Interfacial Reactions between Liquid Indium and Nickel Substrate

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The morphologies and growth kinetics of intermetallic compounds for the interfacial reaction between liquid In and solid Ni substrate in the temperature range from 225 to 500°C are examined in this study. Experimental results showed that the thickness of intermetallic compounds formed during the $Ni_{(s)}/In_{(l)}$ interfacial reaction increased with the reaction temperature and the square root of reaction time. The x-ray diffraction pattern revealed the formation of intermetallic compounds $Ni_{10}In_{27}$ (T<300°C) and Ni_2In_3 (T>300°C). Moreover, the activation energies for the interdiffusion of Ni and In atoms in the $Ni_{10}In_{27}$ and Ni_2In_3 are 94.74 and 33.51 kJ/mol, respectively. Using the Ta thin film as a diffusion mark, the formation mechanism of intermetallic compounds during interfacial reaction was clarified.

Key words: Activation energy, indium, intermetallic compound, nickel

INTRODUCTION

Soldering is a low-temperature joining process commonly used for electronic packaging.[1] During soldering, the solder alloy melts and reacts with the substrate to form intermetallic compounds at the joining interface. The formation of intermetallic phases at the solder joint could cause mechanical failure during thermal or power cycling.[2] Therefore, a knowledge of intermetallic phases produced by soldering in electronic packaging is essential. Among many solder alloys, Pb-Sn solders have been most commonly used.[3] However, since Pb will induce environment pollution, the development of Pb-free solders should thus be of vital importance for the electronic industry in the future. Several Pb-free solders[4,5] have been developed for electronic packaging. Jin et al.[6] developed a Bi-43%Sn solder containing Fe dispersoid particles, which had better microstructure stability and superior creep resistance compared to the Pb-Sn eutectic solder. The growth kinetics of Ni-Sn intermetallic phases at the liquid Sn and solid Ni interface has been investigated by Kang et al.[7] In their work, both Ni_3Sn_4 and Ni_3Sn_2 were observed and parabolic kinetics was obeyed for the growth of intermetallic compounds.

The In-alloy solders possess a longer fatigue life than conventional Pb-Sn solders for flip-chip interconnections in thermal shock tests between room temperature and liquid nitrogen.[8] Some studies have been performed on the interfacial reactions between In and Cu. Kao[9] found that $Cu_{11}In_9$, Cu_7In_3, and Cu_2In formed in the solid Cu/liquid In interface. Manna et al.[10] studied the interdiffusion between In and bulk Cu and Cu-In alloy isothermally annealed at 373, 398, and 423K for varying lengths of time. They found the growth rates of intermetallic layers to follow parabolic kinetics. The activation energy for Cu (In) interdiffusion was 26.07 kJ/mol and for Cu-In (In) was 26.42 kJ/mol. With the exception of these efforts, no other information is yet available on the interfacial reaction between In and Ni.

In the present work, the morphologies and growth kinetics of intermetallic compounds during the reaction of liquid In with solid Ni were analyzed in the temperature range from 225 to 500°C. For the identification of intermetallic compounds, both electron microprobe (EPMA) and x-ray diffraction (XRD) were employed.

EXPERIMENTAL

Nickel substrates (15 mm × 15 mm) were cut from a 0.8 mm thick high-purity Ni plate (Ni-99.5%). Their surfaces were prepared by grinding with 1500 grit SiC paper and polishing with 0.3 µm Al_2O_3 powder.

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Indium plates (In-99.99%) with dimensions of $3 \times 3 \times 3$ mm[3] were laid on the Ni substrates. The SMQ TACFLUX 005 flux was used in this test. Table I lists the characteristics of this flux.

