High Temperature Characterization of Binary and Ternary Bi Alloys Microalloyed with Cu and Ag

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The s-orbital energy level (Mk) of alloying elements in a Bi cluster was used to determine the composition for alloys of this system for use as Pb-free high-temperature solders. Binary Bi-Cu and Bi-Ag alloys with ΔMk of 0.013–0.343 and ternary Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu alloys with ΔMk of 0.180 and 0.379, respectively, were fabricated and tensile tested at 423 K; here, ΔMk is the compositional average of Mk . The flow stress and fracture strain at 423 K increased after the alloying elements were added to the alloys. The relationships between the 0.2% proof stress, ultimate tensile strength or fracture strain, and ΔMk were similar to those determined previously through tests performed at 293 K. Thus, these relationships could be useful for predicting the stress and fractures strain levels based on ΔMk , regardless of the temperature and alloy composition. Moreover, a transition from ductility to brittleness was observed at 348–373 K for both ternary alloys. In addition, the melting points of the ternary alloys lay between 536 and 538 K, indicating that the alloys would be suitable as high-temperature solders. The contact angles of molten droplets of 10 of the experimental binary and ternary alloys on a Cu plate as determined at 973 K were 24–30°. This confirmed that the alloys exhibited good wettability with respect to Cu. Finally, the ternary Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu alloys showed thermal conductivities of 12.1 and 15.9 W/m/K, respectively, at 373 K; these were lower than that (30.4 W/m/K) of Pb-5Sn. [doi:10.2320/matertrans.MAW201710]

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1. Introduction

Solder alloys with high-melting points are used widely in power semiconductor packaging. High-lead-content alloys, which have been employed as high-temperature solder alloys, have a solidus temperature of more than 533 K¹. In recent years, owing to the RoHS (The Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment Regulations 2012) and End of Life Vehicles Directives of EU, lead-free high-temperature solder alloys have been promoted in the electronics industry². Therefore, significant efforts are being devoted all over the world towards the development of lead-free solders. However, there have not been significant advances in the development of lead-free solders for high-temperature applications^{3,4}. Several research groups have focused on Au-Sn, Zn-Sn, and Bi-Ag system alloys as potential lead-free alloys, based on their thermal and electricity properties and their melting points^{5–12}. However, Au system alloys find limited use as high-temperature solders because of the high cost of Au⁵. The applicability of Zn system alloys is also limited because of the oxidability of Zn^{6–9}. On the other hand, the melting point of Bi is 544 K, which is similar to that of conventional high-temperature Pb-Sn solders^{10–12}. Moreover, Bi is not only cheap but is also not harmful to human health and the environment. Thus, Bi system alloys are being considered for use as Pb-free alloys for high-temperature solders^{13,14}.

So far, high-performance alloys have been developed

through trial-and-error experiments performed based on a few empirical rules. In order to develop new alloys more efficiently, a theoretical design approach is strongly needed. The concept of d-electrons based on the theoretically determined electronic structures of alloys using discrete variational (DV)- $X\alpha$ ^{15–17} cluster calculations was proposed by Morinaga *et al.*^{18,19} This concept was first used in the case of austenitic Ni, C, and Fe alloys, wherein the phase boundary as well as a few physical and mechanical properties were predicted based on electronic parameters such as the d-orbital energy level and bond order. Moreover, the compositional optimization of Al²⁰ system alloys as a simple metal was performed based on the s-orbital energy level (Mk)^{15–17}. The relationship between the dislocation density (or hindrance to dislocation migration) and ΔMk has also been investigated previously²¹. It was concluded that the ΔMk value could be used as an indicator of the level of solid-solution hardening in ternary Al-1.5Mn-xMg alloys consisting of a mono phase.

