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Interfacial Reactions of Liquid Sn and Sn-3.5Ag Solders With Ag Thick Films

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The interfacial reactions of liquid Sn and Sn-3.5Ag solders with Ag thick films are investigated in the temperature range from 250-325 °C, and the morphology of intermetallic compounds formed after such soldering reactions is observed. In kinetics analysis of the growths of intermetallic compounds, it was found that both Sn/Ag and Sn-3.5Ag/Ag reactions were interfacial-controlled, and the growth rates for both cases were similar. The rate of Ag dissolution into liquid solder attendant on the formation of interfacial intermetallic compounds after Sn/Ag reaction was about four times higher than that after Sn-3.5Ag/Ag reaction, as evidenced by experimental results.

Keywords Ag dissolution, Ag_3Sn intermetallic compound, Ag thick film, Sn/Ag, Sn-3.5Ag/Ag, soldering reactions

1. Introduction

In a previous work by the authors, the intermetallic compounds and their growth kinetics during the soldering reactions between liquid Sn and Ag plates were studied.[1] The results showed that, along with the formation of Ag_3Sn intermetallic compounds at Sn/Ag interface, the Ag substrate dissolved severely into the molten solder. Typically, such an erosion phenomenon on the Ag substrate can be alleviated by the addition of the Ag element into the Sn solder, in which case the growth kinetics of interfacial intermetallic compounds will also be affected. Because Ag thick films have been widely used for the manufacturing of hybrid integrated circuits (HIC), resistors, ceramic capacitors, and multilayer chip inductors, it makes sense to conduct a further investigation of Sn and Sn-Ag solders reacted with Ag thick films. For the present experimental investigation, a eutectic Sn-3.5Ag alloy was used, which has been recognized as one of the promising candidates for Pb-free solders in the electronics industry. This study compared the growth kinetics of interfacial intermetallic compounds and dissolutions of Ag thick films between Sn/Ag and Sn-3.5Ag/Ag soldering reactions.

2. Experimental

For the preparation of the Ag thick film, the surface of an alumina substrate was coated with silver paste (composition: Ag 75-80 wt.%, glass 1-5 wt.%, resin 1-5wt.%, Terpineol 5-10 wt.% and Diethyl Phthalate 5-10 wt.%) using a screen printer. Specimens were first heated at 150 °C for 10 min and then sintered at 850 °C for 10 min in an air furnace. After the specimens were sintered, they were cooled to room temperature. The sintered Ag thick film on the alumina substrate possessed a thickness of 10 μm and low porosity. The Sn-3.5Ag solder was prepared by vacuum melting into an ingot and homogenized at 100 °C for 50 h. Afterward, both the Sn and Sn-3.5Ag solders were rolled into 0.2 mm thick foils. For the study of interfacial reactions, the solder foil was cut to the same size as the Ag/Al_2O_3 substrate, placed on the Ag/Al_2O_3 substrate, and then heated in an IR furnace under a vacuum of 10^{-3} torr. To eliminate the oxidation factor in soldering, a flux of SMQ TACFLUX 005 (Indium Co., Utica, NY) was applied before testing.

Soldering reactions took place at temperature ranging from 250-325 °C for various periods of time. After the reaction, the soldered specimens were cut along the cross section, ground with SiC paper, polished with 1 and 0.3 μm Al_2O_3 powders, and observed by scanning electron microscopy (SEM). For kinetics analysis, the thicknesses of intermetallic compounds were calculated by dividing the total areas of interfacial intermetallics by the widths of the intermetallics on the micrographs. The dissolved thickness (X_D) of the Ag thick film was estimated as follows: $X_D = X_I - X_R - X_{IM}^{Ag} = X_I - X_R - (3/4)X_{IM}$, where X_I is the initial thickness of the Ag thick film, X_R is the residual thickness of the Ag thick film, X_{IM} is the thickness of the interfacial intermetallic compound, and X_{IM}^{Ag} signifies the partial thickness of Ag in the intermetallic compound. The intermetallic compound in this study was Ag_3Sn as analyzed by electron probe microanalysis (EPMA). The difference in atomic size between Ag and Sn notwithstanding, the partial thickness (X_{IM}^{Ag}) of the Ag thick film contained in the Ag_3Sn intermetallic compound was about $(3/4)X_{IM}$.