Interfacial reactions were carried out at temperatures ranging from 225 and 500°C in an infrared furnace for various periods of time in a vacuum of 10^{-3} Torr. After the reactions, In was selectively etched from the Ni/In specimens using an aqueous solution of 7g NH_4F + 10 ml H_2O_2. The intermetallic compounds were analyzed using XRD. In order to examine the growth kinetics of intermetallic compounds during interfacial reactions, the cross sections of all specimens were observed with a scanning electron microscope (SEM) and average thicknesses of the intermetallic layer were given for the analyses at five points. The In contents in intermetallic compounds were further examined by EPMA. The measurements are known to be within ±0.05 at.%. Combining the results of XRD and EPMA analyses, the intermetallic compounds that form through the interfacial reactions between liquid In and Ni substrate were identified. For further clarification of the formation mechanism of intermetallic compounds in the interfacial reaction, the original $Ni_{(s)}/In_{(l)}$ interfaces were marked by sputtering-deposition of a Ta thin film on the partial region of Ni substrates. From the phase diagram, it can be seen that Ta will not react with Ni and In, the deposition of Ta thin film acted as a diffusion barrier at $Ni_{(s)}/In_{(l)}$ interface. The original $Ni_{(s)}/In_{(l)}$ interface can thus be identified.

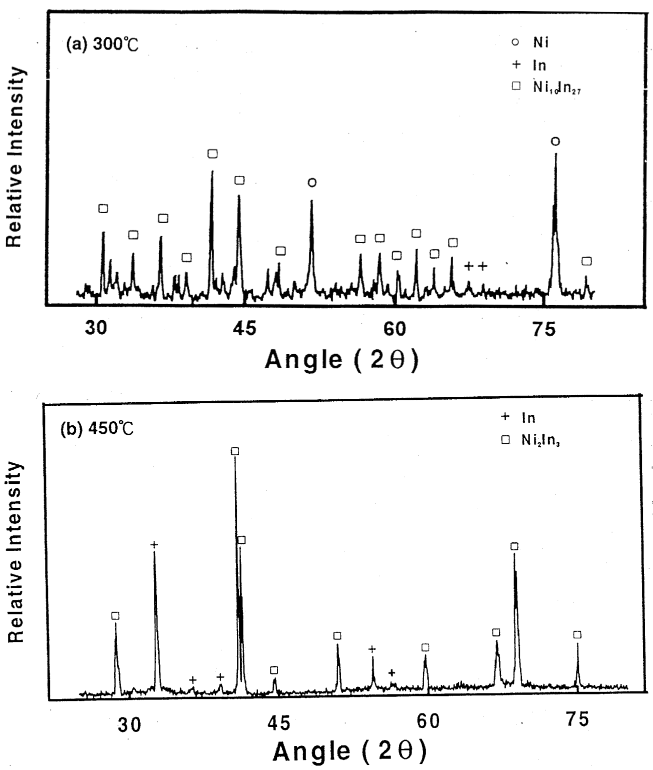

Fig. 1. Typical x-ray diffraction patterns of the $Ni_{(s)}/In_{(l)}$ interfacial reaction products formed below and above 300°C: (a) 300°C, and (b) 450°C.

RESULTS AND DISCUSSION

When the specimens were heated above the melting temperature of In (157°C), the molten In reacted with Ni substrate and immediately formed intermetallic compounds (Ni_xIn_y) at the $Ni_{(s)}/In_{(l)}$ interface. According to the Ni-In phase diagram, several intermetallic phases such as Ni_3In, Ni_2In, $Ni_{13}In_9$, NiIn, Ni_2In_3, and $Ni_{10}In_{27}$ could form. However, the x-ray diffraction patterns only revealed the phases Ni, In, and $Ni_{10}In_{27}$ for the samples reacting below 300°C (Fig. 1a). When the reaction temperatures increased above 300°C, Ni, In, and Ni_2In_3 were detected (Fig. 1b). The chemical compositions of interfacial reaction products were also analyzed by using EPMA, the results are shown in Table II. In Table II, average data were given for the analyses at five points, revealing that the primary intermetallic compound formed below 300°C was $Ni_{10}In_{27}$, and above 300°C changed to Ni_2In_3.

