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Intermetallic Reactions in Reflowed and Aged Sn-58Bi BGA Packages with Au/Ni/Cu Pads

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The reflow of Sn-58Bi solder joints in a BGA package with Au/Ni/Cu pads has been performed by employing various temperature profiles, which results in the formation of $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ intermetallic flakes in the solder matrix. The reflow operation performed at a peak temperature of 180 °C for a melting time of 80 s gives a ball shear strength of 9.1 N, which decreases drastically to lower values between 6.4 and 4.6 N after further aging at temperatures from 75 to 125 °C. Double layers of intermetallic compounds with the compositions of $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4/Ni_3Sn_4$ can be found at the solder/pad interfaces of the aged Sn-58Bi solder joints. Ball shear testing of the reflowed specimens shows ductile fracture through the solder matrix, which changes to brittle cleavage fracture mainly along the $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$ intermetallic layer after aging at various temperatures. The measurement of ball shear strengths (S) reveals a linear relation with the thicknesses (X) of $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$ intermetallic layers: $S = 7.13 - 0.33X$.

Keywords aging, ball shear strength, intermetallics, reflow, Sn-58Bi solder BGA

1. Introduction

Eutectic Sn-58wt.%Bi alloy has been considered a promising Pb-free solder for low-temperature applications. This alloy possesses the merits of low melting point (138 °C), high tensile strength (Ref 1), and good creep resistance (Ref 2, 3). On the other hand, the Au/Ni metallization has been one of the most commonly used surface finishes for printed circuit boards (PCB) in electronic packages. The Au thin film provides the beneficial effects of oxidation protection and wetting improvement for Cu pads, while the Ni layer acts as a diffusion barrier between Au and Cu. During the reflow process, the Au surface finish dissolves quickly into the solder matrix and a liquid/solid reaction occurs at the interface of Sn-58Bi solder and Ni layer. The resultant intermetallic formation affects the bonding efficiency of the solder joints. In addition, the aging effect caused by heat generated from operating the electronic devices leads to intermetallic growth, and this has become quite an important issue for the reliability of the packages (Ref 4).

The intermetallic reactions occurred at the interfaces between Sn-58Bi solders and Ni substrates have been intensively investigated (Ref 5-8). After aging the Sn-58Bi/Ni solder joints at 85, 100, and 120 °C, Chen et al. reported the formation of Ni_3Sn_4 intermetallic compounds at the interfaces, and the growth kinetics of these Ni_3Sn_4 intermetallics was analyzed and an activation energy of 90 kJ/mol obtained. Chiu et al. (Ref 6) further studied the interfacial reactions between Sn-58Bi solders and Ni substrates at temperatures ranging from 200 to 400 °C. They found a $Ni_3(Sn_{0.99}Bi_{0.01})_4$ intermetallic phase with the composition of $Ni_{41.5}Sn_{57.9}Bi_{0.6}$ formed at the interface, and the intermetallic growth was diffusion-controlled with an activation energy of 28.3 kJ/mol. Kang et al. (Ref 7) also investigated the intermetallic reaction of a liquid Sn-58Bi solder with Ni(0.5-2.0 μm)/Cu(4 μm)/Si substrate and reported the appearance of Ni_3Sn_4 intermetallic compounds at the Sn-58Bi/Ni interface. The growth kinetics of such an interfacial intermetallic was also diffusion-controlled. Young et al. (Ref 8) used electro- and electroless-plated Ni on Cu plates to react with Sn-58Bi solder at 145 and 185 °C. They found that by increasing the phosphorus content, the electroless-plated Ni could act as a good reaction barrier between Sn-58Bi solder and Cu substrate. As the soldering temperature rose, the growth of Ni_3Sn_4 intermetallic compound was accelerated, which allowed the Cu atoms to join in the reaction. In this case, the morphology of the Sn-58Bi/Ni interface would change from faceting to a saw-tooth type.

In a reflowed Sn-37Pb solder BGA package with Au/Ni surface finish, the dissolved Au atoms were found to form flake-shaped $AuSn_4$ intermetallics in the solder matrix, and further aging of the reflowed specimen caused the $AuSn_4$ intermetallic phase to migrate from the solder matrix to the Sn-37Pb solder/Ni layer interface (Ref 9). According to the explanation of Ho et al., it has been the Ni layer that attracts $AuSn_4$ intermetallics and causes their migration to the Ni/Cu pads (Ref 10). However, the behavior of $AuSn_4$ intermetallics in a Sn-3.5Ag solder BGA package with Au/Ni/Cu pads could be quite different. In this case, the $AuSn_4$ intermetallic flakes after aging would continue to remain in the solder matrix. The discrepancy might be attributed to the peening effect of Ag_3Sn precipitates in the Sn-3.5Ag solder matrix on the $AuSn_4$ intermetallic flakes (Ref 11).

In this present study, the morphology and compositions of various intermetallic phases formed in a Sn-58Bi BGA package with Au/Ni surface finish after reflow and aging processes are

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identified. The growth kinetics of intermetallics formed at solder/pad interfaces are analyzed. Finally, the bonding strengths of the solder joints are measured via ball shear testing.

