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Experimental investigation of Sn/Ni/Cu interactions at high temperatures

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Interest in environmentally conscious products has been growing steadily in recent years. In the electrical manufacturing industry, the practical use of Pb-free solder is increasing to satisfy the RoHS directive (Directive 2002/95/EC of the European Parliament and of the Council on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment) in Europe. Although high-melting point solder, (containing more than 85 mass% Pb), applied to power devices such as power transistors and thyristors is not restricted by the RoHS directive at present [1], alternative solder will be indispensable in the near future.

Sn-based alloys have been in general use for solder joints because they have good wettability and workability properties. However, for the practical use of Sn-based alloys as a high-melting point solder, improvement of the heat resistance of them is essential because the melting point of Sn (504 K) is lower than that of Sn-85 mass% Pb. Yamamoto *et al*. have reported that the heat resistance of Sn-based alloys can be improved by using interactions of Sn-based alloys and metal substrates to change them completely to intermetallic compounds (IMCs) [2]. But developing the IMCs adequately by the reported method would make the time required in the joining process unacceptably long.

In this study, Sn/Ni/Cu interactions were examined at high temperatures in a short time in order not to remarkably decrease manufacturing efficiency. Ni is widely used as a barrier layer on Cu pads on printed wiring boards. Sharif *et al*. [3, 4] and He *et al*. [5–7] have studied Sn/Ni interactions. They have analyzed the state of the interface after tens of minutes, several hours, and several days at 473–543 K. On the other hand, we examined the Sn/Ni/Cu interactions at temperatures of 573 K or more for a few seconds, assuming practical joining conditions. For the interactions, pure Sn and Cu plated by Ni were respectively selected as an Sn-based alloy and a metal substrate to achieve the basic Sn/Ni/Cu interaction.

After Sn/Ni/Cu interaction, pure Sn changes to Sn–Ni–Cu alloy by dissolution of Ni and Cu in molten Sn, and the liquidus line temperature of it rises rapidly. As can be seen in Fig. 1 [8], the liquidus line temperature of the Sn–Ni alloy can be raised to 573 K or more by adding 1 mass% of Ni. The microstructures of Sn–Ni–Cu alloy have IMCs consisted of Sn, Cu, and Ni in Sn-matrix. Because these IMCs can keep solid phase even after Sn-matrix become liquid phase, it is expected that an Sn–Ni–Cu alloy have a good heat resistance at high temperature conditions demanded from the high-melting point solder. Though these IMCs might cause to decrease the wettability in the case of using Sn–Ni–Cu alloy in soldering, this method enables to solder in good wettability condition because of using pure Sn at first.

Samples were prepared in a pure Sn sheet with dimensions of 15 mm × 20 mm×0.1 mm and a 0.5-μm-thick electroless plating layer of Ni on the surface of an oxygen-free copper (OFC) substrate with dimensions of 15 mm×20 mm×0.3 mm. Fig. 2a shows the above pure Sn sheet and the Ni-plated OFC substrate. These were set as shown in Fig. 2b for the Sn/Ni/Cu interactions in air at peak temperatures of 523–723 K and in a peak holding time of 5 s. These heat treatments were carried out by using a hot plate.

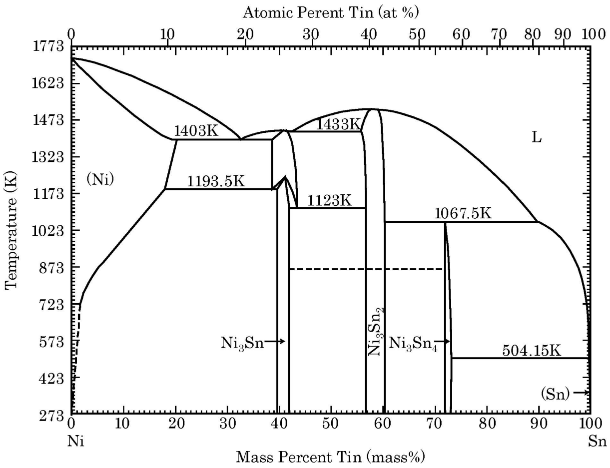

Figure 1 Sn-Ni binary system phase diagram.

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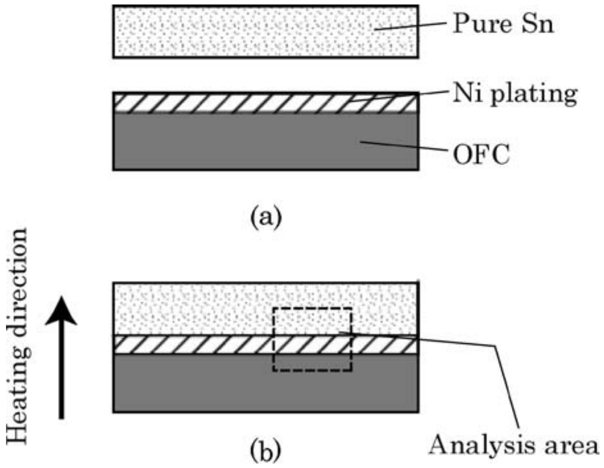

Figure 2 Materials used in Sn/Ni/Cu interaction.

