Properties of Soldering Cu/Fe Alloy Produced by Powder Metallurgy

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In order to develop an advanced soldering material, the Cu/Fe alloys were produced by using powder metallurgy and the soldering properties were examined. Thermal conductivity of Cu/Fe alloy decreased with the increase in the volume fraction of pores, while it increased with the increase in the volume fraction of Cu particles. Wettability of Cu/Fe alloy was better than that of conventional Fe plating. Comparing the consumption amounts under the same wettability, the amount of Cu/Fe alloy consumed was smaller than that of Fe plating consumed.
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1. Introduction

The core of a conventional soldering iron for a soldering robot is made of Cu, which has a high thermal conductivity, and its surface is covered by Fe plating. Once the whole of Fe plating is consumed during soldering, resulting in the loss of function of the soldering iron.¹⁾ Nowadays, due to the environment concern that Pb is harmful to human health, conventional Sn-Pb soldering has been switched into Pb-free soldering in electronic packaging.²⁻⁴⁾ Because the practically used Pb-free solder (Sn-Ag-Cu system) contains a large amount of Sn and has a high melting point compared with the conventional Sn-Pb eutectic solder, the use of Pb-free solder causes a significant increase in the consumption of the soldering iron, resulting in an increase in the number of times which the soldering iron is changed and a reduction in production efficiency owing to production discontinuance. However, there are few reports regarding new soldering materials which may be used as an alternate for soldering iron.

In the present study, in order to develop an advanced soldering material, Cu/Fe alloys were prepared by using powder metallurgy and density, thermal conductivity, wettability, reactivity between fused Pb-free solder and Cu/Fe alloy and consumption of soldering Cu/Fe alloy were investigated.

2. Experimental Procedure

High purity carbonyl Fe powder (Mitsuwa Chemical Co. Ltd.: Fe; 99.5 mass%, maximum particle diameter; 5 μ m, mean particle diameter; 3.3 μ m) and high purity Cu powders (Cu; 99.8 mass%, symbol 10Cu: maximum particle diameter; 10 μ m, mean particle diameter; 6.5 μ m, symbol 45Cu: maximum particle diameter; 45 μ m, mean particle diameter; 18.3 μ m, and symbol 100Cu: maximum particle diameter;

100 μ m, mean particle diameter; 72.8 μ m) were used. Figure 1 shows secondary electron (SE) images of powders used. All the powders are spherical.

The Cu/Fe powders having various Cu volume fractions (0, 4.5, 8.9, 18.1 and 27.5 vol%) were compacted under an uni-axial pressure of 88.4 MPa, followed by sintering at 1223 K for 10 h in vacuum (0.1 Pa). The density of sintered compact was measured by Archimedes method (Alfa Mirage Co. Ltd.: MD-300S). Thermal conductivity of sintered compact disk having a diameter of 10 mm and 1.5 mm thickness was measured by laser flash method (Rigaku Co. Ltd.: LF-TCM).

Pb-free solder of the Sn-3.0Ag-0.5Cu system including a flux (Senju Kinzoku Co. Ltd.: ECO SOLDER RMA02P3M705-1.0) was used. The fused solder was held on the surface of sintered compact at 653 K for various times to examine reactivity between Pb-free solder and Cu/Fe alloy. Then the microstructure of the longitudinal section of sintered compact was examined using an electron probe micro-analyzer (EPMA). The fused solder (0.03 g) was held at 653 K on the surface of sintered compact in air to measure contact angle. The consumption of soldering Cu/Fe alloy was examined using a soldering robot (Japan Unix Co. Ltd.: UNIX-412).¹⁾ In the consumption test, soldering Cu/Fe alloy was heated to testing temperature, and then maintained till the steady state in which no change in temperature achieved. Thereafter, Pb-free solder of 10.5 mm length was supplied to the center of the soldering Cu/Fe alloy automatically and then held for 7.25 s, followed by compressed air cleaning at the center of soldering Cu/Fe alloy (angle of air cleaning nozzle to soldering Cu/Fe alloy: $\pi/2$, air pressure: 0.49 MPa, nozzle diameter: 1.5 mm, blowing time: 0.3 s). We designate the process from solder supply to compressed air cleaning as one cycle. The consumption test was carried out to 5000 cycles.