2. Experimental

The Sn-58Bi solder BGA package used in this study contained a Si dummy die on a resin substrate, encapsulated with molding compound. Each substrate was fitted with 49 (7×7) Cu pads which were electroplated with 5 μm thick Ni, and immersion coated with 0.5 μm thick Au. The eutectic point (T_e) of Sn-58Bi as measured by a differential scanning calorimeter (DSC) was 138 °C. The Sn-58Bi (wt.%) solder balls of 0.4 mm in diameter were dipped in rosin mildly activated (RMA) flux, placed on the Au/Ni surface finished Cu pads, and then reflowed in a hot-air furnace. The reflow furnace was installed with five heating zones. Temperature profiles with various peak temperatures (T_{max}) and melting times (Δt_m, $T > T_e$) as shown in Fig. 1 were employed for the soldering process. In addition, a certain number of specimens after reflow at a peak temperature 180 °C for a melting time of 80 s were further aged at 75, 100, 115, and 125 °C for various times ranging from 100 to 1000 h.

The reflowed and aged Sn-58Bi BGA packages were cross-sectioned through a row of solder balls, ground with 2000 grit SiC paper and polished with 0.3 μm Al_2O_3 powder. The microstructure of solder joints was observed using a scanning electron microscope (SEM). The chemical compositions of

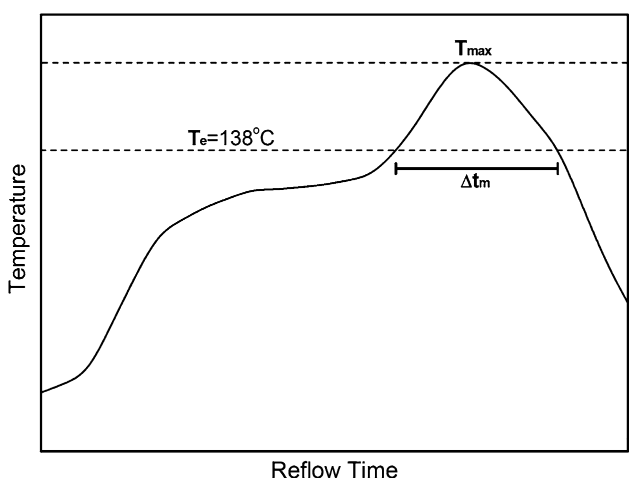

Fig. 1 Temperature profile for the reflow process of Sn-58Bi solder BGA package in this study (T_{max} = peak temperature, Δt_m = melting time for $T > T_e$, T_e: eutectic point)

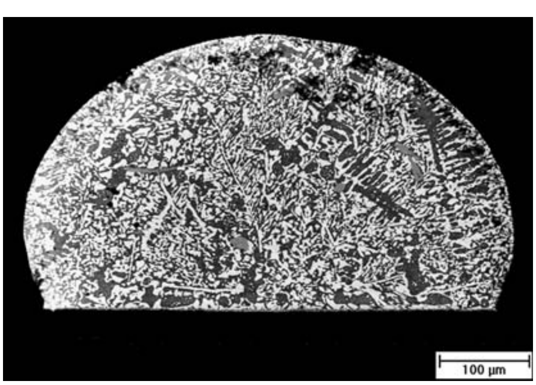

Fig. 2 Typical morphology of a solder ball in Sn-58Bi BGA package after reflow

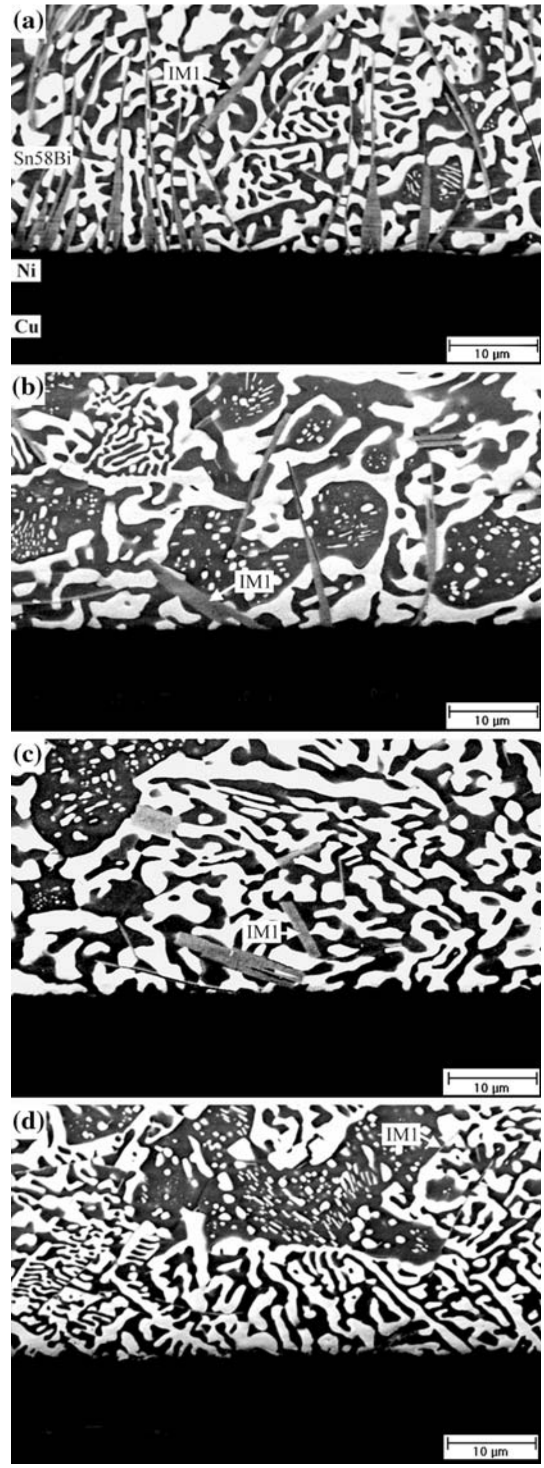

Fig. 3 Microstructure of the Sn-58Bi solder joints reflowed at various peak temperatures for a melting time of 60 s: (a) 160 °C, (b) 170 °C, (c) 180 °C, and (d) 190 °C