3. Results and Discussion

The typical micrographs of intermetallic compounds formed during interfacial reactions between liquid Sn and Ag thick films are shown in Fig. 1. It can be seen that the intermetallic compounds at the Sn/Ag interface have a scallop-type morphology. EPMA analyses indicate that these interfacial intermetallic compounds are in the Ag_3Sn phase. Through selective etching out of the Sn solder from the reacted Sn/Ag specimens,

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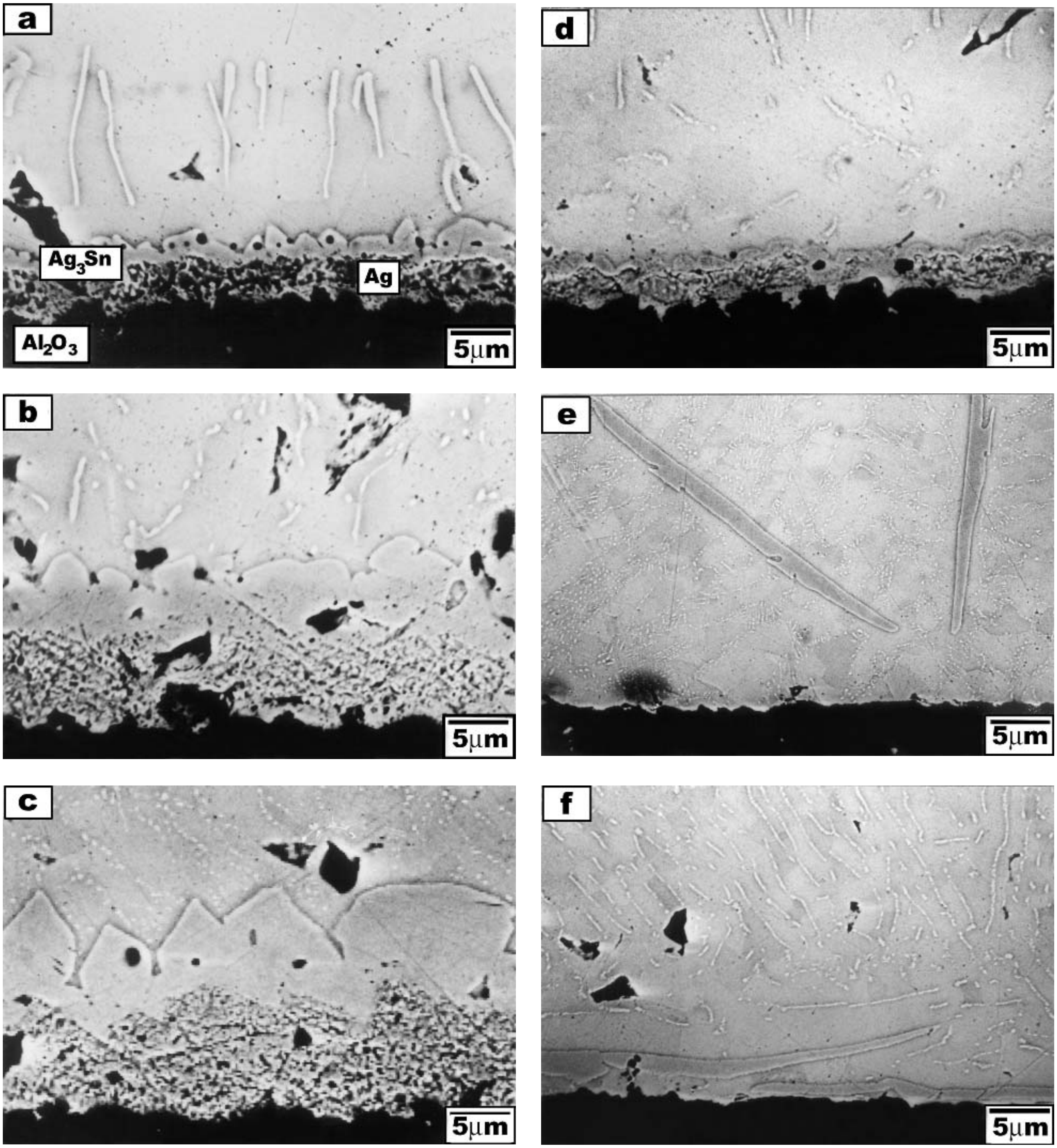