Figure 2 shows a schematic illustration of the longitudinal section of soldering Cu/Fe alloy that the mixture of Cu and Fe powders was compacted under an uni-axial pressure of 88.4 MPa, followed by sintering at 1223 K for 10 h in vacuum (0.1 Pa). To prevent the spreading of fused solder, a Cr

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Fig. 1 SE images of powders used. (a) Fe, (b) 10Cu, (c) 45Cu and (d) 100Cu.

Fig. 2 Schematic illustration of the longitudinal section of soldering Cu/Fe alloy.

plating is applied on the upper and hind sides of the soldering Cu/Fe alloy. The shape of every soldering Cu/Fe alloy before the consumption test was measured using a projector. The shape of longitudinal section of soldering Cu/Fe alloy after the consumption test was examined using EPMA (SE image). The consumption amount, which is the decrease in thickness of soldering Cu/Fe alloy, was measured at positions ① (near the Cr plating) and ② (the center of the solder contact plane) in Fig. 2.

3. Results and Discussion

Figure 3 shows SE images of the longitudinal section of Cu/Fe alloys. The white parts are Cu particles. In 10Cu/Fe alloy (Fig. 3(a)), plastic deformation of Cu particles is observed. In 45Cu/Fe alloy (Fig. 3(b)), irregularity of the surface of Cu particles appears. These are because the plastic deformation of soft Cu particles due to hard Fe particles occurs during compaction. As shown in Figs. 3(a) and 3(b), a number of pores were observed. As shown in Fig. 3(c), uniform dispersion of Cu particles could be achieved even when Cu particles were very large.

Figure 4 shows the changes in density and relative density (the ratio of measured density to theoretical density calculated from the volume fraction of Cu particles) of sintered compact with the volume fraction of Cu particles. The density of sintered Fe is smaller than that of pure bulk Fe (7.87 Mg/m^3).⁵⁾ Also the relative density of sintered Fe is smaller than 1 (full density). This is due to the presence of pores in the sintered Fe. Because density of pure bulk Cu (8.93 Mg/m^3)⁵⁾ is larger than that of pure bulk Fe, it is expected that density of Cu/Fe alloy increases with the increase in the volume fraction of Cu particles. However, as shown in Fig. 4, the obtained results showed opposite behavior. Considering both the pores in sintered compact and the volume fraction of Cu particles, the density is given by

Fig. 3 SE images of the longitudinal section of Cu(27.5 vol%)/Fe alloys. (a) 10Cu/Fe alloy, (b) 45Cu/Fe alloy and (c) 100Cu/Fe alloy.

$$\rho = \rho_{\text{Fe}}(1 - V_p - V_{\text{Cu}}) + \rho_{\text{Cu}}V_{\text{Cu}} \quad (1)$$

where ρ_{Fe} , ρ_{Cu} and ρ is the density of pure bulk Fe, Cu and density of sintered compact, respectively, V_p is volume fraction of pores (1-relative density) and V_{Cu} is volume fraction of Cu particles.

Figure 5 shows the relationship between density calculated from eq. (1), ρ_{cal} , and measured density, ρ_{exp} . The values of ρ_{cal} agree well with those of ρ_{exp} . Thus, density of sintered Cu/Fe alloy depends on both the volume fraction of pores and the volume fraction of Cu particles.

Fig. 4 Changes in density and relative density of sintered compact with the volume fraction of Cu particles.

Fig. 5 Comparison between calculated density, ρ_{cal} , and measured one, ρ_{exp} .

Figure 6 shows the relationship between thermal conductivity of sintered compact and the volume fraction of Cu particles. The thermal conductivity of sintered Fe is smaller than that of pure bulk Fe ($78.2 \text{ W/(m}\cdot\text{K)}$).⁶⁾ This may be due to the presence of pores in sintered Fe. Since thermal conductivity of pure bulk Cu ($397 \text{ W/(m}\cdot\text{K)}$)⁶⁾ is larger than that of pure bulk Fe, it is expected that thermal conductivity of Cu/Fe alloy increases as the volume fraction of Cu particles increases. However, as shown in Fig. 6, the obtained results showed opposite behavior. This suggests that κ vary depending on both the pores and the Cu particles. From multi-regression analysis of thermal conductivity using the volume fractions of pores and Cu particles, thermal conductivity is given by

$$\kappa = 79.9 - 176 V_p + 172 V_{\text{Cu}}^2 \quad (2)$$

Fig. 6 Relationship between thermal conductivity of sintered compact and the volume fraction of Cu particles.

