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Effect of Ag addition to Zn–12Al alloy on kinetics of growth of intermediate phases on Cu substrate

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ABSTRACT

Zn–Al–Ag solders based on eutectic Zn–12Al alloy containing 0.5–1.5 at.% Ag are developed for ultra high temperature applications. Wettability tests carried out on Ag-doped Zn–Al alloys on Cu substrates showed the formation of Cu–Zn phases at the interface. Wettability studies were performed with the use of flux at 500 °C for 15, 30, 60, 180, 240, 900, 1800 and 3600 s, and for 240 s at 460, 480, 520, 550 °C, respectively. Experiment was designed this way in order to demonstrate the effect of Ag addition on the kinetics of formation and growth of CuZn, Cu_5Zn_8, $CuZn_4$ phases, which were identified with EDS analysis. In addition to improving spreadability of Zn–Al–Ag alloys, Ag increases their melting temperature, electrical resistivity, and coefficient of thermal expansion.

1. Introduction

Over the recent years research groups put a lot of effort into finding Pb-free and Cd-free solder alloys that could be used for high temperature soldering [1]. In particular group of alloys based on Zn–Al system could be used for soldering as high as at 400 °C. Although binary near-eutectic Zn–Al alloys show no intermetallic phases in the bulk (similarly to Pb–Sn solders) and are relatively cheap, their wetting performance on Cu and corrosion resistance is poor, therefore attempts were made to test the effect of third component on performance of solders. As pointed out in [2] ternary Zn–Al–Cu solders show good characteristics such as high solderability, small electrical resistivity, and good mechanical property for the ultra high temperature applications. During interaction of liquid Zn–Al solder and solid Cu substrate formation of intermetallic compounds (IMC) from Cu–Zn system is observed at the solder/substrate interface.

It is known from the studies on wetting of SAC solders on Cu that small addition of Zn (~1%) to SAC solder inhibits the growth of intermetallic phases from Cu–Sn system at the solder/substrate interface. However, for higher Zn concentrations in SAC solder Cu_5Zn_8, $AgZn_3$, Ag_5Zn_8 IMC particles start to appear [3], since they are thermodynamically more stable than Cu_6Sn_5. By analogy it is expected that addition of Ag to Zn–Al eutectic should inhibit the growth of intermetallic phases (IMPs) from Cu–Zn system, because Ag_5Zn_8 is thermodynamically more stable than Cu_5Zn_8. From cognitive point of view it is interesting if it is possible to obtain a "miscibility gap" (miscibility gap $a_1 + a_2$) at the solder substrate interface as calculated in [4] on the phase diagram of Al–Cu–Zn system. It is, on the other hand, experimentally confirmed that the (a1 + a2) miscibility gap of fcc–Al solid solution exists at temperatures even above 351 °C at the low Cu side of the Al–Zn–Cu ternary system [5]. Considering the effect of Cu (diffusing form substrate) to Zn–Al alloy and local saturation of Zn in alloy, formation of IMPs from Cu–Zn system may lead to formation of miscibility gap. Problem is there are no thermodynamic data for Al–Ag–Cu–Zn quaternary system, therefore based on Al–Cu–Zn phase diagram assessed by [6] an attempt will be made to describe thermodynamic properties and crystallization of solder on Cu substrate. Present work is the first that gives analysis of the effect of Ag content in Zn–Al–Ag solder on IMPs growth on Cu and kinetics versus time and temperature of joining.

2. Experimental

High purity metals Zn, Al (99.999%), and Ag (99.99%) were used for alloys preparation. Similarly to [7], Zn–Al–Ag alloys were prepared in a glovebox filled with high purity Ar (99.9999%), with levels of O_2 and H_2O kept below 1 ppm, and the lowered content of N_2 (although it was not monitored), owing to Ar gas circulating through high temperature purification system filled with Ti shavings heated to 850 °C. Carefully weighted amounts of metals were melted in graphite crucibles in resistance furnace then cast to graphite molds or sucked into quartz capillaries. Compositions of the studied alloys are reported in Table 1. Wetting tests were performed on Cu (99.9%) substrates.