Fig. 1 Micrographs of the interfacial intermetallic compounds and matrix precipitates formed during soldering reaction between liquid Sn and the Ag thick film. **(a)** 250 °C, 20 min. **(b)** 250 °C, 25 min. **(c)** 250 °C, 30 min. **(d)** 300 °C, 7 min. **(e)** 300 °C, 15 min. **(f)** 300 °C, 18 min

the Ag_3Sn phase is further confirmed by x-ray diffractometry (XRD) to be present in the remaining intermetallic compounds, as shown in Fig. 2. The intermetallic compounds formed during the interfacial reactions of Sn thin film, and Sn-Pb and Sn-Ag solders with Ag substrates, have been reported in the literature to be in the Ag_3Sn phase,[2-8] which is consistent with the results of the current study.

Figure 1 illustrates that the Ag thick film dissolves into the pure Sn matrix for a distance of about 13 μm after soldering reaction at 250 °C for 20 min. The dissolved Ag atoms result in the formation of needle-like precipitates near the Ag/Sn interface, which are also shown to be in the Ag_3Sn phase as analyzed by EPMA. No Ag_3Sn precipitates appear in the Sn matrix aside from this region. After the soldering reaction at

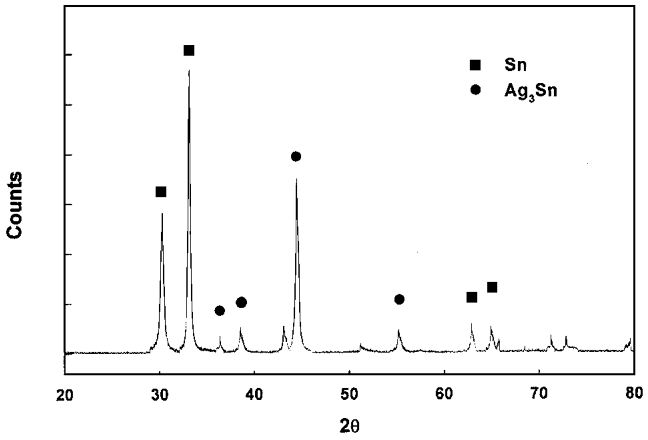

Fig. 2 Typical x-ray diffraction patterns of the intermetallic compounds formed at the interface between liquid Sn and Ag thick film after selectively etching out the Sn unreacted solder

Table 1 Thicknesses of Interfacial Intermetallic Compounds Under Various Conditions (a)

T, °C	t, min	X_{IM}, μm	X_R, μm	X_{IM}^{Ag}, μm	X_D, μm
250	20	2.2	4.8	1.7	3.5
250	25	4.8	4.1	3.6	2.3
250	30	6.6	3.2	5.0	1.8
275	9	2.3	3.2	1.7	5.0
275	15	5.4	2.8	4.0	3.2
275	20	7.0	1.0	5.2	3.4
300	7	1.6	3.2	1.2	5.6
325	5	2.8	1.6	2.1	6.4

(a) The thicknesses of residual Ag thick Films (X_R), created intermetallic compounds (X_{IM}), dissolved Ag thick films (X_D), and the partial thickness of Ag in the created intermetallic compounds (X_{IM}^{Ag}) after soldering reactions between liquid Sn and Ag thick films at various temperatures (T) for various times (t)

Table 2 Thicknesses of Interfacial Intermetallic Compounds Under Various Conditions