Fig. 7 Comparison between calculated thermal conductivity, κ_{cal} , and measured one, κ_{exp} .

where κ is thermal conductivity of sintered compact. Substituting $V_p = 0$ and $V_{Cu} = 0$ in eq. (2), we obtain $\kappa_{cal} = 79.9 \text{ W}/(\text{m}\cdot\text{K})$. This value, which indicates thermal conductivity of pore-free sintered Fe, is compatible with thermal conductivity of pure bulk Fe ($78.2 \text{ W}/(\text{m}\cdot\text{K})$).⁶⁾

Figure 7 shows the relationship between thermal conductivity calculated from eq. (2), κ_{cal} , and measured one, κ_{exp} . The values of κ_{cal} agree well with those of κ_{exp} . Thus, thermal conductivity of sintered Cu/Fe alloy decreases with the increase in the volume fraction of pores, while it increases with the increase in the volume fraction of Cu particles. As shown in Fig. 6, the values of κ at $V_{Cu} = 9 \text{ vol\%}$ in 10Cu/Fe and 45Cu/Fe alloys are smaller than that of sintered Fe. This is because the decrease in κ due to large V_p (Fig. 4) is superior to the increase in κ due to small V_{Cu} . When V_{Cu} exceeds 9 vol%, the values of κ increase with increasing V_{Cu} . This is because V_p is almost unchanged by varying V_{Cu} (Fig. 4), while κ increases with increasing V_{Cu} .

Fig. 8 EPMA analysis of the longitudinal section of 10Cu(27.5 vol%)/Fe alloy that fused solder was held on the surface at 653 K for 24 h. (a) SE image, (b) Sn $K\alpha$ -ray image, (c) Fe $K\alpha$ -ray image and (d) Cu $K\alpha$ -ray image.

Figure 8 shows EPMA analysis of the longitudinal section of 10Cu(27.5 vol%)/Fe alloy when fused solder was held on the surface at 653 K for 24 h. In SE image, the upper part is solder, the lower part is Cu/Fe alloy and the middle part is reaction layer. It is found that the reaction layer consists of two different layers. The result of EPMA quantitative analysis (point analysis) of the encircled area (Fig. 8(a)) in the lower reaction layer indicated Cu : Fe : Sn = 0.98 : 32.01 : 67.01 in at%. This suggests that the lower reaction layer consists of FeSn_2 . The formation of FeSn_2 during soldering was also detected in case of Fe plating.¹⁾ As shown in area analysis, few Cu is found in Cu/Fe alloy near the

Fig. 9 Relationship between the thickness of reaction layer in Cu(27.5 vol%)/Fe alloys and holding time. (a) lower reaction layer (FeSn_2) and (b) all reaction layer.

reaction layer though Cu is detected in Cu/Fe alloy a little way off the reaction layer. On the other hand, Fe still remains in Cu/Fe alloy near the reaction layer and FeSn_2 is detected at Cu-poor region (once a Cu particle). In accordance with the Fe-Sn equilibrium phase diagram,⁷⁾ Fe undissolves within the liquid Sn at 653 K but FeSn_2 is formed. In accordance with the Cu-Sn equilibrium phase diagram,⁸⁾ Cu dissolves into the liquid Sn at 653 K. As Cu content in liquid Sn increases, Cu-Sn compound crystallizes partially. These results suggest that preferential dissolution of Cu in Cu/Fe alloy into Sn in fused solder occurs, followed by the reaction between Sn and Fe. The upper layer (Cu-Sn compound) may be formed by reaction between Sn and Cu which is swept away from the lower reaction layer on the process of the formation of FeSn_2 .

Figure 9 shows the relationship between the thickness of reaction layer in 10 Cu(27.5 vol%)/Fe alloys and holding time at 653 K. The results of conventional Fe plating are also plotted in Fig. 9.¹⁾ As shown in Fig. 9(a), the thickness of lower reaction layer (FeSn_2) of 10Cu/Fe alloy having small Cu particles is almost equivalent to that of Fe plating. However, when a diameter of Cu particles is large. As shown in Fig. 9(b), the changes in thickness of all reaction layer

Fig. 10 Relationship between contact angle for sintered compact and the volume fraction of Cu particles.

(lower reaction layer (FeSn_2) + upper reaction layer (Cu-Sn compound)) are similar to those of lower reaction layer (Fig. 9(a)). As mentioned above, the thickness of lower reaction layer increases when a diameter of Cu particles is large. This is because the growth of lower reaction layer is enhanced by the behavior that the formation of large amounts of FeSn_2 occurs at Cu-poor region (once a Cu particle) below lower reaction layer (Fig. 8), too.

