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EFFECTS OF PLATING CONDITION ON THE GROWTH OF Cu-Sn INTERMETALLIC COMPOUNDS OF 80Sn-20Pb ELECTRODEPOSITS ON Cu-BASED LEADFRAME ALLOY

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ABSTRACT

Alloy deposits of 80Sn-20Pb, electroplated on a Cu-based leadframe alloy from an organic sulfonate bath, were aged at 100, 150, and 180 °C to form Cu-Sn intermetallic compounds at deposit/substrate interface. The growth rate of Cu-Sn intermetallic compounds layer [ε (Cu_3Sn) + η (Cu_6Sn_5)] on aging, followed a parabolic time dependence, exhibited significant difference depending on the deposition condition; it was fastest in an extremely fine deposit formed using pulse current in bath without grain refiner, but slowest in one using dc current in bath with grain refiner. Effects of grain refiner on the growth of Cu-Sn intermetallic compound were discussed.

1. INTRODUCTION

Pb-Sn alloys are usually electrodeposited on copper alloys, especially copper based leadframe alloys for soldering electronic components in the packaging processes. The Pb-Sn on copper alloy produces Cu-Sn intermetallic compounds during soldering process or when the integrated circuited (IC) chips are exposed at elevated temperatures [1, 2]. Although the intermetallic compounds contribute to strong bonding through mutual interdiffusion between Pb-Sn deposit and copper alloy [3], they have detrimental effects on mechanical properties of solder joints because of their brittleness. As the integrated chips are increasingly used in elevated temperature environments such as automobile, nuclear power plants, airplane and etc., the intermetallic compounds are likely to form during operation and reduce the reliability of the solder joints providing both mechanical support and electrical conduction. In view of this importance, extensive study has been done on the crystal structure [4, 5] and morphology [2, 6-8] of Cu-Sn intermetallic compounds, and their effects on mechanical properties of solder [9,10] and on solderability [2, 8]. Most of these studies are concerned with 60Sn-40Pb eutectic alloy of solidified structure. However, similar studies on the electrodeposits of Pb-Sn alloys, especially 80Sn-20Pb, are very limited.

The objective of this study is to elucidate the effects of microstructure of 80Sn-20Pb deposits, as influenced by electrodeposition condition, on the growth of Cu-Sn intermetallic compounds during aging.

2. EXPERIMENTAL PROCEDURE

A rectangular cell (15×8×7 cm^3) was used for the electroplating of 80Sn-20Pb on the Cu-based leadframe alloy (PMC-102M) of 0.3 mm thick, and chemical compositions of which is presented in Table I. 80Sn-20Pb plate was used as the anode. The cathode sheets (PMC-102M) were successively degreased with acetone, washed with distilled water, cleaned in alkaline solution, and activated for 30 seconds in 10 % methane sulfonic acid prior to the plating. All the chemicals used were reagent grade.

Table I. Chemical Composition of the PMC-102M Alloy (wt.%)

Cu	Ni	Si	P	Mg
bal.	1.5	0.3	0.03	0.05

Plating was conducted at room temperature using either dc current or pulse current in methane sulfonic solutions with magnetic stirring at 100 rpm. The distance between anode and cathode was maintained at 10 cm throughout the plating. The compositions of plating bath are shown in Table II. Three different plating conditions, developed in previous study [11], were used to produce the 80Sn-20Pb deposits with different morphologies ; deposit with coarse grain was obtained in bath A at a current density of 10 A/dm^2, and that with fine grain was obtained either in bath A using pulse current of 10 A/dm^2 with 10 % duty cycle and 10 Hz pulse frequency, or in bath B using dc current of 8 A/dm^2. Thickness of 80Sn-20Pb deposits was in the range of 8 to 10 μm irrespective of deposition condition.

Table II. Bath Composition for Eectrodeposition of 80Sn-20Pb

Chemicals	Composition	
	Bath A	Bath B
Pb^{2+}	11 g/ ℓ	7.4 g/ ℓ
Sn^{2+}	28 g/ ℓ	28 g/ ℓ
CH_3SO_3H	103 g/ ℓ	103 g/ ℓ
Additive (TALIN HSM 96)	-	60 mℓ/ ℓ

In order to form the Cu-Sn intermetallic compounds at Sn-Pb deposit/substrate (PMC-102M) interface, the electroplated samples were aged for 3, 12, 24, 48, 72, and 120 hours at 100, 150, and 180 °C in a vacuum tube furnace. The chemical composition across the intermetallic phases of aged samples was measured by energy dispersive X-ray spectroscopy (EDS) attached to a scanning electron microscope (SEM). The interface morphology of η phase (Cu_6Sn_5) between the intermetallic phase and Sn-Pb deposit was observed by SEM after removing the Sn-Pb deposit layer by etching in a solution of 10 g NaOH +7 g Ortho-Nitrophenol + 100 g distilled water for 20 s at 60 °C.

