation of Sn-Cu-In alloys affected by the relative content of the retarding In and the enhancing Cu additive.

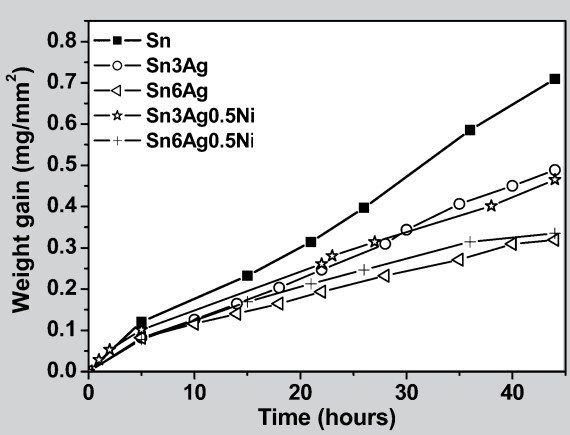

Figure 6. Oxidation curves of Sn-Ag-Ni alloy system.

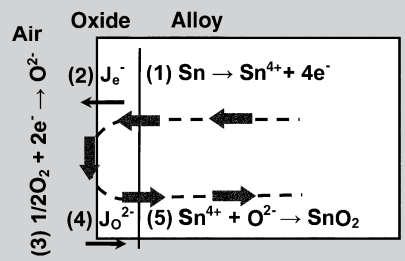

Figure 7. Sn surface oxidation process.

surface oxidation. The ultimate oxidation behavior of the ternary solder alloys would highly depend on the relative concentration ratio of the two additives. Here, we also like to understand what the ultimate oxidation behavior of the Sn-based ternary solders would be if they are alloyed with two retarding additives, for instance, Ag and Ni. Would these two additives exhibit an accumulative effect on the oxidation behavior? Figure 6 shows the oxidation curves of Sn-Ag-Ni and Sn-Ag alloys. We find that the oxidation curve of the Sn3Ag0.5Ni alloy is very similar to the oxidation curve of Sn3Ag alloy. Similarly, the oxidation curve of the Sn6Ag0.5Ni alloy is very close to the oxidation curve of the Sn6Ag alloy. It means that the oxidation-retarding effect from Ag and Ni additives can not be aggregated together on the oxidation of Sn-Ag-Ni alloys.

DISCUSSION

Mechanism of Sn Surface Oxidation

The entire Sn surface oxidation process can be described by five consequent sub-steps, illustrated in Figure 7.[2] At first, the Sn atoms reduce as Sn^{4+} cations at the oxide/Sn interface. Second, the electrons released from the ionization of Sn atoms diffuse through the oxide layer to reach the outer surface of the surface oxide layer. In the third step, O_2 gas molecules adsorb the released electron from Sn ionization and form O^{2-} ions on the oxide surface. Then, the O^{2-} ions diffuse through the oxide layer and reach the oxide/Sn interface. Finally, O^{2-} ions react with Sn^{4+} ions and form Sn oxide phase at the oxide/Sn interface. It has been reported that the most outer Sn oxide phase is SnO.[3] The SnO phase eventually would transform to SnO_2 phase after prolonged annealing. The density difference between SnO and SnO_2 phase is about 5%.[3] So, the SnO-SnO_2 phase transformation would generate an internal stress, which leads to cracking and pores in the Sn surface oxide layer. As a result, the Sn surface oxide layer usually appears in a porous structure.[3] The porous structure of the Sn surface oxide layer enables a fast O^{2-} diffusion through the Sn surface oxide layer.

Effect of Additives on Surface Oxide Formation

Upon reviewing the mechanism of the Sn surface oxidation, we know that metallic additives (M) could affect the surface oxidation of Sn(M) alloys during Sn ionization and oxide formation at the oxide/Sn(M) interface. Table I lists electromagnetic field (EMF) values and Gibbs free energies of the oxide formation of In, Ni, Sn, Cu, and Ag.[4] As Sn alloyed with the additives with more negative EMF value than Sn, the additives have a higher tendency to ionize than Sn does at the oxide/molten solder interface. Therefore, the additives with more negative EMF value would likely ionize first and possibly suppress the Sn ionization. In addition, if the additives' Gibbs free energy of oxide formation is larger than that of Sn, the additives would be more prone to forming their oxide phases on the surface of the molten solders than Sn. On the contrary, if Sn is alloyed with additives with a higher EMF value than Sn, Sn ionization would dominate. Thus, Sn oxide would be the dominant oxide phase on the surface of molten Sn(M) alloys. So, EMF values and Gibbs free energies of oxide formation of the additives in solder alloys can roughly give us an idea about the possible major oxide phase on the surface. The resultant surface oxide phase and its structure are the key factors affecting the O^{2-} ions diffusion in the oxide layer, which likely is the controlling step for the surface oxidation.