T, °C	t, min	X_{IM}, μm	X_R, μm	X_{IM}^{Ag}, μm	X_D, μm
250	20	2.4	7.9	1.3	0.2
250	28	4.6	5.7	3.4	0.8
250	32	5.6	5.6	4.2	0.3
275	20	2.5	6.3	1.9	1.8
275	24	4.7	5.7	3.5	0.8
275	28	5.5	5.3	4.2	0.6
300	12	4.8	5.7	3.6	0.7

(a) The thicknesses of residual Ag thick films (X_R), created intermetallic compounds (X_{IM}), dissolved Ag thick films (X_D), and the partial thickness of Ag in the created intermetallic compounds (X_{IM}^{Ag}) after soldering reactions between liquid Sn-3.5 Ag and Ag thick films at various temperatures (T) for various times (t)

250 °C for 25 min or more, or as the reaction temperature is raised to above 275 °C for various time periods, the Ag_3Sn precipitates are seen to distribute fully in the Sn matrix. In this case, the needle-like Ag_3Sn precipitates are broken into particles located preferentially at grain boundaries of the Sn matrix. Figure 1 also shows that the residual Ag thick film has become porous after the soldering reaction. Such a porous structure of the remaining Ag thick film may be correlated to the severe dissolving of Ag Atoms through the grain boundaries of the sintered Ag thick film.

The micrographs in Fig. 1 also show that the scallop-shaped Ag_3Sn intermetallic compounds at the Sn/Ag interface grow with increasing reaction temperature and time. As the Sn/Ag soldering reaction approaches the end, a number of large intermetallic bands appear in the Sn matrix, as shown in Fig. 1(e) and (f). EPMA analyses indicate that their compositions are the same as those of the interfacial Ag_3Sn intermetallic compounds. From the Ag-Sn phase diagram, it can be seen that these large Ag_3Sn intermetallic bands result from the decomposition of liquid solder bearing excessively dissolved Ag atoms into the Ag_3Sn phase (intermetallic bands) and the eutectic phase (Ag_3Sn fine particles embedded in the Sn matrix) during the solidification process. However, a certain amount of intermetallic bands are found to settle along the Sn/Al_2O_3 interface where the Ag thick film has been consumed (Fig. 1f). It seems that the Ag_3Sn intermetallic bands have been preferentially formed ahead of the Sn/Al_2O_3 interface prior to the conclusion of the Sn/Ag soldering reaction. At that moment, the previously created scallop-shaped Ag_3Sn intermetallic compounds are split away from the remainder of the thin Ag layer, which has been prone to dissolve exhaustively into the liquid Sn solder. The drastically increased Ag concentration in the liquid Sn solder ahead of the Sn/Al_2O_3 interface results in the preferential decomposition of solder during the solidification process to form the intermetallic bands. These intermetallic bands will float away from the Sn/Al_2O_3 interface into the liquid solder matrix because of their poor bonding with the Al_2O_3 ceramic substrate.

The morphology of the interfacial intermetallic compounds formed during the soldering reaction between liquid Sn-3.5Ag and Ag thick films (shown in Fig. 3) is similar to that during the Sn/Ag soldering reaction. In both cases, there are also similar appearances of precipitates in the solder matrix. However, the precipitate-free region at the early stage of Sn/Ag soldering reaction (Fig. 1a) cannot be found with the Sn-3.5Ag/Ag reaction (Fig. 3a), which indicates that most of the precipitates formed in the latter case have originated from the Ag alloying element contained in the Sn-3.5Ag solder. It also results in a thicker residual Ag thick film after Sn-3.5Ag/Ag soldering reaction at 250 °C for 20 min (Fig. 3a) as compared with the Sn/Ag reaction (Fig. 1a). In addition, the structural porosity of the remaining Ag thick film after Sn/Ag soldering reaction can obviously be alleviated for the Sn-3.5Ag/Ag reaction (Fig. 3). At the final stage of the Sn-3.5Ag/Ag soldering reaction, the floating of large intermetallic bands can also be observed (Fig. 3e, f). Figure 3(e) gives a strong indication that such floating intermetallic bands have been stripped from the solder/Al_2O_3 substrate interface.