3. RESULTS AND DISCUSSION

3.1 Effects of deposition condition on microstructure of deposits

Microstructure of electrodeposits depends on applied current density (or cathodic polarization), type of current, and bath composition. Fig. 1 shows the surface morphology of 80Sn-20Pb electrodeposits formed respectively in bath A using dc current of 10 A/dm^2, in the same bath using pulse current of 10 A/dm^2 with duty cycle, 10 % and pulse frequency, 10 Hz, and in solution containing grain refining additive (bath B) using dc current of 8 A/dm^2. While the microstructure of 80Sn-20Pb electrodeposit formed using dc current in bath A was very coarse and angular, those formed using either pulse current in bath A or dc current in bath B were extremely fine and round. According to the classical electrodeposition mechanism proposed by Erdey-Gruz and Volmer [12], the critical radius of electrodeposited nucleus for stable growth is inversely proportional to the cathodic overpotential. Mor eover, nucleation rate of electrodeposit is proportional exponentially to the cathodic overpotential. Th-

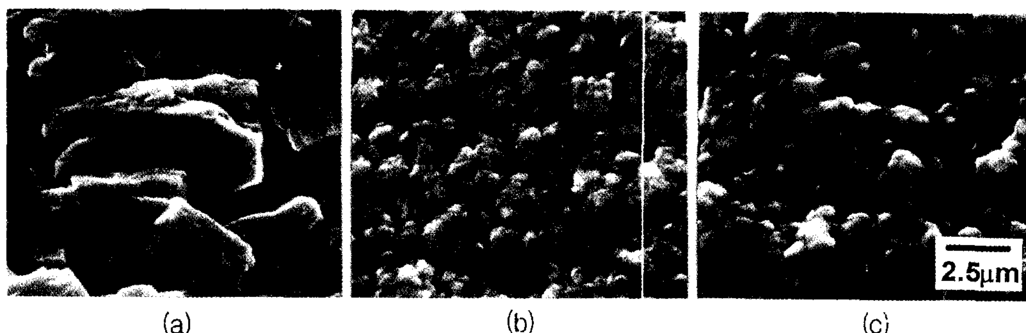


Fig. 1. Scanning electron micrographs on the surface morphology of 80Sn-20Pb electrodeposit formed in (a) bath A at 10 A/dm^2, (b) in bath A using pulse current of 10 A/dm^2 with 10 % duty cycle & 10 Hz frequency, and (c) in bath B at 8 A/dm^2.

us, the higher the cathodic overpotential, the finer is the grain size of electrodeposit.

The cathodic polarization for electrodeposition of Sn-Pb alloy on PMC-102M alloy in bath B was 600 mV greater than that in bath A at 10 A/dm^2, a deposition condition for producing 80Sn-20Pb [11]. Thus,the extremely fine deposit of 80Sn-20Pb, as shown in Fig.1(b), results from the high cathodic overpotential arising by a polarizing effect of grain refiner added in bath B.

Grain refinement of electrodeposits by increasing the cathodic overpotential is also achieved in pulse plating in which the cathodic overpotential increases with increasing the peak current density. Generally, the electrodeposits formed using by pulse current becomes gradually fine with reducing duty cycle and/or pulse frequency for a given average current density. The pulse plating condition applied in this work produced high peak current density of 100 A/dm^2 with a resultant high overpotential, thereby forming an extremely fine deposit of 80Sn-20Pb as shown in Fig. 1(c).

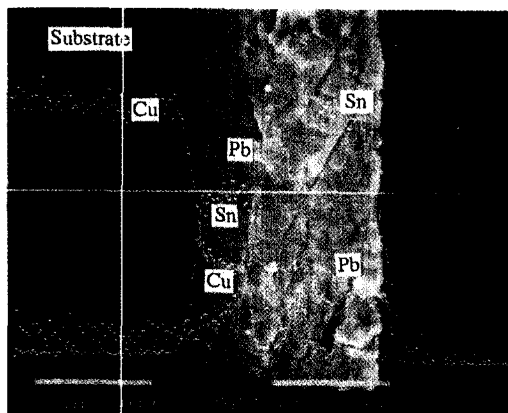


Fig. 2. Elemental EDS line profile for cross section of 80Sn-20Pb deposited on PMC-102 alloy using pulse current in bath A and then aged for 120 hours at 150 °C.