Enhancing Effect of Cu Additive

Our present results have shown that the Cu additive would greatly enhance the surface oxidation of Sn(Cu) alloys. Since the Cu additive has a larger EMF value than Sn, Sn could be assumed to ionize before Cu does. In addition, Gibbs free energy of Cu oxide formation is much smaller than that of Sn oxide formation. So, the Sn oxide forma-

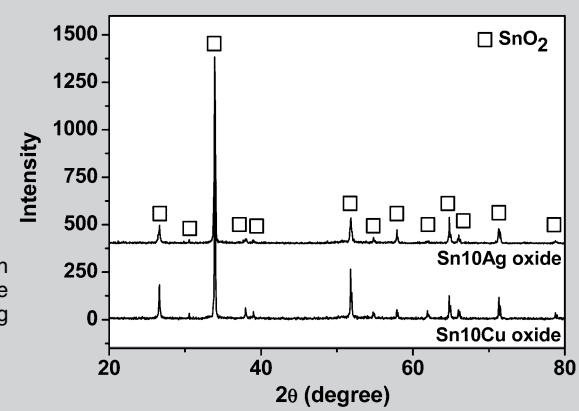

Figure 8. XRD diffraction patterns on the surface oxide layer of Sn10Cu and Sn10Ag alloys.

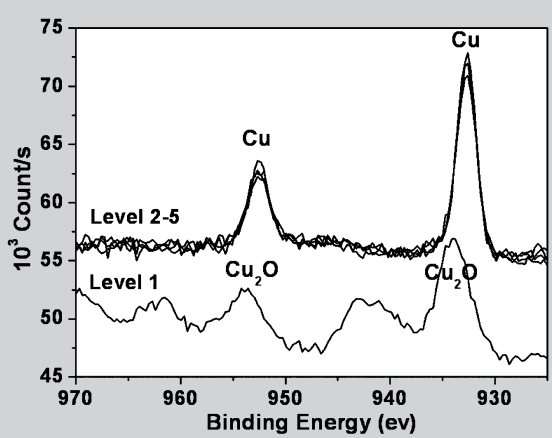

Figure 9. Spectrum of binding energy of Cu solutes in the surface oxide layer of Sn3Cu alloy.

tion should be the predominant process on the surface of Sn(Cu) alloys. While Sn oxides are forming on the surface of the molten Sn(Cu) solders, how does the Cu additive respond to the Sn surface oxide formation? It is very crucial for understanding the oxidation enhancing mechanism of the Cu additive. The Cu additive would either incorporate in the Sn surface oxide or retreat back to the molten Sn(Cu) alloys. X-ray diffraction and ESCA were used to analyze the composition and phase structure of the surface oxide on the Sn(Cu) alloys after a short 10 minutes oxidation time. Figure 8 is the XRD diffraction pattern of the surface oxide layer on the oxidized Sn(Cu) alloy. The diffraction pattern of the surface oxide layer of the oxidized Sn(Cu) shows that the surface oxide only consists of Sn oxide (SnO_2 phase). No Cu oxide can be detected on the surface oxide layer. Figure 9 shows the spectrum of the binding energy of Cu atoms dissolved in the surface SnO_2 layer. Five surface layers on the surface Sn oxide of the oxidized Sn3Cu alloy were analyzed. The depth of each layer is 800 Å. The binding energy of the Cu solute atoms in the first surface oxide layer matches with the Cu-O binding energy of the Cu_2O phase. In the second layer and beyond, the binding energy of the Cu solute atoms belongs to the Cu-Cu binding energy. It implies that while the Sn oxide formed on the surface of the molten Sn3Cu, the Cu additives incorporated into the SnO_2 oxide layer as elemental Cu impurities. The incorporated Cu solute atoms eventually oxidized as Cu oxide phase after prolonged oxidation time. ESCA depth profiling results indicate that the Sn surface oxide phase dissolves a certain percentage of Cu and the Cu concentration in the Sn surface oxide ranges from 3.5 at.% to 6.4 at.%.