Melting temperatures of the solder alloys (Table 1) were determined from heating curves obtained by differential scanning calorimetric (DSC) measurement at a heating rate of 10 °C/min, under argon 5 N flow of 30 ml min^{-1}, in Al_2O_3 cell. The

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Table 1
Chemical composition of alloys with melting temperature obtained from DSC measurement.

Alloys	Chemical composition		Melting temperature (°C)
	at.%	wt.%	
ZnAl	Zn–12Al	Zn–5.3Al	383.7
ZnAl + 0.5Ag	Zn–12Al–0.5Ag	Zn–5.3Al–0.9Ag	385.2
ZnAl + 1Ag	Zn–12Al–1Ag	Zn–5.2Al–1.8Ag	387.8
ZnAl + 1.5Ag	Zn–12Al–1.5Ag	Zn–5.2Al–2.6Ag	386.6

Table 2
Temperature dependence of CTE for Zn, Zn–Al and Zn–Al–Ag alloys.

Alloy (at.%)	Range of temperature (°C)	CTE, 10^{-6} K^{-1}
Zn	−50 to 200	29.87
Zn–12Al	−50 to 200	23.97
Zn–12Al–0.5Ag	−50 to 200	24.03
Zn–12Al–1.0Ag	−50 to 200	25.27
Zn–12Al–1.5Ag	−50 to 200	29.75

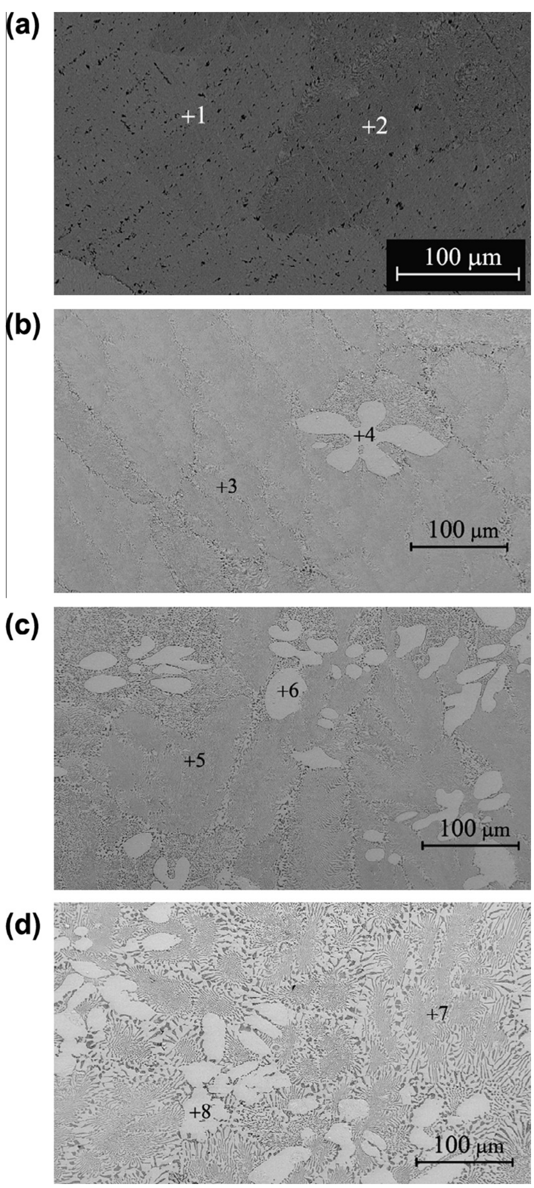

Fig. 1. Microstructure of as-cast solders: (a) Zn12Al and Zn12Al–XAg, (b) 0.5, (c) 1.0, and (d) 1.5, respectively.