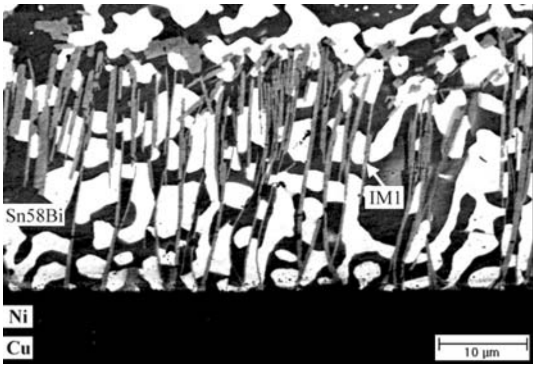

Fig. 4 Intermetallic flakes IM1 tend to form at a distance away from the solder/pad interface after reflowing at 160 °C for a longer melting time of 80 s

various intermetallic phases were analyzed via an energy dispersive x-ray spectrometer (EDX) installed in the SEM. The bonding strengths of the solder joints were measured by ball shear tests, for which the shear rate and shear height were set at 0.1 mm/s and 80 μm, respectively.

3. Results and Discussion

The typical morphology of Sn-58Bi solder balls reflowed on Au/Ni/Cu pads in BGA packages is shown in Fig. 2. The solder ball contains a eutectic lamellar microstructure of pure Bi phase (in white) and β-Sn solid solution (in black). In addition, some flake-shaped intermetallics in the color of gray appear in the solder matrix. EDX analysis indicates that the chemical composition (at.%) of these gray intermetallic flakes is Au:Ni:Sn:Bi = 13.05:6.84:65.63:14.48, which corresponds to the $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ phase (IM1). Metallographic observations of a higher magnification in Fig. 3 reveal that the distribution of these flake-shaped IM1 intermetallic compounds is dependent on the reflow conditions. On the reflow profile having lower peak temperatures (T_{max}), the $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ intermetallic flakes tend to position vertically at the solder/pad interface (Fig. 3a). However, the increase in the peak temperature causes them to form in the solder matrix (Fig. 3b-d). These intermetallic flakes also tend to appear at a distance away from the solder/pad interface on the reflow profile having longer melting time (Fig. 4 and 5). In this case, they will either stay in the interior of the solder matrix or move farther to the outer surface of the solder ball (Fig. 5). Together with the migration of intermetallic compounds, the intermetallic flakes also coarsen into thicker plates (Fig. 5) or even cubic blocks (Fig. 5). It has been mentioned that the Au thin film on Au/Ni/Cu pads dissolves quickly at the onset of the reflow process. Subsequently, the exposed Ni layer will also dissolve into the liquid solder. However, the dissolution rate of Ni is much slower than that of the Au film (Ref 12). The dissolved Au and Ni atoms in liquid Sn-58Bi solder react predominantly with the Sn element to form $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ intermetallic flakes (IM1) in between the Bi lamellae. The increase in peak temperature (T_{max}) or melting time (Δt_m) of the reflow profile causes these Au and Ni atoms to diffuse to greater distances and precipitate farther away from