The typical morphologies of $Ni_{(s)}/In_{(l)}$ interfacial microstructure in dependence of reaction temperatures and times are shown in Fig. 2. Small nuclei of intermetallic compounds are found randomly along the Ni/In interface at 250°C for 15 min, which revealed the early step of interfacial reaction (Fig. 2a). A continuous intermetallic layer grew slowly with the increase of reaction time (Fig. 2b). At 450°C, the continuous intermetallic layer formed even after a

Table I. The Characteristics of SMQ TACFLUX 005 Flux

Flux Type	Flash Point	Solid Content	Viscosity (25°C)	Max. use Temp.	Residue Removal
RMA	66°C	14%	68,000±10% cps	300°C	Water

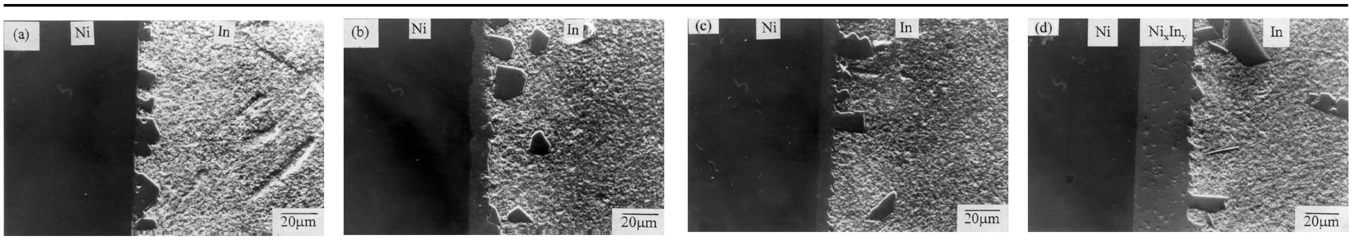

Fig. 2. Typical morphologies of the $Ni_{(s)}/In_{(l)}$ interfacial reaction products formed under various temperatures at various times: (a) 250°C, 15 min, (b) 250°C, 135 min, (c) 450°C, 15 min, and (d) 450°C, 135 min.

Table II. Chemical Compositions Obtained Across the Intermetallic Layer Formed during $Ni_{(s)}/In_{(l)}$ Interfacial Reaction (at.%)

	Positions Measured Across the Ni-In Intermetallic Layer								
	5μm	10 μm	15 μm	20 μm	25 μm	30 μm	40 μm	50 μm	60 μm
250°C	Ni-29.62	Ni-29.25							
	In-70.38	In-70.75							
275°C	Ni-27.76	Ni-26.16	Ni-26.74						
	In-72.24	In-73.84	In-73.26						
300°C	Ni-28.96	Ni-28.01	Ni-28.47	Ni-28.02	Ni-27.95				
	In-71.04	In-71.99	In-71.53	In-71.98	In-72.05				
450°C		Ni-36.75		Ni-36.18		Ni-37.36	Ni-37.32	Ni-36.73	
		In-63.82		In-63.82		In-62.64	In-62.68	In-63.27	
500°C		Ni-38.06		Ni-37.60		Ni-38.36	Ni-39.06	Ni-38.79	Ni-38.52
		In-61.94		In-62.40		In-61.64	In-60.94	In-61.21	In-61.48

short reaction time of 15 min (Fig. 2c). Reaction at such an elevated temperature for a longer time caused the appearance of a very thick and uniform intermetallic layer (Fig. 2d). It was also found that during the interfacial reactions, some products showed poor adhesion with the Ni substrate and separated from the interface to form many intermetallic islands in the In matrix. The remaining intermetallic products grew as a continuous layer along the $Ni_{(s)}/In_{(l)}$ interface. EPMA analyses confirmed that both the intermetallic islands and the continuous intermetallic layer possessed the same In content.

The average thicknesses (ΔX) of the intermetallic layers were measured and plotted against the square root of the reaction time (t) in Fig. 3

$$\Delta X = K\sqrt{t}$$

where K is the growth rate constant. From the curves of Fig. 3, the growth rate constants were calculated and listed in Table III. The standard deviation for intermetallic layers was between 0.1 and 0.2 μm. In Fig. 3, it can be seen that the growth of intermetallic compounds followed a parabolic law, implying that the growth of the intermetallic layer was diffusion controlled; i.e., the Ni and In atoms interdiffused through the intermetallic compound layer to result in the growth of intermetallic compounds. In this case, the Arrhenius equation can be used to express the growth rate constant for the intermetallic layer:

$$K = A\exp\left(-\frac{Q}{RT}\right)$$

where A is a constant, Q is the activation energy, R is the gas constant, and T is the absolute temperature.