We were able to determine the Mk value of a few alloying elements in a Bi cluster model by using the DV- $X\alpha$ cluster method²². It was observed that there exists a relationship between the ultimate tensile strength or fracture strain at 293 K and ΔMk in the case of binary Bi-Cu/-Ag/-Zn alloys with near-eutectic compositions and that this relationship was in keeping with the results of tensile tests performed at 293 K for ternary Bi-Ag-Cu alloys²². These ternary alloys exhibited the desired properties, namely, a ultimate tensile strength of 20 MPa and fracture strain of 5% at 293 K²³. The mechanical properties of the alloys such as their tensile properties and hardness could be predicted based on the

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ΔMk value. However, the high-temperature properties of the Bi system alloys were not investigated.

In this study, the high-temperature tensile properties were measured on binary and ternary Bi-Cu-Ag system alloys proposed by ΔMk parameter. In contrast, the melting points, thermal conductivities, and wettabilities with respect to Cu of the alloys at high temperatures were also measured, in order to evaluate their suitability for practical applications. The desired characteristics of the high-temperature solders were considered to be a melting point higher than 533 K¹⁾, and a contact angle on Cu of less than 90°.

2. Experiment Procedure

2.1 Materials and fabrication process

Stick-like Bi (purity of 99.99%), granular Ag (purity of 99.99%), and laminar Cu (purity of 99.9%) were placed in a graphite crucible, which was then set in an electric furnace in air. The diameters of the Bi and Ag samples were 2–3 mm, while the thickness of the Cu sample was 1 mm. Once all the starting materials had melted, the melt was mixed with a ceramic stick at 773 K and held at this temperature for 1.8 ks. Next, the melt was poured into a casting mold heated to 773 K. The resulting ingot which had a diameter of 15 mm and height of 115 mm, was air cooled to 293 K. The compositions of the experimental alloys are listed in Table 1.

2.2 Characterization of alloys at high temperatures

The microstructures of the alloys were observed using scanning electron microscopy (SEM). Tensile tests were performed on the alloys at 323, 348, 373, 423, and 473 K in air using a mechanical testing machine (Autograph DCS-R-5000, Shimadzu Corporation, Japan); the tests were performed using an initial strain rate of $3.4 \times 10^{-4} \text{ s}^{-1}$. The dimensions of the gauge section of the tensile test specimens were 6 mm (diameter) $\times$ 20 mm (length). In addition, the fracture surfaces of the tensile samples were observed by SEM. Differential scanning calorimetry (DSC) was used to characterize the melting points of the alloys. Rectangular samples with dimensions of $3 \times 3 \times 3 \text{ mm}^3$ were employed for the purpose. The DSC measurements were performed in an Ar atmosphere. A heating rate of 5 K/min was used, and the temperature was varied from 293 to 673 K, with the samples being held for 300 s at 673 K. As shown in Fig. 1,

the contact angles between molten droplets of the experimental alloys and a Cu plate (purity of 99.9%) were measured in the atmosphere-controlled chamber with Mo heaters. Figure 2 shows profiles of press and temperature of Cu plate. First, the vacuum furnace was evacuated to $1.5 \times 10^{-3} \text{ Pa}$ and then heated to 973 K while using Ar as the shielding gas at a flow rate of $1.67 \times 10^{-5} \text{ m}^3/\text{s}$ up to a pressure of $1.0 \times 10^5 \text{ Pa}$. Then, a droplet of the molten alloy being tested was placed on the Cu plate at 973 K and photographed after 120 s. The volume of the droplets of the alloys was approximately 111 mm³. The surface of the Cu plate was finished to the polishing by Al₂O₃ particles paste with 0.3 μm . Further, the thermal conductivities of the alloys were measured using a laser flash thermal constant measurement system (TC-700, ULVAC-RIKO Inc., Japan)⁹⁾ at 293, 323, and 373 K. The test samples, which had dimensions of 10 (diameter) $\times$ 1 mm³ were also finished to the polishing by Al₂O₃ particles paste with 0.3 μm .

2.3 Electronic parameter representing alloying effects

An s-orbital energy level exists above the Fermi energy level of an MBi₇ cluster²²⁾ consisting of an alloying element M that is surrounded by Bi atoms. Therefore, the alloying effects were inevitably involved in this Mk parameter. The Mk level decreases with an increase in the electronegativity of pure metals but increases with an increase in the atomic

Fig. 1 Apparatus of contact angle tests.