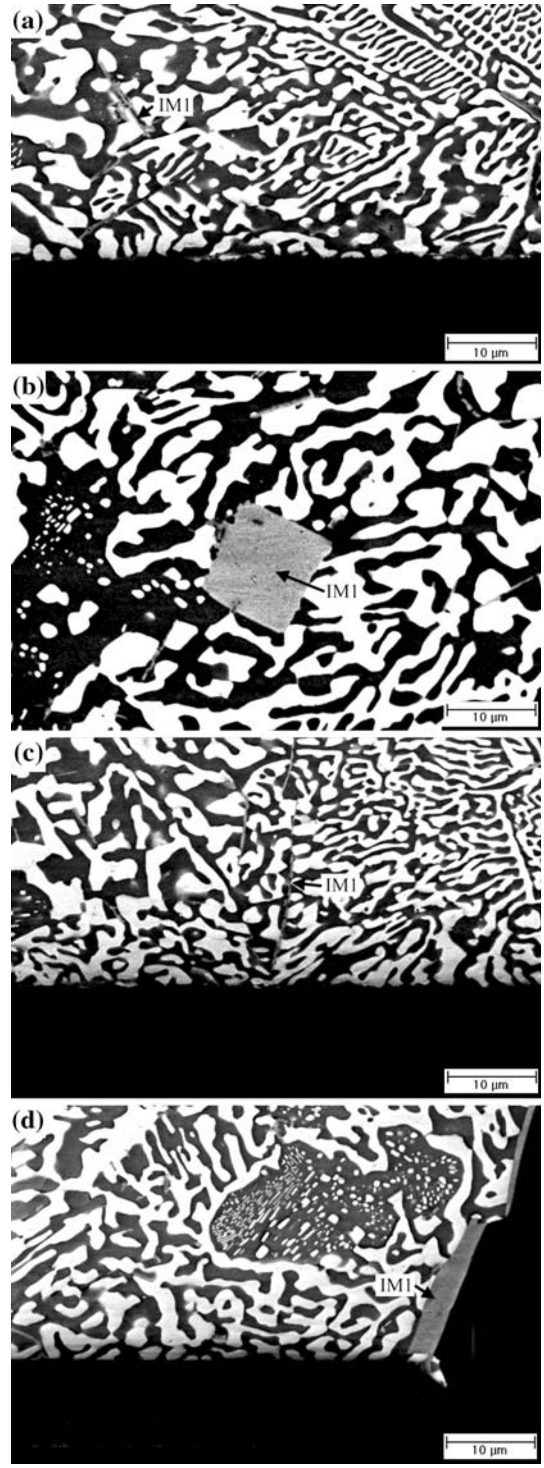

Fig. 5 Microstructure of the Sn-58Bi solder joints reflowed at the peak temperatures of 160 °C (a, b) and 190 °C (c, d) for a longer melting time of 140 s

the solder/pad interface. It is the surface tension that causes them to coarsen into thicker plates or cubic blocks.

The specimens reflowed at the peak temperature of 180 °C for the melting time of 80 s have been further aged at temperatures ranging from 75 to 125 °C for various times from 100 to 700 h. It can be seen in Fig. 6 and 7 that a gray layer of intermetallic phase (IM2) appears at the solder/pad interface,

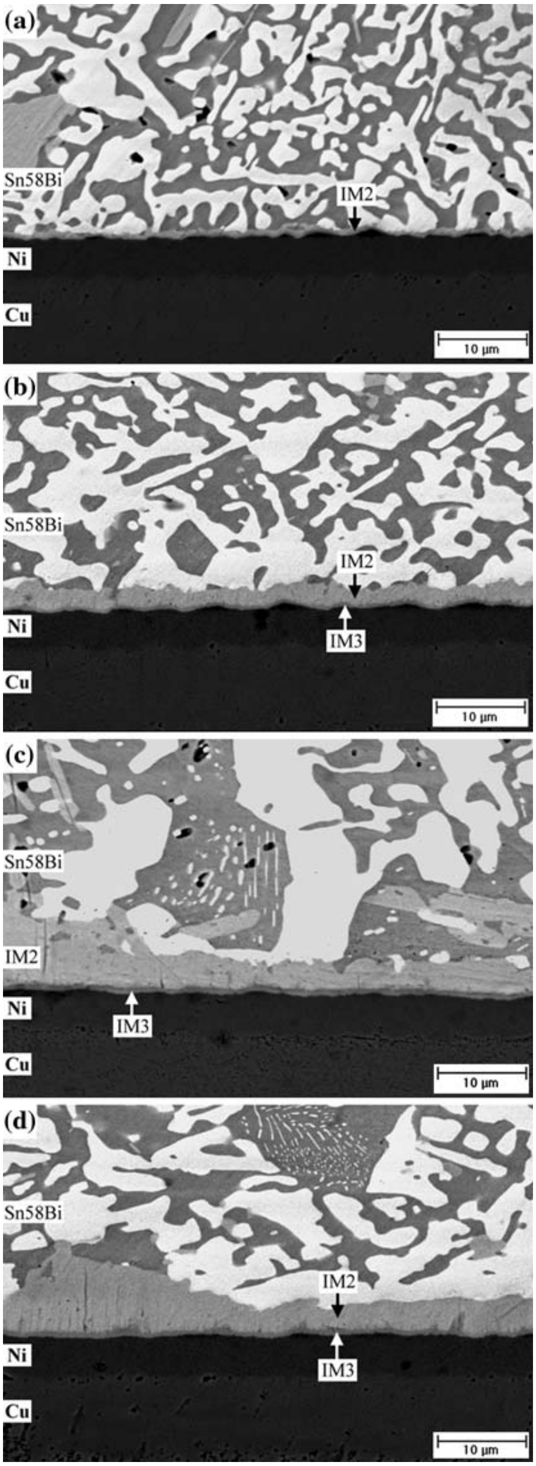

Fig. 6 Microstructure of the Sn-58Bi solder joints after aging at various temperatures for 100 h: (a) 75 °C, (b) 100 °C, (c) 115 °C, and (d) 125 °C