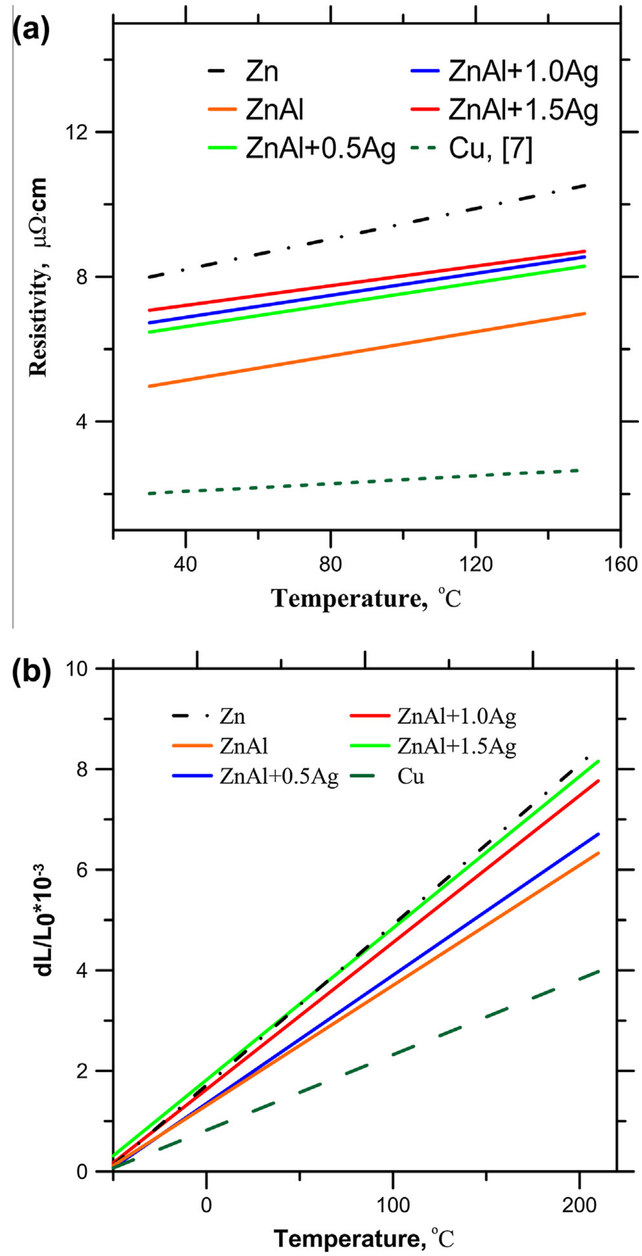

Fig. 2. Temperature dependence of Zn, Zn–Al and Zn–Al–Ag for (a) electrical resistivity and (b) thermal expansion.

coefficient of thermal expansion (CTE) of alloys were determined from thermomechanical analysis (TMA) measurement at a heating rate of 5 °C/min, from −50 to 200 °C, under argon 5 N gas flow of 20 ml min^{-1}, and shown in Table 2 respectively. Electrical resistivity measurements were made using 4-point method, with the use of a high-current source Keithley 6220 (with an accuracy of 100 mA) coupled with nanovoltometer Keithley 2182 (range, 10 mV with an accuracy 1 nV). The length of samples was from 10 cm to 25 cm. Experiment proceeded as follows: range of temperature was from 30 to 150 °C and heating step was 10 °C; at each temperatures the sample was held from 3 to 6 h.

Prior wetting tests copper substrates were electro-polished and then degreased with acetone. Wettability measurements were made using flux Alu700 in a protective atmosphere of nitrogen and mass of the solder samples used for wetting test was 0.5 g. The wetting tests were conducted at temperatures: 460, 480, 500, 520, 550 °C, for 8 min to determine the activation energy of the phase-forming. In order to determine the kinetics of growth of the IMPs and the exponent n in Eq. (1) the tests were performed at 500 °C for different wetting times: 15, 30, 60 s and 3, 8, 15, 30 and 60 min. Short wetting times were an indication for the determination of the sequence of appearing of phases. Wettability tests were performed for the eutectic Zn12Al and Zn12Al with additives of 0.5, 1.0 and 1.5 at.% Ag. As described in [8], the spreading area of 0.5 g samples of solder was calculated after wetting tests