Table 1 Compositions of binary and ternary Bi system alloys and their ΔMk values.

Alloy (mass%)	ΔMk
Bi-0.15Cu	0.013
Bi-0.25Cu	0.021
Bi-0.5Cu	0.042
Bi-0.75Cu	0.062
Bi-1.0Cu	0.082
Bi-2.5Ag	0.176
Bi-5.0Ag	0.343
Bi-2.0Ag-0.5Cu	0.180
Bi-5.0Ag-0.5Cu	0.379

Fig. 2 Profiles of (a) temperature of Cu plate and (b) pressure in atmosphere of melting process.

radius; this is in keeping with the relationship determined by using the MAI_{18} cluster as a model of face-centered cubic Al^{24}). It is well known²⁵⁾ that the energy level determined through $X\alpha$ calculations is representative of the electronegativity itself^{26–29)}.

The value of the Mk parameter in the MBi_7 cluster model was calculated using an octahedron of triclinic Bi. Using the Mk parameter, the ΔMk value for Bi alloys was defined using the compositional average, as given in eq. (1):

$$\Delta Mk = \sum X_M |Mk_M - Mk_{\text{Bi}}| \quad (1)$$

where X_M is the molar fraction of the alloying element M, Mk_M is the Mk value of the alloying element M, and Mk_{Bi} is the Mk value of the mother metal Bi.

3. Results and Discussion

3.1 Microstructures

The microstructures of the as-cast Bi system alloys with the elements Cu or Ag are shown in Fig. 3. Pure Bi is a monophase of Bi and consists of equiaxial grains with a size of $45\text{ }\mu\text{m}$. A primary Cu phase and a eutectic consisting of Bi and Cu are observed in the case of the Bi-0.15-1.0 Cu alloys. The size of the primary Cu phase in the Bi-Cu alloys increases with an increase in the Cu content. A primary Ag solid solution (hereafter called the Ag S.S.) and the eutectic of the Bi and Ag S.S. are observed in Bi-5.0Ag. In contrast, only the eutectic of the Bi and Ag S.S. is observed in Bi-2.5Ag.

The microstructures of the Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu alloys consisted of primary phases and a typical eutectic structure composed of Bi, a Ag S.S., and a Cu S.S. in normal eutectic cells formed alternately, as shown in Figs. 3 (i) and (j). In the Bi-5.0Ag-0.5Cu alloy, which had a large Ag content, an irregular region consisting of a darker needle-like primary Ag S.S. and a light-contrast primary Bi phase surrounding the primary Ag S.S. were also observed; this was indicative of the crystallization of Bi in the depleted region of the Ag S.S. owing to the formation of the primary Ag S.S. because of atomic diffusion under the nonequilibrium state (see Fig. 3 (h)).

3.2 Tensile properties at high temperatures

3.2.1 Stress-strain behaviors

Figure 4 shows the nominal stress-strain curves for 7 of the binary Bi system alloys as determined through tensile tests at 423 K; that for pure Bi is shown as a reference. Typical softening can be seen in the stress-strain curves as compared to the curves obtained at 293 K²²⁾. The ultimate tensile strength and fracture strain of pure Bi were 4.2 MPa and 15.4%, respectively. Thus, pure Bi exhibited the lowest ultimate tensile strength and fracture strain. For the Bi-0.15/0.25/0.5/0.75/1.0 Cu alloys, the ultimate tensile strengths were 4.4, 4.9, 5.2, 5.8, and 5.4 MPa, respectively. Further, the fracture strains of these alloys were at least twice as large as that of pure Bi, even though their ultimate tensile strength and flow stress values were only slightly greater than those of Bi. In contrast, the ultimate tensile strength values of the Bi-2.5/5.0Ag alloys were 8.8 and 9.9 MPa, respectively; these are 2.1 and 2.4 times greater,

Fig. 3 Compositional images of (a) pure Bi and (b) Bi-0.15Cu, (c) Bi-0.25Cu, (d) Bi-0.5Cu, (e) Bi-0.75Cu, (f) Bi-1.0Cu, (g) Bi-2.5Ag, (h) Bi-5.0Ag, (i) Bi-2.0Ag-0.5Cu, and (j) Bi-5.0Ag-0.5Cu alloys.

respectively, than that of pure Bi. Moreover, the fracture strains of the two Bi-Ag alloys were similar to those of the Bi-Cu system alloys. Thus, the tensile properties of the Bi alloys at 423 K improved with the addition of the alloying

elements, namely, Cu and Ag.