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectrometry (EDX) were employed to observe the microstructures and analyze the Sn/Ni/Cu interfaces after the heat treatments. The dotted-line rectangle in Fig. 2b indicates the SEM observation area of Sn/Ni/Cu interfaces. Differential scanning calorimetry (DSC) was also employed to determine the melting point of the Sn/Ni/Cu interfaces. Samples were extracted from the Sn/Ni/Cu interfaces by 10 mg. And they were heated up to 773 K and then cooled to room temperature at 0.08 K/s in accordance with the Japan Industrial Standards (JIS) [9]. In addition, heating rate at 1.0 K/s was also adopted in assuming a rapid heating case.

Firstly, Figs 3–5 show the microstructures of the Sn/Ni/Cu interface after heat treatments at 573–723 K for 5 s. From the result at 573 K shown in Fig. 3, IMCs appear to be formed as layer at the Sn/Ni/Cu interface and as grain in Sn-matrix though Ni is difficult to dissolve in molten Sn at the usual soldering temperature [10]. At heat treatments at 623 K (Fig. 4) and 723 K (Fig. 5), the size and the distribution density of the IMCs were greater. The dendritic shape of the IMCs seen in Fig. 5 indicates that the microstructure of Sn/Ni/Cu interface depends on the heat treatment temperature.

Secondly, the compositions of the IMCs were investigated by EDX analysis. The results from EDX revealed that the atomic ratio of the sum of Cu and Ni content to Sn content in the IMCs in the Sn-matrix was approximately 6:5. Therefore it was confirmed that $(Cu,Ni)_6Sn_5$ were formed in Sn-matrix. In addition, the EDX results revealed that the atomic ratio of the sum of Cu and Ni content to Sn content in the IMCs in the layer at the Sn/Ni/Cu interface was approximately 3:1. This result indicates $(Cu,Ni)_3Sn$ were formed at the Sn/Ni/Cu interface. Cu and Ni are elements that lie next to each other in the periodic table of elements; therefore their atomic radii are similar. Thus, they might to be interchangeable during Sn/Ni/Cu interactions.

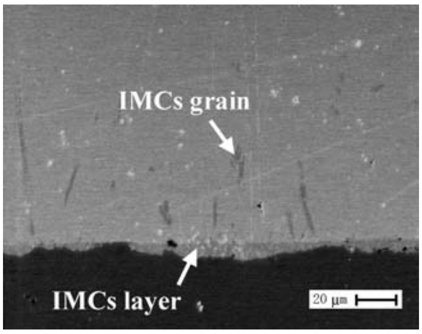

Figure 3 Sn/Ni/Cu interface at heat treatment at 573 K.

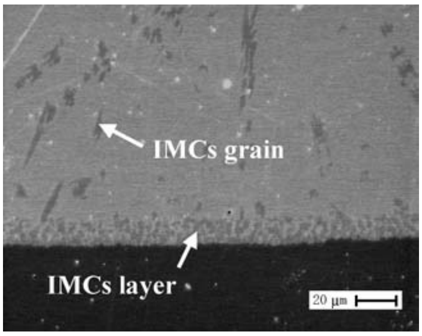

Figure 4 Sn/Ni/Cu interface at heat treatment at 623 K.

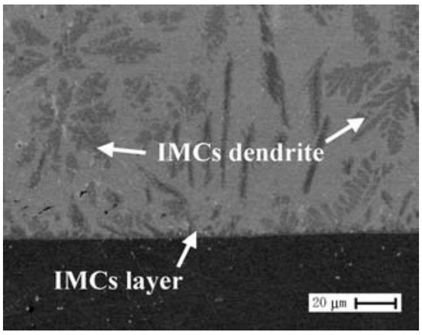

Figure 5 Sn/Ni/Cu interface at heat treatment at 723 K.

Thirdly, DSC thermal analysis of samples extracted from Sn/Ni/Cu interfaces was employed in accordance with JIS for measuring the solidus and liquidus temperatures directly. The results from DSC revealed the solidus temperatures were constant at 503 K regardless of the heat treatment temperatures. On the other hand, the liquidus line temperatures depended on the heat treatment temperature. Fig. 6 shows the results of DSC analysis in cooling process of samples at heat treatments at 623–723 K. The temperatures of an exothermic peak mean the liquidus line temperatures. These results show that the exothermic peaks appeared at heat treatments at 623 K or more. And the peaks became clearer with the increase in the heat treatment temperature. The liquidus line temperature rose up to 670.5 K at heat treatment at 723 K.