The thicknesses of the interfacial intermetallic compounds (X_{IM}) formed during the soldering reactions of liquid Sn and Sn-3.5Ag with Ag thick films under various conditions are summarized in Tables 1 and 2. The data are plotted against the

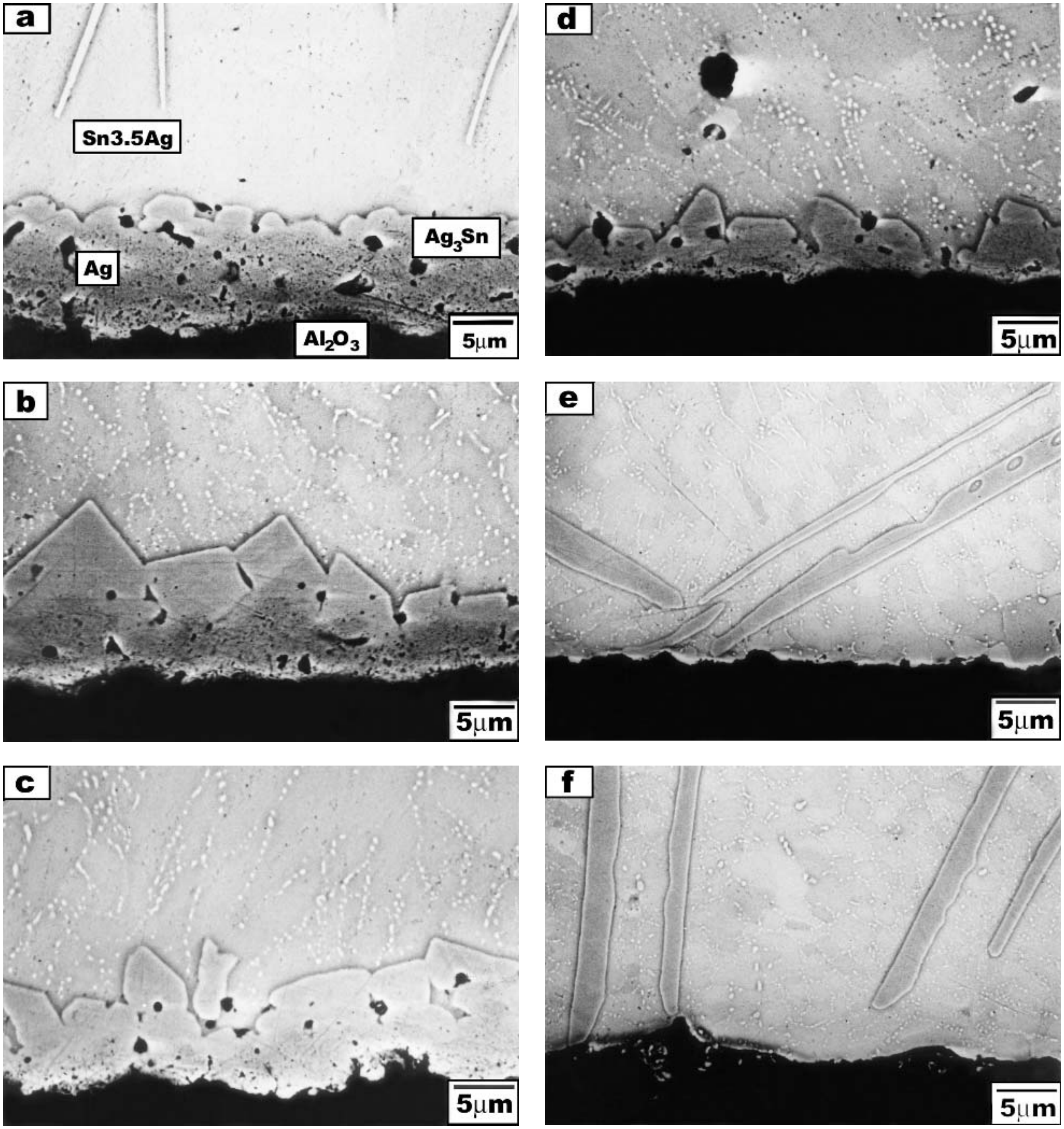

Fig. 3 Micrographs of the interfacial intermetallic compounds and matrix precipitates formed during soldering reaction between liquid Sn-3.5Ag and the Ag thick film. **(a)** 250 °C, 20 min. **(b)** 250 °C, 28 min. **(c)** 250 °C, 32 min. **(d)** 300 °C, 12 min. **(e)** 300 °C, 16 min. **(f)** 300 °C, 20 min