3.2.2 Temperature dependence of tensile properties

Figures 5 (a) and (b) shows the nominal stress-strain curves as determined at various temperatures of the ternary Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu alloys. The flow stress values of both alloys decreased with the increase in the test temperature, owing to the softening of the alloys. Therefore, the stress-strain curves were obtained at different test temperatures. In general, during plastic deformation, the alloys

Fig. 4 Stress-strain curves at 423 K for Bi-0.15Cu²²⁾, Bi-0.25Cu, Bi-0.5Cu²²⁾, Bi-0.75Cu²²⁾, Bi-1.0Cu, Bi-2.5Ag, and Bi-5.0Ag alloys and pure Bi²²⁾. *Range of reduction in area (%) after failure.

Fig. 5 Stress-strain curves of (a) Bi-2.0Ag-0.5Cu and (b) Bi-5.0Ag-0.5Cu alloys at 293, 323, 348, 373, 423, and 473 K. *Range of reduction in area (%) after failure.

experienced simultaneous work hardening and dynamic recovery, phenomena which have opposite effects on plastic deformation. Dislocation annihilation occurred more quickly than did dislocation generation, resulting in the weakening of the hardening phenomenon, as the test temperature was increased. This behavior has also been observed in the case of solder materials³⁰⁾.

Both alloys showed a fracture strain of more than 17% even at 348 K. The temperature dependence of the 0.2% proof stress and fracture strain of the ternary alloys is shown in Fig. 6. The 0.2% proof stress decreased with an increase in the temperature. In particular, between 323 and 348 K the temperature dependence of the 0.2% proof stress was stronger than that seen between 293 and 473 K in the case of Bi-2.0Ag-0.5Cu. In contrast, the fracture strain increased sharply from 5.9 to 42.4% between 323 and 348 K; this resulted in a transition from ductility to brittleness in this temperature range. Further, the ductile-to-brittle transition occurred at approximately 348 K in the case of Bi-5.0Ag-0.5Cu. It was found that the decrease in the 0.2% proof stress was correlated to a significant increase in the fracture strain at temperatures between 323 and 373 K. Therefore, these data confirmed the ductile-to-brittle transition temperature. The Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu alloys underwent ductile fractures at 348 and 373 K, respectively, with dimples being present on the fracture surfaces. The fracture surfaces of the alloys at temperatures higher and lower than the ductile-to-brittle transition temperatures are shown in Fig. 7. The ductile and brittle fracture surfaces shown correspond to the deformation behaviors at temperatures higher and lower than the ductile-to-brittle transition temperatures.

Fig. 6 0.2% proof stress and fracture strain at 293–473 K for (a) Bi-2.0Ag-0.5Cu and (b) Bi-5.0Ag-0.5Cu alloys.

Fig. 7 SEM images of fracture surfaces of Bi-2.0Ag-0.5Cu specimens tensile tested at (a) 323 K and (b) 348 K, and Bi-5.0Ag-0.5Cu specimens tensile tested at (d) 348 K and (e) 373 K. (c) High-magnification image of area marked by black rectangle area in (b).

Fig. 8 SEM images of fracture surfaces at 423 K of (a) pure Bi²² and (b) Bi-0.15Cu, (c) Bi-0.5Cu, (d) Bi-5.0Ag, (e) Bi-2.0Ag-0.5Cu, and (f) Bi-5.0Ag-0.5Cu alloys, and high-magnification images of fracture surfaces of (g) pure Bi and (h) Bi-0.15Cu, (i) Bi-0.5Cu, (j) Bi-5.0Ag, (k) Bi-2.0Ag-0.5Cu, and (l) Bi-5.0Ag-0.5Cu alloys. The high-magnification images (g)–(l) correspond to areas enclosed in black rectangles in (a)–(f), respectively.