Finally, Fig. 7 shows the result from DSC analysis at heating rate 1.0 K/s of samples at heat treatments at 573 and 723 K in assuming a rapid heating case. Until two DSC curves reach 550 K, they show almost the same

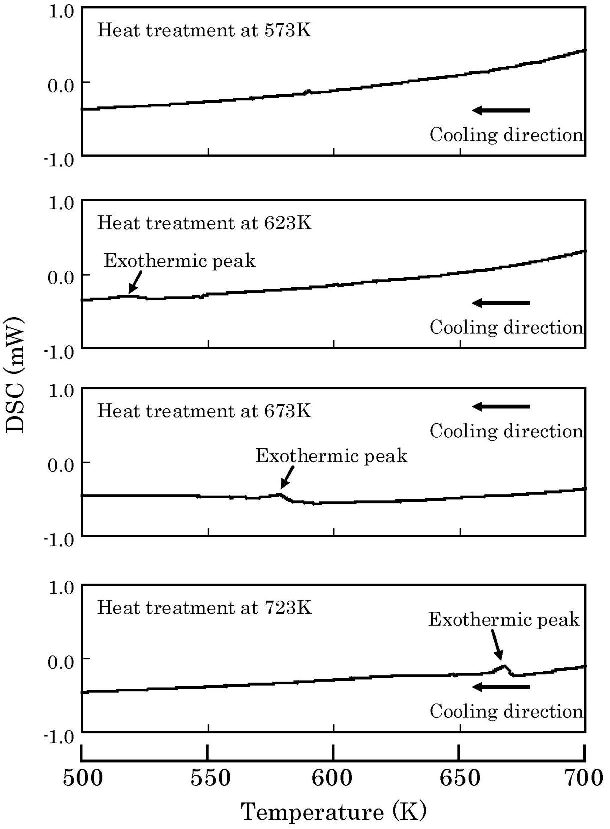

Figure 6 DSC results for Sn/Ni/Cu interface in cooling process (cooling rate 0.08 K/s).

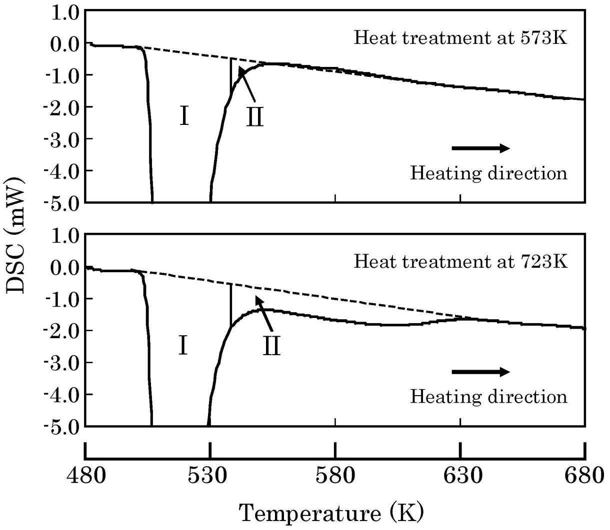

Figure 7 DSC results for Sn/Ni/Cu interface in heating process (heating rate 1.0 K/s).

behavior. When exceeding 550 K, they show the different. It is thought that they show the two different endothermic reactions which occurred when Sn-matrix in the samples changes from solid to liquid and when the IMCs dissolved in molten Sn gradually. So the endothermic peaks divided into two at 538 K for convenience. The first parts caused by Sn-matrix melting present I and the second parts caused by IMCs dissolving present II. Compared with endothermic values of part I to ones of part II, the ratio of endothermic value of part II is 1.09% at heat treatment at 573 K. Otherwise the ratio of it is 9.97% at heat treatment at 723 K. This means that the IMCs remaining in the state of solid phase after Sn-matrix melting increased greatly at heat treatment at 723 K. It is expected that the increase in these IMCs contributes to the improved the heat resistance of Sn/Ni/Cu interface.

These experimental results revealed Sn/Ni/Cu interactions at high temperatures in a short time. The results from SEM observation show that increasing the heat treatment temperature caused the growth of the size and dissolution of the IMCs. The growth was also confirmed by the results from DSC analysis. Because these IMCs can keep solid phase even after Sn-matrix become liquid phase, it is expected that an Sn/Ni/Cu interface formed a lot of IMCs in Sn-mtrix have a good heat resistance. In future the improvement of the heat resistance will be confirmed actually by measuring a mechanical strength of Sn/Ni/Cu interface at the high temperature conditions demanded from high-melting point solder.

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