Figure 10 shows the relationship between contact angle for sintered compact and the volume fraction of Cu particles. Contact angle decreases with the increase in the volume fraction of Cu particles. This is because wettability of Sn/Cu system is better than that of Sn/Fe system. There is no influence of Cu particle size on contact angle. This is because the area fraction of Cu in the contact area is almost equal independent on Cu particle size. It is thought that Cu particle size dependence of the reaction layer thickness (Fig. 9) relate to the reaction toward the interior rather than on the surface.

Figure 11 shows the relationship between contact angle and fusing temperature. Contact angle decreases as fusing temperature is high. Comparing these contact angles at the same fusing temperature, contact angle of 10Cu(27.5 vol%)/Fe alloy is lower than that of Fe plating. It is found from Fig. 11 that contact angle equivalent to that of Fe plating at 653 K can be achieved at lower temperature (616 K) in 10Cu/Fe alloy.

Figure 12 shows the shape (SE image) of the longitudinal section of soldering Cu/Fe alloy after the consumption test. The consumption amount at position ① in Fig. 2 is larger than that at the position ②. This is because the reaction is promoted by the retained solder, which cannot be blown away during compressed air cleaning. The consumption at the bottom of Cu/Fe alloy is also observed. These phenomena are similar to those of Fe plating.¹⁾

Figure 13 shows the relationship between the amount of soldering Cu/Fe alloy consumed and temperature of consumption test. The results of Fe plating are also plotted in Fig. 13.¹⁾ The symbols ① and ② in Fig. 13 correspond to the positions ① and ② in Fig. 2, respectively. Under the same temperature, the amount of Cu/Fe alloy consumed is larger

Fig. 11 Relationship between contact angle and fusing temperature.

Fig. 12 Shape of the longitudinal section of soldering Cu/Fe alloy after the consumption test.

than that of Fe plating consumed. However comparing the consumption amounts under the same wettability, the amount of Cu/Fe alloy consumed is smaller than that of Fe plating consumed. Once the whole of Fe plating is consumed by soldering, resulting in the loss of function of the soldering iron. The increases in the number of exchanging the soldering iron and reconditioning time brings about a reduction in production. However, in case of soldering Cu/Fe alloy shown in Fig. 2, it is possible for Cu/Fe alloy to use for a long time till the whole of Cu/Fe alloy is consumed, resulting in the decreases in the exchanging number and reconditioning time. This brings about an increase in production efficiency.

Fig. 13 Relationship between the amount of soldering Cu/Fe alloy consumed and temperature of consumption test.

4. Conclusions

In order to develop an advanced soldering material, the Cu/Fe alloys were produced by using powder metallurgy and its density, thermal conductivity, wettability, reactivity between Pb-free solder and Cu/Fe alloys and consumption of soldering Cu/Fe alloys were examined. The results obtained are as follows.

- (1) Thermal conductivity of Cu/Fe alloy decreased with the increase in the volume fraction of pores, while it increased with the increase in the volume fraction of Cu particles.
- (2) Wettability of Cu/Fe alloys was better than that of conventional Fe plating.
- (3) Under the same soldering temperature, the amount of Cu/Fe alloy consumed was larger than that of Fe plating consumed. However, comparing the consumption amounts under the same wettability, the amount of Cu/Fe alloy consumed was smaller than that of Fe plating consumed.

REFERENCES

- 1) H. Sueyoshi, H. Odo, S. Mizokuchi, S. Abe and K. Saikusa: *Mater. Trans.* **47** (2006) 1221–1226.
- 2) K. Suganuma: *Materia Japan* **38** (1999) 919.
- 3) T. Suga: *Materia Japan* **38** (1999) 920–922.
- 4) T. Nishimura: *Materia Japan* **43** (2004) 651–654.
- 5) Japan Inst. Metals: *A Data Book on Metals* (Maruzen, Tokyo, 2007) p. 10.
- 6) Japan Inst. Metals: *A Data Book on Metals* (Maruzen, Tokyo, 2007) p. 11.
- 7) ASM International: *ASM Handbook Vol. 3 Alloy Phase Diagrams*, (ASM International, Ohio, 1992) p. 2-203.
- 8) ASM International: *ASM Handbook Vol. 3 Alloy Phase Diagrams*, (ASM International, Ohio, 1992) p. 2-178.