reaction time as shown in Fig. 4. For each soldering temperature in this study, there were fewer than three reliable measurements obtained because the as-sintered Ag thick film possesses only a thickness of 10 μm. Despite insufficient data for kinetics analysis, the plots in Fig. 4 are approximately linear, which implies that the growths of interfacial intermetallic compounds during both reactions of Sn and Sn-3.5Ag solders with Ag thick films are interface-controlled. However, in our previous study on the interfacial reaction between liquid Sn solder and Ag plates, the growth kinetics of Ag_3Sn intermetallic compounds was shown to be diffusion-controlled.[1] Such a discrepancy also appeared in our previous studies on the interfacial reactions of In49Sn solder with Ag plates[9] and Ag thick films.[10] This type of linear growth kinetics of the intermetallic compounds should be attributed to the penetration of liquid solder through the interfacial glass phase between the sintered

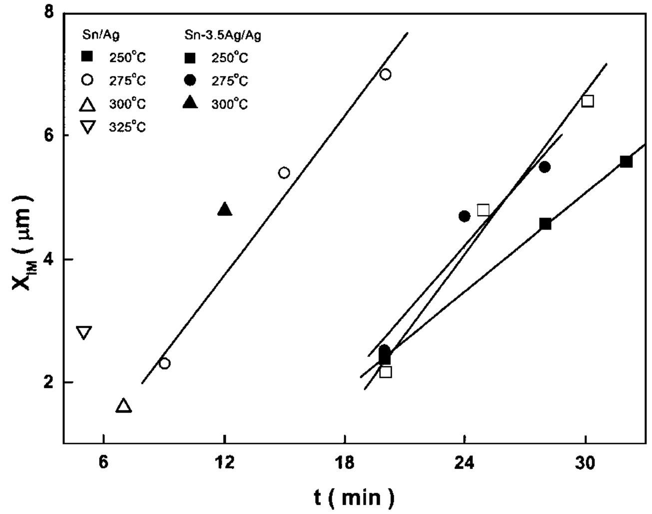

Fig. 4 The thickness of interfacial intermetallic compounds (X_{IM}) formed during soldering reactions of liquid Sn and Sn-3.5Ag with Ag thick films as a function of reaction time (*t*)

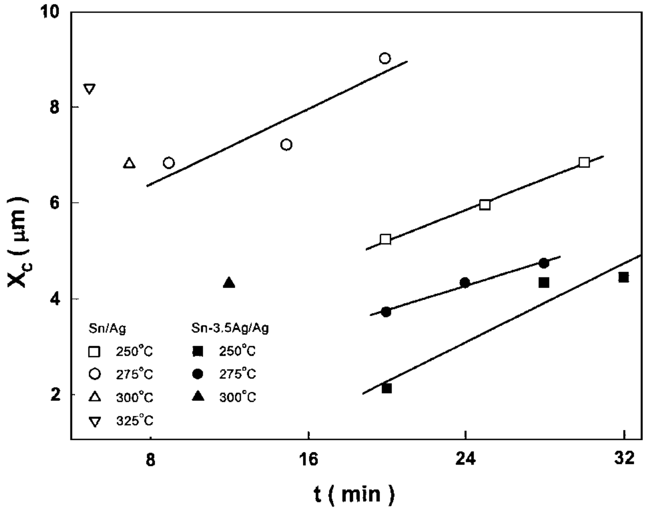

Fig. 5 The thickness of consumed Ag thick films ($X_c = X_I - X_R$) after soldering reactions of liquid Sn and Sn-3.5Ag with Ag thick films as function of reaction time. (X_I and X_R, respectively, signify the Ag thick film in its original and residual forms.)