3.2 Growth of intermetallic compounds by aging

It has been reported [13,14] that the η (Cu_6Sn_5) phase forms initially at the copper alloy/Sn-Pb interface when the copper alloy plated with Sn-Pb is aged at elevated temperatures, and then the ε (Cu_3Sn) phase forms later at η/substrate interface Fig. 2 shows EDS line profile for cross section of pulse plated sample aged for 120 hours at 150°C. The formation of ε phase at the η/substrate interface is indicated by two step reductions of copper concentration line across the intermetallic layer in the EDS profile. A Pb-rich zone was formed between the intermetallic layer and the deposit layer due to a segregation of Pb as tin diffused from the Sn-Pb layer into the intermetallic layer during aging.

Effects of deposition condition on the growth of Cu-Sn intermetallic compounds during aging at 150°C are presented in Fig. 3, showing that the thickness of the intermetallic compound layer increased parabolically with aging time, but depended on deposition condition. The intermetallic compounds in pulse plated sample grew most fast probably due to a high diffusion rate of Sn provided by an extremely fine microstructure. On the other hand, that deposited in solution containing additive (bath B) grew most slowly in spite of almost same microstructure as shown in Fig. 1. This is probably

because the additive, incorporated at grain boundary of electrodeposits during plating, inhibits a grain boundary diffusion of Sn to form the intermetallic phases.

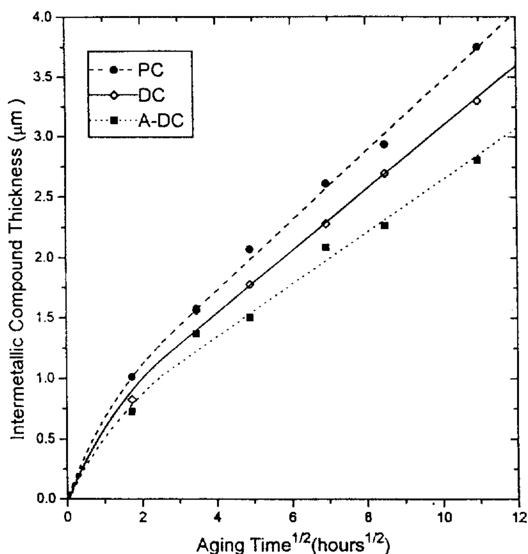


Fig. 3. Thickness of intermetallic compounds layers as a function of aging time for 80Sn-20Pb electrodeposits formed under different plating condition.

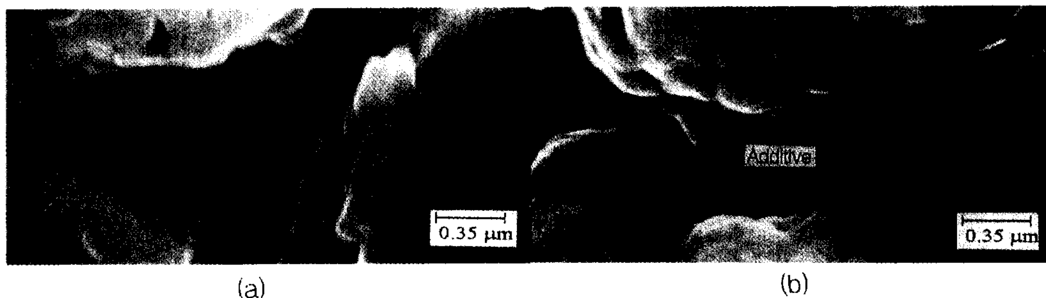
Fig. 4 compares the surface of 80Sn-20Pb electrodeposits formed repectively in bath A with that in solution containing grain refining additive(bath B). Small substances adsorbed at grain boundary were observed only at electrodeposits formed in bath B (Fig. 4(b)). These substances were confirmed as additve previously [11] and presumed to be incorporated into the grain boundary of deposits.

3.3 Morphology of η intermetallic compounds

The surface morphologies of η phase for samples aged for 72 hours were observed by a scanning electron microscope after removing the Sn-Pb layer (outer layer) by etching, and the results are presented in Fig. 5. Evidently, the surface morphology of η phase is significantly influenced by deposition condition ; whereas an interface morphology between Sn-Pb and η phase, or the surface morphology of η phase on sample deposited using either dc or pulse current in solution without additive (bath A) were observed to be rounded, that of sample deposited in solution containing the additive (bath B) appeared to be angular and coarser. The dependence of grain morphology of η phase for aged sample on the deposition condition is probably due to the difference in diffusion rate of Sn and /or Cu atoms that is influenced by the microstructure of Sn-Pb deposit. For sample deposited in bath B, the grain refining additive incorporated in Sn-Pb deposits presumably retards the growth of intermetallic layer in the thickness direction by delaying the diffusion rate of Cu and/or Sn atoms across the η phase/deposit interface. Instead, the growth of intermetallic layer of the same sample in the lateral direction appears to be promoted, thereby forming the angular and coarse grain, as confirmed in Fig. 5(c).