3.2.3 Fracture morphology

The typical fracture surfaces of the Bi-0.15/0.5Cu and Bi-5.0Ag alloys and pure Bi after the tensile tests at 423 K are shown in Fig. 8 (a)–(d) and (g)–(j). The pure Bi sample has a wavy fracture surface with undeveloped voids; however, the decrease in area (2–12%) was the lowest in this case. In contrast, as shown in Figs. 8 (b), (c), (d), (h), (i), and (j), the fracture ends of the Bi-0.15/0.5Cu and Bi-5.0Ag alloys tested at 423 K had a dimple-like pattern consisting of several cavities, which were elongated along the stress axis close to failure. This resulted in a very large decrease in area, in keeping with the data shown Figs. 4 and 5. In addition, the fracture surface of Bi-0.15Cu, which showed the lowest fracture strain, not only exhibited a ductile-fracture-like pattern but also a partially brittle-fracture-like pattern, even at 423 K.

The Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu specimens, which showed fracture strains of 43.4 and 35.6%, respectively, had their areas reduced by 10–90 and 71–87%, respectively. This was indicative of ductile failure and a heterogeneous and homogeneous increase in all three dimensions along the stress axis close to failure, respectively. Further, the fracture ends of the Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu specimens had a dimple-like pattern consisting of several cavities of different sizes.

3.2.4 Relationship between tensile properties at 423 K and ΔMk

Figure 9 shows the relationship between the 0.2% proof stress, the ultimate tensile strength or fracture strain at 423 K (see Figs. 4 and 5), and ΔMk . The 0.2% proof stress and ultimate tensile strength increased with an increase in ΔMk till approximately 0.18 and then remained almost constant; this was regardless of the type and amount of binary

and ternary alloying elements used. This relationship at 423 K was similar to that seen at 293 K²²⁾. The 0.2% proof stress and ultimate tensile strength of pure Bi for a ΔMk of 0.00 could be also fitted using the relationship between the parameters and the ΔMk value for the experimental alloys. It is interesting to note that the measured stress levels of pure Bi agreed with those obtained by the extrapolation to ΔMk .

On the other hand, the fracture strains of the binary and ternary Bi system alloys increased with an increase in ΔMk till approximately 0.08 and then remained almost constant. Thus, it can be assumed that the tensile properties of binary and ternary Cu- and Ag-containing Bi alloys at 293 K as determined based on ΔMk ²²⁾ can be used to evaluate their properties at 423 K.

The number of slip systems also in the Bi alloys increased with an increase in the temperature. In addition, the effect of the precipitates on the retardation of the migration of dislocations was different for the different slip planes. Therefore, it may be considered that the relationship between the fracture strain and ΔMk changed with the increase in the test temperature. On the other hand, as shown in Fig. 3, the morphologies of the alloys changed with an increase in the amounts of the alloying elements. Thus, the phenomena arising from the retardation of dislocation migration, such as solid-solution hardening, precipitation hardening, and the Orowan effect, also changed. It may also be considered that the relationship between the alloy strength and ΔMk was not proportional to the change. Moreover, when the amounts of the alloying elements added were low levels, the relationship between the alloy strength and ΔMk was linear for both the binary and the ternary Bi system alloys.

3.3 Melting points

Figure 10 showed the DSC heating curves of the ternary Bi system alloys. The solidus temperatures of the Bi-2Ag-0.5Cu and Bi-5.0Ag-0.5Cu alloys were 536 and 538 K, because of the eutectic structure shown in Fig. 3 (i) and (j), respectively. Based on these results, it can be surmised that the compositionally optimized Bi-Ag-Cu system alloys are suitable for use in practical applications requiring a melting point higher than 533 K¹⁾.

Fig. 9 Relationship between (a) 0.2% proof stress and ultimate tensile strength and (b) fracture strain at 423 K and ΔMk for experimental Bi system alloys.