An Arrhenius diagram of ln K vs 1/T is given in Fig. 4. The diagram consists of two straight lines intersecting at approximately 300°C, which indicates that two kinds of intermetallic compounds grew in different temperature ranges during the $Ni_{(s)}/In_{(l)}$ interfacial reaction. The activation energies for the straight line above and below 300°C, as determined from Fig. 4, were 94.74 and 33.51 kJ/mol, respectively. According to the XRD and EPMA analyses presented above, the interfacial reaction in the temperature range from 300 to 500°C resulted in an Ni_2In_3 intermetallic compound. Below 300°C, the $Ni_{10}In_{27}$ compound was found. This implied that the activation energies for the interdiffusion of Ni and In atoms in the Ni_2In_3 and $Ni_{10}In_{27}$ intermetallic compounds were 94.74 and 33.51 kJ/mol, respectively.

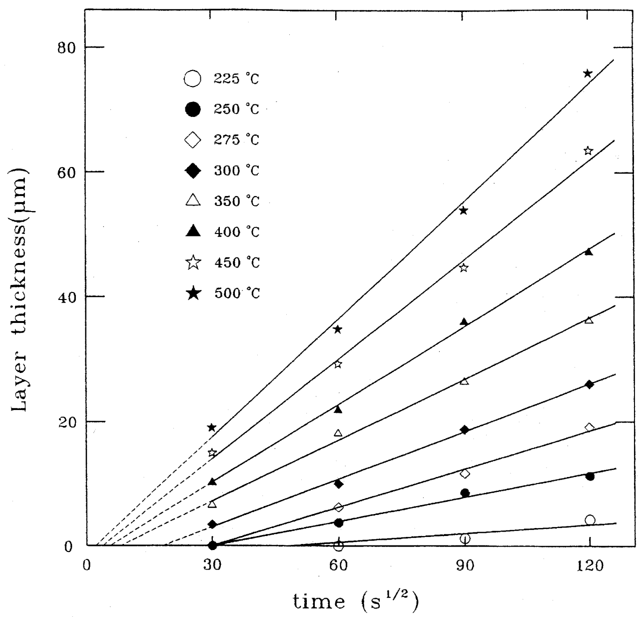

Fig. 3. Thickness of intermetallic compound layers as a function of the square root of reaction time under the reaction temperature range from 225 to 500°C.

Through the employment of Ta thin film on Ni substrate as a diffusion barrier for the $Ni_{(s)}/In_{(l)}$ interfacial reaction, it was found that the reaction fronts of intermetallic compounds migrated toward Ni substrate and molten In (Fig. 5). EPMA analyses showed that the intermetallic compounds on both sides of the Ta diffusion mark possessed the same In contents. It was also shown that the ratios of migration distance toward Ni substrate to that toward molten In were about 2.25 and 2.10 for the interfacial reactions below and above 300°C, respectively. The ratio of migration distance toward Ni substrate to that toward In solder should correspond to the ratio of diffusivity (D) of In and Ni in the respective intermetallic compounds.

Table III. Growth Rate Constants of Intermetallic Layers Formed during the $Ni_{(s)}/In_{(l)}$ Interfacial Reaction

Temperature(°C)	Growth Rate Constant (cm^2s^{-1})
225	3.32×10^{-11}
250	1.30×10^{-10}
275	1.59×10^{-10}
300	6.56×10^{-10}
350	1.06×10^{-9}
400	1.76×10^{-9}
450	2.80×10^{-9}
500	3.92×10^{-9}