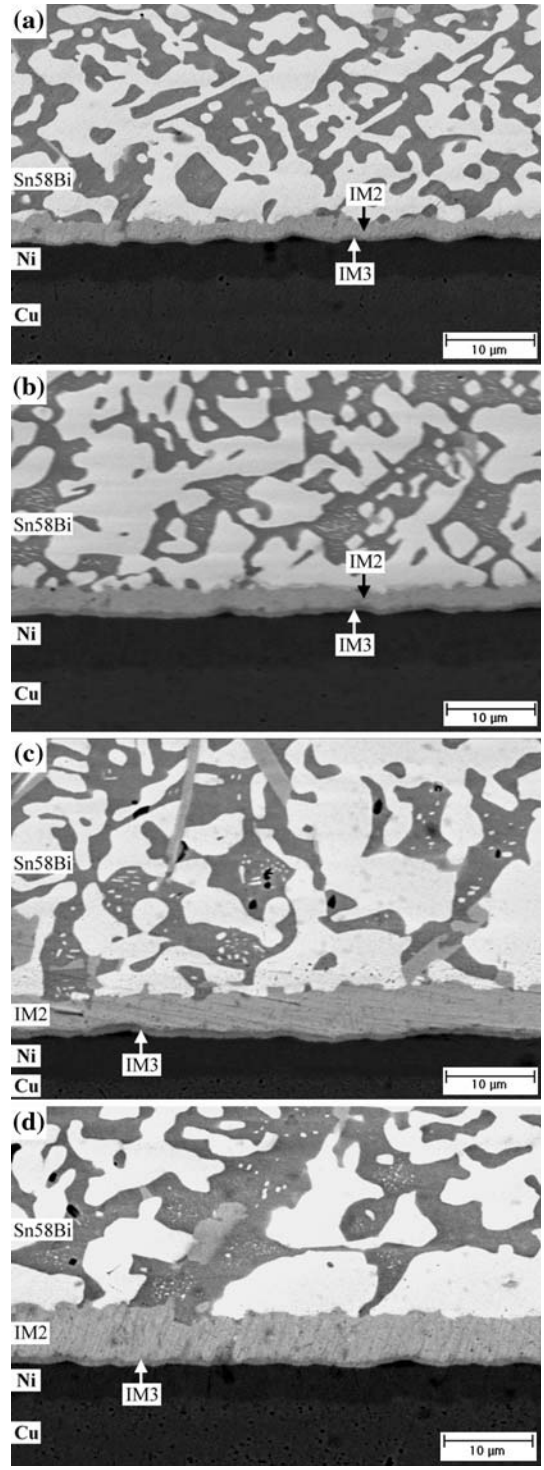

Fig. 7 Microstructure of the Sn-58Bi solder joints after aging at 100 °C for various times: (a) 100 h, (b) 300 h, (c) 500 h, and (d) 700 h

which grows with the increase of aging temperature and aging time. The chemical compositions of IM2 intermetallic compounds formed in the Sn-58Bi solder joints after aging under various conditions are listed in Table 1. As such a gray interfacial intermetallic phase (IM2) grows, another thin intermetallic phase (IM3, in dark color) forms between IM2 layer and Ni/Cu pad. EDX analysis indicates that the gray and dark intermetallic layers possess compositions of $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$ and Ni_3Sn_4, respectively. It is evident that the $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ intermetallic flakes (IM1) in the solder matrix have migrated to the solder/pad interface, which is similar to the case reported for a Sn37Pb BGA package by Minor and Morris (Ref 9). From Table 1, in which the compositions of IM1 and IM3 are also included for comparison, the interfacial intermetallic phase IM2 has higher Ni and Sn contents than the IM1 flakes in the solder matrix. It implies that the $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ intermetallics (IM1) migrated toward the Ni layers on Cu pads have reacted simultaneously with the Ni atoms, causing its composition to change to $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$. Further increasing the aging time and temperature, the Sn atoms in the Sn-58Bi solder matrix have diffused through the IM2 intermetallic layer to react with the Ni layer on Cu pads to form the Ni_3Sn_4 phase (IM3).

The growth thicknesses (X) of IM2 and IM3 intermetallic layers formed at the solder/pad interfaces after aging at various temperatures are measured and presented as a function of the square root of aging time ($t^{1/2}$) in Fig. 8. All plots show a linear relation, which indicate that the growth kinetics for both IM2 and IM3 intermetallic compounds is diffusion-controlled. The growth rate constants ($K = X/t^{1/2}$) of both intermetallic layers are also calculated from Fig. 8 and plotted in an Arrhenius diagram in Fig. 9. The slopes of both curves give the activation energies (Q) for the growth of IM2 and IM3 intermetallic compounds, which are 58.06 and 80.28 kJ/mol, respectively. Yeh and Huntington (Ref 13) reported that the activation energy for the lattice diffusion of Ni atoms in Sn is 54.2 kJ/mol. This value is quite consistent with the activation energy for the growth of IM2 intermetallics, which confirms the above inference that the diffusion of Ni atoms through the $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ phase causes the change of its composition to $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$. On the other hand, the activation energy for the self-diffusion of Sn as measured by Lange and Hassner (Ref 14) is 93.8 kJ/mol, which is near the value for the intermetallic growth of the IM3 phase. It is also verified that the growth rate of Ni_3Sn_4 intermetallic layer (IM3)