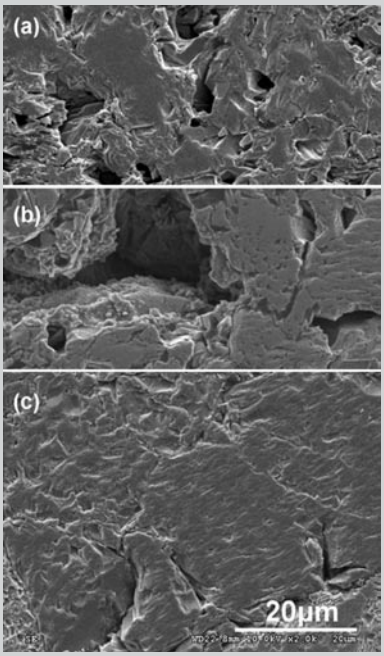

Figure 10. SEM cross-sectional images of the surface oxide of Sn(M) alloys: (a) Sn, (b) Sn3Cu, and (c) Sn3In.

The Cu additive, incorporated in the Sn surface oxide, has two effects on the structure of the Sn surface oxide layer. First, Wagner reports that the Cu solute atoms dissolved in the SnO_2 phase would increase the concentration of O^{2-} anion vacancies, which promotes the atomic diffusion flux of O^{2-} ions.[5] Second, after prolonged annealing, Cu solute atoms would oxidize and form Cu oxide. The formation of Cu oxide inside the Sn surface oxide would cause cracking and facilitate a highly porous surface oxide layer.[6] Figure 10 shows SEM cross-sectional images on the surface oxide of Sn(M) alloys. Big pores can be observed inside the surface oxide of Sn3Cu alloy, which are larger than that in the surface oxide layer of pure Sn cave. The porous surface oxide layer of the Sn3Cu alloys provides more surface diffusion path for O^{2-} ions, which enhances the atomic diffusion flux of O^{2-} ions through the surface oxide layer. So the Cu additive in the Sn(Cu) solders would cause a highly porous surface oxide layer and a higher concentration of O^{2-} vacancies. They are the two main root causes for the oxidation-enhancing effect by the Cu additive.

Retarding Effect of Ag, Ni, and In Additives

The EMF values of Ni and In additives are more negative than that of Sn, so Ni and In additives would be more prone to ionizing and oxidizing than Sn. Figure 11 is the ESCA atomic depth profile on the surface of Sn3In alloy oxidized for 5 minutes at 600°C. The atomic ratio of Sn to In is about 5:1. It is known that SnO_2 and In_2O_3 are miscible and can form a solid solution.[7] So, based on the above two facts, we can estimate that the ratio between SnO_2 and In_2O_3 oxide phases in the surface oxide layer is about 10:1. Figure 10c is an SEM cross-sectional image on the surface oxide of the oxidized Sn3In alloy. We can see that the surface oxide of the Sn3In alloy is relatively dense, compared to other Sn(M) alloys. Thus, the In and Ni surface oxide layers on the molten alloys could serve as a reaction barrier layer retarding the further oxidation formation.[8]

Table I. Electrochemical Potential and Gibbs Free Energy of Metal Oxide Formation of In, Ni, Sn, Cu, and Ag

Reaction	E^0, V	Metal Oxide	$\Delta G°$ (J/mol)
$Ag^+ + e$ Ag	0.7996	AgO	
$Cu^+ + e$ Cu	0.521	CuO	–64793
$Cu^{2+} + 2e$ Cu	0.3419	Cu_2O	–124461
$Sn^{4+} + 2e^-$ Sn^{2+}	0.15	SnO_2	–430398
$Sn^{2+} + 2e$ Sn	–0.1375		
$Ni^{2+} + 2e$ Ni	–0.257	NiO	–173741
$In^{3+} + 3e$ In	–0.3382	In_2O_3	–729731

Unlike other retarding additives (i.e., Ni and In), Ag has a larger EMF value than that of Sn. Yet, instead of having an oxidation-enhancing effect like the Cu additive, the Ag additive reduces the surface oxidation. This implies that the additive with a higher EMF value than Sn would not necessarily promote the Sn ionization and oxidation at the oxide/solder interface. We tend to believe that the key mechanism of the retarding effect by the Ag additive should be the structure of the surface oxide layer.