3.4 Apparent activation energy for the growth of Cu-Sn intermetallic compound

Effects of aging temperature on the growth of Cu-Sn intermetallic compounds at deposit/substrate



(a) (b)

Fig. 4. SEM micrographs of surfaces of 80Sn-20Pb electrodeposits formed (a) in bath A at 10 A/dm^2, and (b) in bath B at 8 A/dm^2

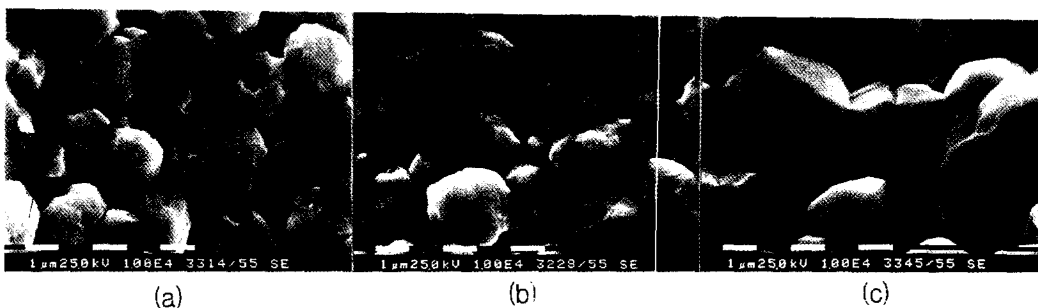


Fig. 5. SEM micrographs showing the surface morphology of η (Cu_6Sn_5) phase formed at the η/80Sn-20Pb deposit interface. The 80Sn-20Pb electrodeposits were formed (a) in bath A at 10 A/dm^2 , (b) in bath A at 10 A/dm^2 of 10 % duty cycle & 10 Hz frequency , and (c) in bath B at 8 A/dm^2 , and then aged for 72 hours at 150 °C.

are presented in Fig. 6. Regression analysis revealed that the data was best fit with a parabolic time dependence as shown in Fig. 6. This suggests that the rate controlling mechanism for the growth of the intermetallic compound is a volume diffusion process.

An apparent activation energy analysis was performed on the growth data. The apparent activation energy remained a generalized parameter because it could not be identified with any one specific, atomic process.. It was assumed that the intermetallic compound layer thickness was represented by the empirical relation[15]:

$$y(t) = y_o + A\, t^n \exp(-Q/RT) \qquad (1)$$

where y(t) is the layer thickness at time, t, y_o is the initial thickness, A is a numerical constant, and n is the time exponent; Q is the apparent activation energy; T is temperature; R is the universal gas constant. The apparent activation energy can be computed from the logarithm-differential of Eq(1):

$$d[\ln(dy/dt)]/d\,(1/T) = -Q/R \qquad (2)$$

Fig. 7 shows Arrhenius plot for the growth of Cu-Sn intermetallic compounds in electrodeposits formed at different deposition conditions. The apparent activation energy for the growth of intermetallic compound in deposit formed repectively in solution containing grain refining additive (bath B), in bath A using dc current, and in bath A using pulse current were computed to be 43.32, 34.36, and 30.53 kJ/mol. The highest value of apparent activation energy for the depsosit formed in bath B due to the fact that grain refining additive inhibits a grain boundary diffusion of Sn to form the intermetallic compounds. In contrast to this,the lowest value of apparent activation energy for deposit formed in bath A using pulse current resutls from a high diffusion rate of Sn provided by an extremely fine microstructure.

4. CONCLUSIONS

1. Addition of grain refining refiner (additive) to methane sulfonic solution increased the cathodic overpotential for electrodeposition of Sn-Pb on Cu based leadframe alloy about 500 mV greater than that in the same solution without the additive at 10 A/dm^2, thereby producing an extremely fine deposit comparable that formed using pulse current with low duty cycle and low frequency.
2. The thickness of Cu-Sn intermetallic compound layer parabolically increased with the aging time, but depended significantly on the microstructure of Sn-Pb electrodeposits that were influenced by dep-