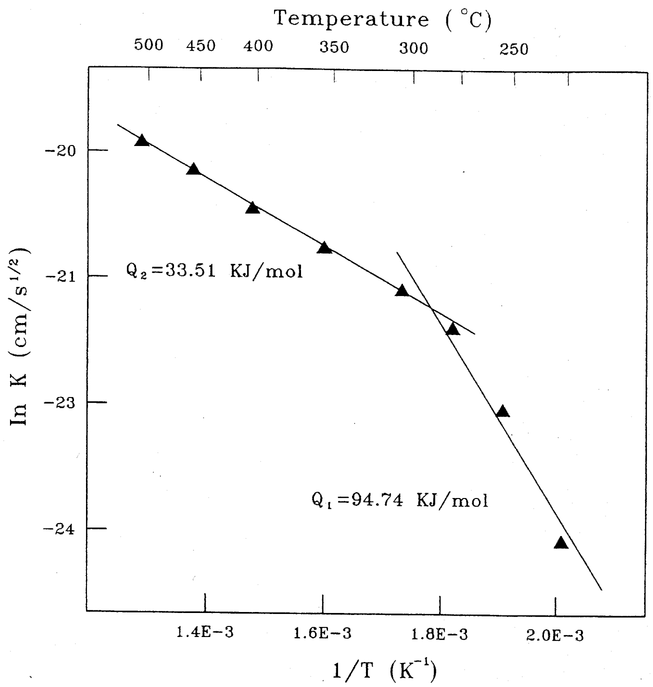

Fig. 4. Arrhenius plots of the growth rate constant (ln K) vs reaction temperature (1/T) during the $Ni_{(s)}/In_{(l)}$ interfacial reaction.

i.e.,

$$\frac{D_{Ni/Ni_{10}In_{27}}}{D_{In/Ni_{10}In_{27}}} = 5.07 \text{ and } \frac{D_{Ni/Ni_2In_3}}{D_{In/Ni_2In_3}} = 4.43.$$

CONCLUSIONS

Two kinds of intermetallic compounds, $Ni_{10}In_{77}$ and Ni_2In_3 for temperatures below and above 300°C, respectively, form when polycrystalline Ni substrates react with liquid In. The thickness of the intermetallic compounds formed during $Ni_{(s)}/In_{(l)}$ interfacial reaction increased with the reaction temperature and the square root of reaction time, which implies that the reaction is diffusion controlled. i.e., during the interfacial reaction of Ni substrate and molten In, Ni, and In atoms interdiffused through intermetallic compounds to cause the growth of intermetallic compounds. The activation energies for the interdiffusion of Ni and In atoms in the $Ni_{10}In_{27}$ (T<300°C) and Ni_2In_3 (T>300°C) are 94.74 and 33.51 kJ/mol, respectively. Using the diffusion mark of Ta thin film, the ratios of the diffusivity for In to Ni in $Ni_{10}In_{27}$ and in Ni_2In_3 were approximately 5.07 and 4.43, respectively.

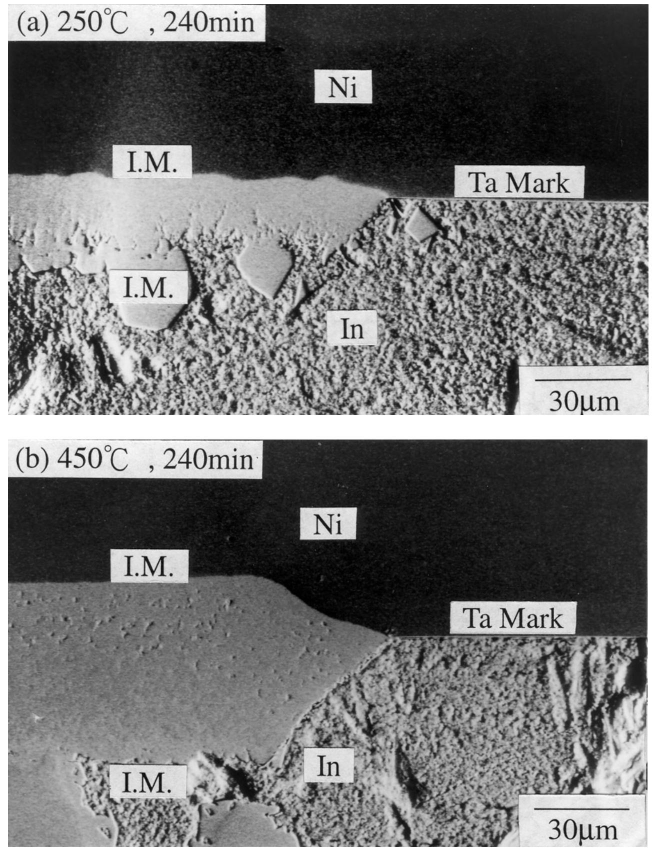

Fig. 5. Migration of reaction of intermetallic compounds at $Ni_{(s)}/In_{(l)}$ interface formed below and above 300°C: (a) 250°C, 240 min, and (b) 450°C, 240 min.

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