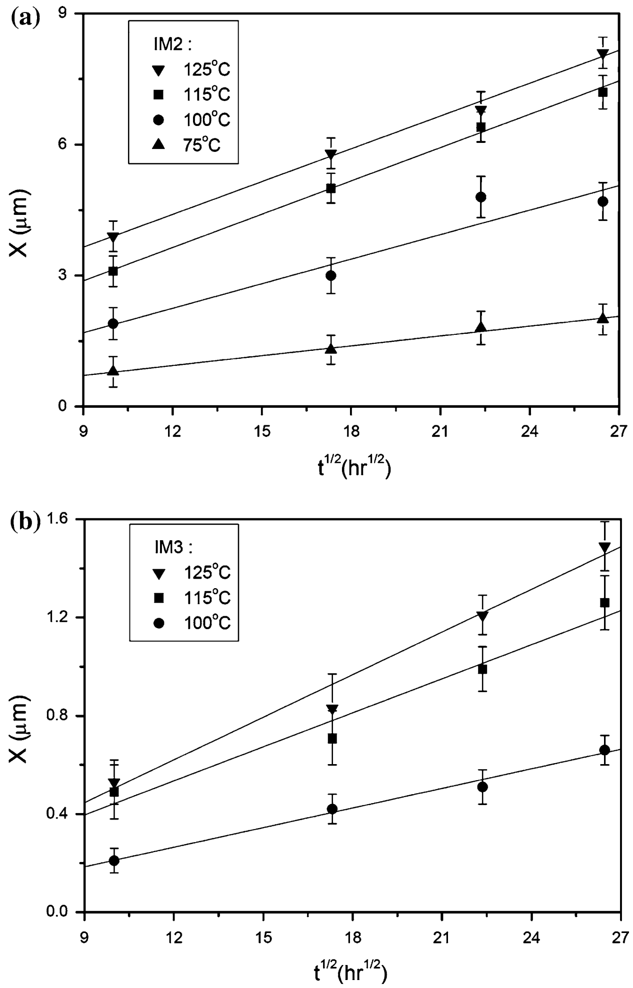

Fig. 8 Thickness (X) of the intermetallic layers formed at the solder/pad interfaces of Sn-58Bi BGA packages after aging at various temperatures versus the square root of time ($t^{1/2}$): (a) IM2 $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$ and (b) IM3 Ni_3Sn_4

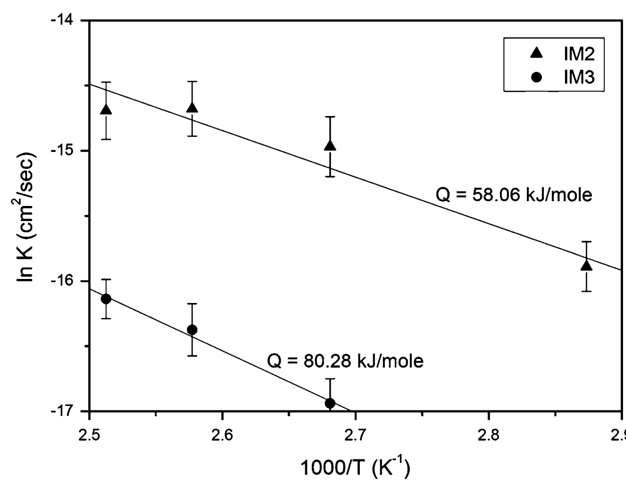

Fig. 9 Arrhenius plot of the reaction constants (K) for the growth of intermetallic layers formed at the solder/pad interface of Sn-58Bi BGA packages after the aging processes: IM2 $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$; IM3 Ni_3Sn_4

Table 1 Chemical Compositions (at.%) of Intermetallic Compounds Formed in Sn-58Bi Solder Joints After the Reflow and Aging Processes

IMC	IM1	IM2				IM3
Process	Reflow	Aging 115 °C, 100 h	Aging 115 °C, 300 h	Aging 125 °C, 100 h	Aging 125 °C, 300 h	Aging
Au	13.05	7.45	6.21	4.34	5.75	0
Ni	6.84	10.61	15.58	15.39	13.64	42.89
Sn	65.63	73.36	70.61	73.47	72.71	57.11
Bi	14.48	8.58	7.60	6.80	7.89	0

IM1: $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ gray intermetallic flakes in the solder matrix after reflowing; IM2: $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$ gray intermetallic layer in the solder/pad interface after aging; IM3: Ni_3Sn_4 dark intermetallic layer in the solder/pad interface after aging

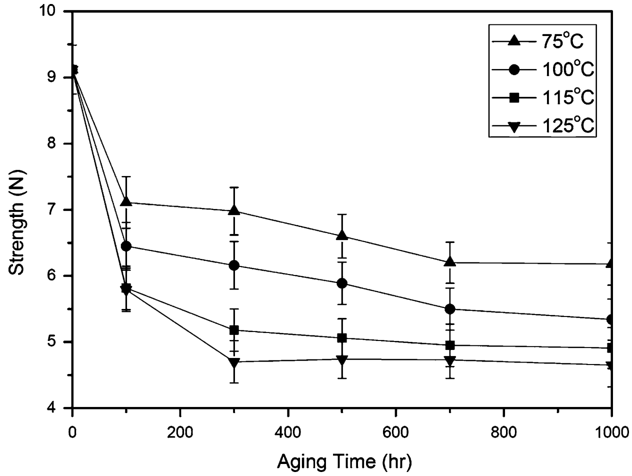

Fig. 10 Ball shear strength of the Sn-58Bi solder joints after aging at various temperatures from 75 to 125 °C (reflow condition: T_{max} = 180 °C, Δt_m = 80 s)

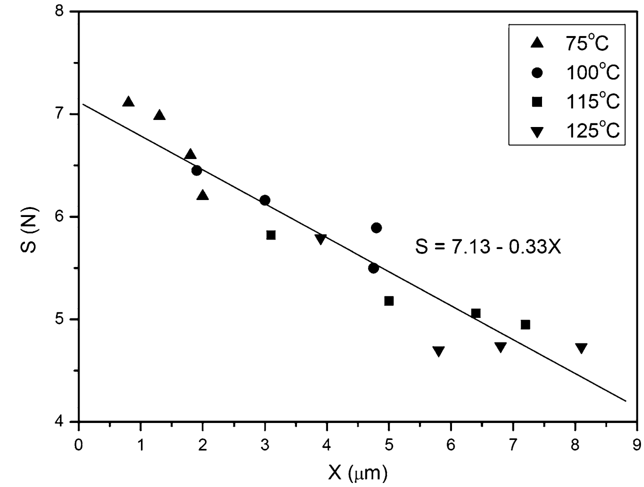

Fig. 11 Ball shear strengths (*S*) of the Sn-58Bi solder joints as a function of IM2 thicknesses (*X*) after various aging times and temperatures