Ag grains. The penetrated liquid solder reacts with the Ag grains at their interfaces, which results in an interfacial controlled growth of the intermetallic compounds. From Fig. 4, it can also be seen that the growth rates of interfacial intermetallic compounds during the Sn/Ag and Sn-3.5Ag/Ag soldering reactions are similar.

From Fig. 1 and 3, it can be observed that accompanying the formation of interfacial intermetallic compounds, a large amount of precipitates appear in the solder matrix. For the Sn/Ag reaction, such precipitates in the Sn matrix should result from the dissolution of Ag atoms from Ag thick films into liquid Sn solder. In fact, the dissolution of the Ag substrate during the Sn/Ag soldering reaction has been evidenced through marking the original Sn/Ag interface with a Ta thin film.[1] Even for the Sn-3.5Ag solder reacted with the Ag thick film, further dissolutions of Ag atoms into the liquid solder are inevitable, though basically the situation can be mitigated to a certain degree. To compare the dissolution of the Ag thick film during the Sn/Ag soldering reaction with that during the Sn-3.5Ag/Ag reaction, the residual thicknesses of Ag thick films (X_R) in both cases are measured and listed in Tables 1 and 2. The difference between the initial thickness (X_I) and the residual thickness (X_R) of Ag thick films gives the thickness (X_C) of Ag thick films consumed after the soldering reactions. Consistent with the growth rate analysis in Fig. 4, the plots for the consumed thickness of Ag thick films as shown in Fig. 5 are also governed by a linear relation.

Because the consumed Ag thick films are used in part to form the interfacial intermetallic compounds and in part to dissolve into the liquid solder, the dissolution amounts of Ag thick films (X_D) can be obtained by subtracting the residual Ag thickness (X_R) and the partial Ag thickness in the created Ag_3Sn intermetallic compounds (X_{IM}^{Ag}) from the initial Ag thickness (X_I). It has been known that the lattice size of Ag (a = 4.086 Å) is near that of Sn (a = 5.831 Å, c = 3.181 Å). The partial Ag thickness in the Ag_3Sn intermetallic compounds (X_{IM}^{Ag}) can thus be roughly estimated as (3/4)X_{IM}. In Tables 1 and 2, the X_D values are also shown for Sn/Ag and Sn-3.5Ag/Ag soldering reactions. It is obvious that the dissolution amounts of Ag thick films during the Sn/Ag reaction are about four-fold larger than those during the Sn-3.5Ag/Ag reaction. In principle, the decrease of the residual Ag thickness (ΔX_R) accompanied by a sequential increase in time (Δt) for the soldering at a definite reaction temperature cannot be lower than the increase of the partial Ag thickness in the intermetallic compounds (X_{IM}^{Ag}) if all of the Ag atoms in the newly grown intermetallic compounds have originated from the consumed Ag thick films. To the contrary, Tables 1 and 2 show evidence that X_{IM}^{Ag} is often greater than ΔX_R, which implies that part of the Ag atoms dissolved into the solder might have turned back to join in the growth of the interfacial intermetallic compounds.

4. Conclusions

During the soldering reactions of Sn and Sn-3.5Ag with Ag thick films, scallop-shaped Ag_3Sn intermetallic compounds appear at their interfaces. Attendant on the growth of such interfacial intermetallic compounds, needle-like precipitates are formed in the solder matrix and then transformed into fine particles to be distributed along the grain boundaries of the solders. At the final stage of soldering reactions, a number of large Ag_3Sn intermetallic bands can be observed in the solder matrix. Kinetic analyses show that the growth of interfacial intermetallic compounds during the Sn/Ag and Sn-3.5Ag/Ag soldering reactions are interface-controlled and the growth rates for both cases are similar. The appearance of precipitates in the Sn matrix during Sn/Ag soldering reaction gives evidence of the Ag dissolution in the Sn solder, which also occurs to the Sn-3.5Ag/Ag reaction. However, the dissolution rate of Ag during Sn/Ag reaction is about four times higher than that during the Sn-3.5Ag/Ag reaction.

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