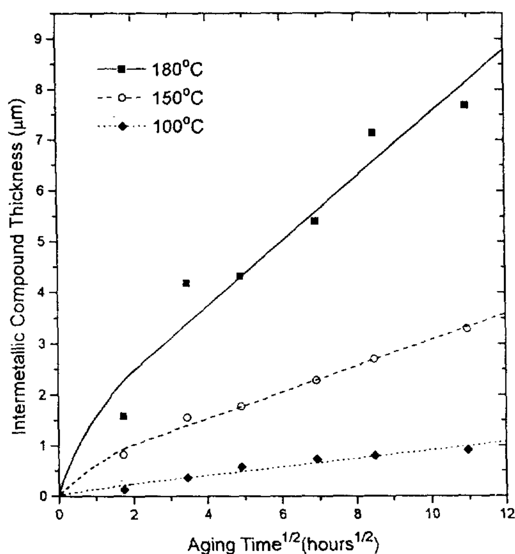


Fig. 6. Effect of aging temperature on the growth of Cu-Sn intermetallic layer at the 80Sn-20Pb deposit/copper leadframe alloy interface.

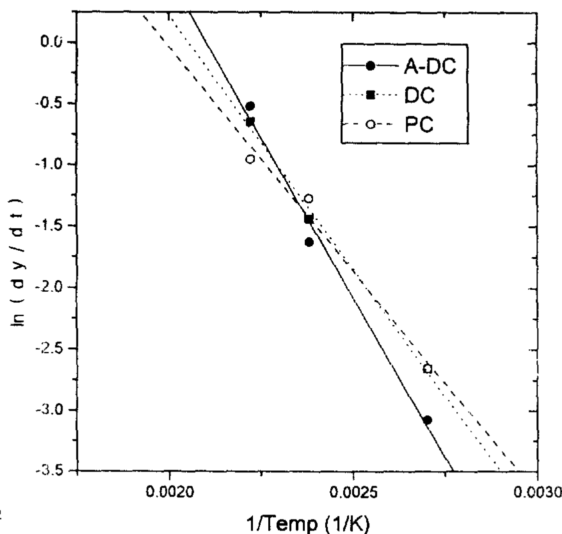


Fig. 7. Arrhenius plot for the growth of intermetallic compound layer of 80Sn-20Pb electrodeposits formed under different plating conditions.

osition condition; it was fastest in the extremely fine deposit formed using pulse current in bath A, but slowest in that formed using dc current in bath containing the additive (bath B) in spite of equivalent grain size.

3. The grain refining additive incorporated in deposits during plating appears to delay the diffusion rate of Sn atom across the deposit/intermetallic layer interface, resulting in slow growth of the intermetallic layer in thickness direction but substantial growth in lateral one.

4. The highest value of apparent activation energy for the growth of intermetallic compound in deposit formed in solution containing grain refining additive (bath B) is due to the inhibiting effect of grain refiner on the diffusion of Sn across the intermetallic/deposit interface.

REFERENCES

[1] P. E Davis , M.E. Warqick, and P J. Kay, Plating and Surface Finishing, 69, 49 (1982).
[2] A. J. Sunwoo, J. W. Morris, Jr., and G. K. Lucey, Jr., Met. Trans. A 23A, 1323 (1992).
[3] M. E. Warwick and S. J. Muckett: Circuit World, 9, 5 (1983).
[4] P. L. Brooks and E. Gilman, Acta Metall., 18, 1181 (1970).
[5] A. GAngulee, G. C. Das and M. B. Bever, Metall. Trans., 4, 2063 (1973).
[6] M. Onishi and H. Fujibuchi, Trans. Inst. Met. Finish, 51, 539 (1975).
[7] K. N. Tu and R. D. Thompson, Acta Metall., 30, 947 (1982).
[8] P. E. Davis, M, E, Warwick and S. J. Muckett, Plat. and Surf. Finish., 70, 49 (1983).
[9] D, Frear, D Grivas, and J. W. Morris, Jr., J. Elect. Mater., 16, 181 (1987).
[10] J. O. G. Paren, D. D. L. Chung, and I. M. Bernstein, J. Mater. Sci., 23, 2564 (1988).
[11] Min-Suk Suh and Hyuk-Sang Kwon, J. Corros. Sci. Soc. of Korea, In press.
[12] T. Erdey-Gruz and M. Volmer, Z.Phys.Chem., 152, 165 (1931)
[13] M. Onishi and H. Fujibuchi, Trans. Jpn. Inst. Met., 16, 539 (1975).
[14] D. A. Unsworth and C. A. Mackay, Trans. Inst. Met. Finish. 54, 85 (1973).
[15] Paul T. Vianco, Paul F. Hlava, and Alice C. Kilgo. J. Elec. Mater. 23, 583 (1994).