Figure 12 is the binding energy spectrum of Ag solutes in the Sn surface oxide layer. The results imply that Ag atoms incorporated in the surface Sn oxide layer exist as elemental Ag impurities. The present analysis agrees with the finding by G. Schimmel and M. Rettenmayr on studying the oxidation of Ag1.2Sn2.9In alloys at 600°C.[9] They found that the surface oxide phase of the Sn-In-Ag alloy is Ag-SnO_2-In_2O_3 and Ag are the solute atoms in the SnO_2-In_2O_3 solid-solution phase. In the previous case of Sn(Cu) alloys, the Cu additives dissolved in the Sn oxide would eventually oxidize and form a Cu oxide phase. The formation of Cu oxide in the Sn oxide surface layer caused porosity in the Sn surface oxide layer. In Sn(Ag) alloys, the Ag additive would also embed in the Sn oxide

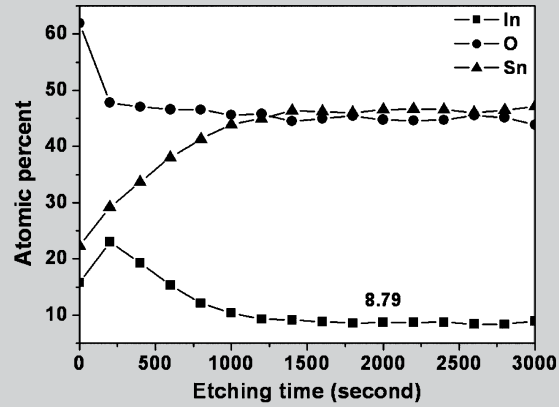

Figure 11. ESCA atomic depth profiling on the oxidized Sn3In alloy.

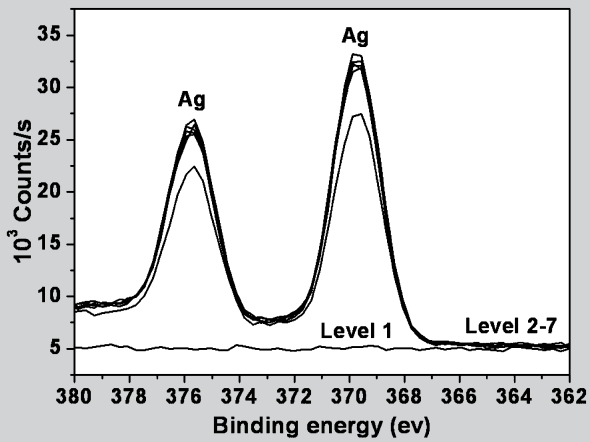

Figure 12. Spectrum of binding energy of Ag solutes in the surface oxide layer of the oxidized Sn3Ag.

layer, but the Ag solutes would not oxidize. So, the surface Sn oxide layer of the oxidized Sn(Ag) alloys is relatively stable and dense. The relatively dense surface SnO_2(Ag) layer should be the main reason for the oxidation retarding effect of the Ag additive.

CONCLUSION

The microstructure of the surface oxide layer is the key factor for the behavior of the surface oxidation. Also, the microstructure of the surface oxide layer is highly influenced by the additives in the solder alloys, which can be roughly anticipated from the additives' EMF values and Gibbs free energies of oxide formation. For example, in the binary Sn-based solders alloyed with the Ni, and In additive with more negative EMF value than Sn, the additives would preferentially form their oxide phases on the surface. The surface oxide would be a mixture of Sn oxide and additives' oxide phases. The mixture surface oxide layers, especially for In and Sn oxides mixture, are very dense and can prevent molten solders from further surface oxidation. On the other hand, alloying with Cu and Ag additives with larger EMF value, the additives have less of a tendency to ionize and oxidize at the oxide/solder interface. They tend to be embedded in the Sn surface oxide layer while the Sn surface oxide layer is forming. A Cu additive incorporated in the Sn surface oxide is found to oxidize in the Sn surface oxide layer eventually. The formation of Cu oxide in the Sn surface oxide layer would cause pores in the Sn surface oxide layer, which is believed to be the main reason for the oxidation-enhancing effect by the Cu additive. An Ag additive would also be embedded in the Sn surface oxide layer, but Ag solutes would not oxidize. Therefore, the Sn surface oxide layer of the Sn(Ag) solder is relatively dense and stable, which is the key for the oxidation-retarding effect of the Ag additive.

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