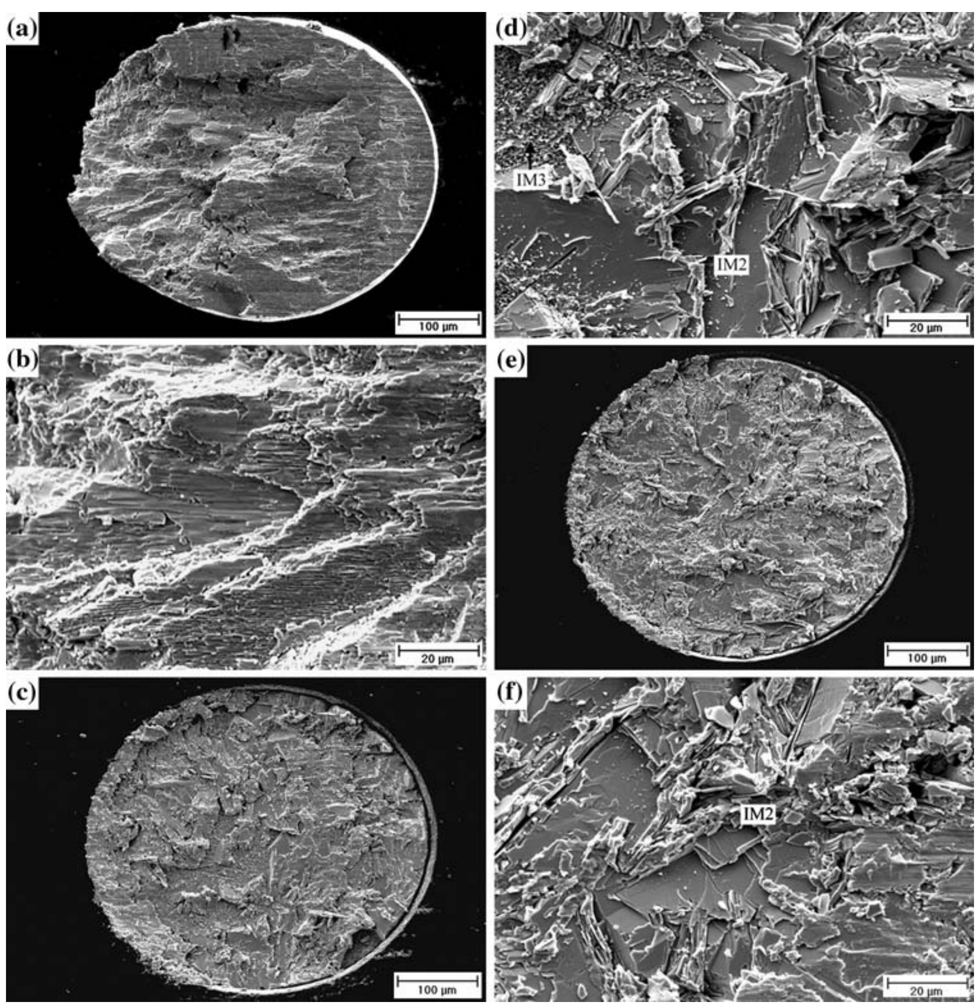

Fig. 12 Typical fractrography of the aged Sn-58Bi solder joints after ball shear tests: (a, b) as reflow; (c, d) 115 °C, 100 h; and (e, f) 115 °C, 300 h

is determined by the diffusion of Sn atoms from Sn-58Bi solder through the IM2 phase containing more than 70 at.% Sn as indicated in Table 1. Ball shear strengths of the Sn-58Bi solder joints after the aging processes are measured and demonstrated in Fig. 10. It can be seen that the bonding strength of the reflowed specimen (T_{max} = 180 °C, Δt_m = 80 s) is 9.1 N, which is higher than the value of a traditional Sn37Pb package (8.7 N) reflowed under the optimized condition (T_{max} = 225 °C, Δt_m = 60 s) (Ref 15). The ball shear strength drops drastically to values between 7.1 and 5.8 N after aging at temperatures between 75 and 125 °C for 100 h. Longer aging times (over 700 h) cause the ball shear strengths to decrease further to values between 6.4 and 4.6 N. In order to clarify the cause for the degradation of solder joints, the ball shear strengths (*S*) of Sn-58Bi BGA packages after aging at various temperatures and times are plotted versus the thickness (*X*) of IM2 intermetallic layers at the solder/pad interfaces. Figure 11 shows that a linear relation exists in this case: $S = 7.13 - 0.33X$. It implies that the growth of IM2 intermetallic compounds leads to the embrittlement of interfaces between Sn-58Bi solder balls and Au/Ni/Cu pads. This result can be reconfirmed from the fractography of the aged Sn-58Bi solder joints after ball shear tests as shown in Fig. 12. It reveals that the fracture occurs to the reflowed Sn-58Bi BGA package through the solder ball with ductile dimple characteristics (Fig. 12a, b). On the contrary, the aged specimens show brittle fracture after ball shear tests. Most areas on the fracture surface of aged specimens contain cleavage planes (Fig. 12c-f). EDX analysis indicates that the composition is $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$ for those fracture zones with cleavage, which corresponds to the interfacial IM2 intermetallic phase. However, many fine particles are also found in certain regions (the upper left region, see fractrography in Fig. 12d), which possess a composition of the IM3 phase (Ni_3Sn_4). The results indicate that the aged Sn-58Bi solder joints fracture mainly along the IM2 intermetallic layer. The fact that there are less fracture paths along the IM3 layer than along the IM2 layer, implies that the latter is much more brittle than the former.