Fig. 10 DSC curves of Bi-2.0Ag-0.5Cu²³⁾ and Bi-5.0Ag-0.5Cu alloys.

Fig. 11 Typical molten droplets of (a) pure Bi, (b) Bi-0.75Cu, (c) Bi-2.0Ag-0.5Cu, and (d) Bi-5.0Ag-0.5Cu on Cu plate.

Table 2 Contact angles between droplets of experimental alloys and Cu plate as measured at 973 K in Ar atmosphere.

Alloy (mass%)	Contact angle (degree)
Pure Bi	25
Bi-0.15Cu	26
Bi-0.25Cu	27
Bi-0.5Cu	29
Bi-0.75Cu	28
Bi-1.0Cu	29
Bi-2.5Ag	25
Bi-5.0Ag	24
Bi-2.0Ag-0.5Cu	28
Bi-5.0Ag-0.5Cu	30

3.4 Wettability

Figure 11 shows typical droplets of pure Bi, Bi-0.75Cu, Bi-2.0Ag-0.5Cu, and Bi-5.0Ag-0.5Cu on a Cu plate at 973 K in an Ar atmosphere. The contact angles for all the experimental alloys are listed in Table 2. It can be seen that the contact angles for all the specimens were 24–30° (i.e., less than 90°), making the alloys suitable for use in practical applications.

3.5 Thermal conductivity

The thermal conductivity (λ) values of the Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu alloys were measured at 293–373 K. Figure 12 shows the temperature and compositional dependence of λ . As can be seen from the figure, λ decreased monotonously with an increase in the temperature; this was the case regardless of the alloy composition. Bi-5.0Ag-0.5Cu showed higher λ values compared with Bi-2.0Ag-0.5Cu, because of large amount of Ag in alloys. As the temperature is increased, the movement of the electrons becomes even more chaotic, resulting in a reduction in conductivity. Moreover, the λ values of the alloys could be estimated using expressions that were functions of the temperature. For the same temperature, the λ values of the designed alloys were lower than those of the conventional Pb-5Sn alloy. However, the λ values of the ternary alloys need to be

Fig. 12 Thermal conductivities of Bi-2.0Ag-0.5Cu, Bi-5.0Ag-0.5Cu, and Pb-5Sn alloys for temperatures of 273–373 K.

increased further in order for the alloys to be practically applicable.

4. Conclusions

- (1) It was found that the 0.2% proof stress, ultimate tensile strength, and fracture strain of the designed binary Bi-Ag/-Cu alloys at 423 K were higher than those of pure Bi. The 0.2% proof stress and ultimate tensile strength of the binary Bi system alloys increased with an increase in ΔMk till approximately 0.18 and then remained almost constant. In contrast, the fracture strain increased with an increase ΔMk till approximately 0.08 and then remained almost constant. The binary Bi system alloys exhibited excellent ductility, showing a fracture strain of more than 30% at 423 K. The relationship between the strength at 423 K and ΔMk was similar to that observed during tests at 293 K.
- (2) The compositionally optimized alloys Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu, which had ΔMk values of 0.180 and 0.379, respectively, showed improved tensile properties at 423 K as compared to those of pure Bi and the binary Bi-Cu alloys. Moreover, a transition from ductility to brittleness was observed at approximately 348–373 K in the case of both ternary alloys. It was found that the manner in which the mechanical properties of alloys can be predicted based on the ΔMk value would also be applicable in the case of the Bi system alloys investigated in this study, regardless of their composition and the tensile test temperature.
- (3) The melting points of the alloys Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu were determined to be 536 and 538 K, respectively; these were within the desired range of melting temperatures for high-temperature solders. Further, the contact angles of molten droplets of 10 of the binary and ternary experimental alloys and a Cu plate at 973 K were determined to be 24–30°. This confirmed that the alloys exhibited suitable wettability with respect to Cu. In addition, the ternary alloys Bi-2.0Ag-0.5Cu and Bi-5.0Ag-0.5Cu showed thermal conductivities of 12.1 and 15.9 W/m/K, respectively, at 373 K; these were lower than that (30.4 W/m/K) of Pb-5Sn.

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