4. Conclusions

Sn-58Bi solder BGA packages with Au/Ni/Cu pads are reflowed at a peak temperatures of 180 °C for a melting time of 80 s results in a ball shear strength of 9.1 N. Fractography after ball shear testing reveals ductile fracture through the solder ball. After the reflow processes, a small number of flake-shaped $(Au_{0.66}Ni_{0.34})(Sn_{0.82}Bi_{0.18})_4$ intermetallic compounds (IM1) appear in the solder matrix. Further aging at temperatures between 75 and 125 °C leads to the migration of IM1 intermetallic flakes from the solder matrix to the solder/pad interface, as well as the change of its composition to the $(Au_{0.30}Ni_{0.70})(Sn_{0.90}Bi_{0.10})_4$ phase (IM2). As the aging time increases, an additional intermetallic phase (IM3) with the composition of Ni_3Sn_4 begins to form at the interface between IM2 and Ni layer on the Cu pad. Aging processes cause the bonding strength of the reflowed specimen to drop drastically from 9.1 N to lower values between 6.4 and 4.6 N. A linear relation between ball shear strengths (*S*) and IM2 thicknesses (*X*) has been obtained: $S = 7.13 - 0.33X$, which implies that the degradation of Sn-58Bi solder joints in this case attributed to the embrittlement of interface caused by the growth of IM2 intermetallic compounds. Fractography of the aged solder joints after ball shear tests reveals brittle cleavage fracture mainly along the IM2 intermetallic layer.

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References

1. W.J. Tomlinson and I. Collier, Mechanical Properties and Microstructures of Copper and Brass Joints Soldered with Eutectic Tin-Bismuth Solder, *J. Mater. Sci.*, 1987, **22**(5), p 1835–1839
2. Z. Mei and J.W. Morris Jr., Characterization of Eutectic Sn-Bi Solder Joints, *J. Electron. Mater.*, 1992, **21**(6), p 599–607
3. C.H. Raeder, L.E. Felton, V.A. Tanzi, and D.B. Knorr, The Effect of Aging on Microstructure, Room-Temperature Deformation, and Fracture of Sn-Bi/Cu Solder Joints, *J. Electron. Mater.*, 1994, **23**(7), p 611–617
4. T.H. Chuang, S.Y. Chang, M.D. Cheng, and S.S. Wang, Challenges for the Application of Lead-Free Solders on Ball Grid Array Packages, *Bull. College Eng. N.T.U.*, 2003, **89**, p 101–110
5. C. Chen, C.E. Ho, A.H. Lin, G.L. Luo, and C.R. Kao, Long-Term Aging Study on the Solid-State Reaction Between 58Bi42Sn Solder and Ni Substrate, *J. Electron. Mater.*, 2000, **29**(10), p 1200–1206
6. M.Y. Chiu, S.Y. Chang, Y.H. Tseng, Y.C. Chan, and T.H. Chuang, Characterization of Intermetallic Compounds Formed During the Interfacial Reactions of Liquid Sn and Sn-58Bi Solders with Ni Substrates, *Zeitschrift fuer Metallkunde/Mater. Res. Adv. Tech.*, 2002, **93**(3), p 248–252
7. S.K. Kang, R.S. Rai, and S. Purushothaman, Interfacial Reactions During Soldering with Lead-Tin Eutectic and Lead (Pb)-Free Tin-Rich Solders, *J. Electron. Mater.*, 1996, **25**(7), p 1113–1120
8. B.L. Young and J.G. Duh, Interfacial Reaction and Microstructural Evolution for Electroplated Ni and Electroless Ni in the Under Bump Metallurgy with 42Sn58Bi Solder During Annealing, *J. Electron. Mater.*, 2001, **30**(7), p 878–884
9. A.M. Minor and J.W. Morris Jr., Inhibiting Growth of the Au0.5Ni0.5Sn4 Intermetallic Layer in Pb-Sn Solder Joints Reflowed on Au/Ni Metallization, *J. Electron. Mater.*, 2000, **29**(10), p 1170–1174
10. C.E. Ho, Y.M. Chen, and C.R. Kao, Reaction Kinetics of Solder-Balls with Pads in BGA Packages During Reflow Soldering, *J. Electron. Mater.*, 1999, **28**(11), p 1231–1237
11. C.C. Chi and T.H. Chuang, Intermetallic Reactions in Sn-3.5Ag Solder Ball Grid Array Packages with Ag/Cu and Au/Ni/Cu Pads, *J. Electron. Mater.*, in press
12. B. Meagher, D. Schwarz, and M. Ohring, Compound Growth in Platinum/Tin-Lead Solder Diffusion Couples, *J. Mater. Sci.*, 1996, **31**(20), p 5479–5486
13. D.C. Yeh, Extreme Fast-Diffusion System: Nickel in Single-Crystal Tin, *H.B. Phys. Rev. Lett.*, 1984, **53**(15), p 1469–1472
14. W. Lange and A. Hassner, Messung der Volumenselbstdiffusion im polykristallinen Zinn, *Phys. Stat. Solidi.*, 1961, **1**(1), p 50–61
15. C.L. Yu, Interfacial Reactions in Sn37Pb, Sn3Pb2Ag and Sn3.5Ag BGA Packages, Ph.D. Thesis, Institute of Materials Science and Engineering, National Taiwan University (2001)