

Materials Characterization 48 (2002) 341-346

MATERIALS CHARACTERIZATION

# Effects of zinc additions on the microstructure and melting temperatures of Al–Si–Cu filler metals

L.C. Tsao, M.J. Chiang, W.H. Lin, M.D. Cheng, T.H. Chuang\*

Institute of Materials Science and Engineering, National Taiwan University, 1 Roosevelt Road, Sec. 4, Taipei 106, Taiwan, ROC

Received 2 July 2002; accepted 4 July 2002

## Abstract

For the development of a low-melting-point filler metal for brazing aluminum alloys, a series of Al–Si–Cu– Zn alloys has been studied. Through differential thermal analysis (DTA) analysis, the melting temperatures of such Al–Si–Cu–Zn filler metals were determined. The results show that the addition of 10–30 wt.% copper into the traditional Al–12 wt.% Si filler metal causes its solidus temperature to decrease by about 60 °C. An addition of 10–30 wt.% zinc into such Al–Si–Cu ternary alloys will cause their solidus temperatures to drop further to a value lower than 500 °C. Metallographic observations indicate that the addition of zinc into the Al–Si–Cu alloys inhibits the formation of the Al–Si, Al–Cu and Al–Si–Cu eutectic phases. The remaining phases are a CuAl<sub>2</sub> intermetallic compound, an  $\alpha$ -Al solid solution and silicon particles. © 2002 Elsevier Science Inc. All rights reserved.

Keywords: Al-12Si alloy; Al-Si-Cu filler; DTA analysis

# 1. Introduction

Among a variety of bonding technologies, brazing has been widely adopted as a reliable method for joining aluminum components [1], wherein the Al– 12 wt.% Si alloy is recognized as the most popular filler metal [2,3]. Although a sound joint can be achieved for certain aluminum alloys using this traditional filler metal, its brazing temperature is high in relation to the melting points of these aluminum alloys. As a result, aluminum workpieces during brazing may be partially molten due to the uneven distribution of the temperature within the industrial

*E-mail address*: tunghan@ccms.ntu.edu.tw (T.H. Chuang).

furnace. The higher brazing temperature can also cause the degradation of the mechanical properties of aluminum alloys. Even in the more extreme cases of many important engineering aluminum alloys such as 2024, 5083 and 7075 Al alloys, brazing with the traditional Al–12Si filler metal is impractical due to the fact that the solidus temperatures of these aluminum alloys are lower than the eutectic point of the Al–12Si alloy.

In order to solve this problem, many efforts have been made to develop low-melting-point filler metals with a satisfactory bonding strength for brazing most of the aluminum engineering alloys. Kayamoto et al. [4] developed a series of Al–Ge–Si–Mg filler metals with quite low melting points and sufficient joint strengths for brazing the 6061 aluminum alloy. However, germanium is approximately 400 times the price of aluminum, making such filler metals excessively

<sup>\*</sup> Corresponding author. Tel.: +886-2236-3031; fax: +886-2236-34562.

<sup>1044-5803/02/\$ –</sup> see front matter C 2002 Elsevier Science Inc. All rights reserved. PII: S1044-5803(02)00276-0

expensive for most applications. Humpston et al. [5] and Jacobson et al. [6] further reported an Al-5Si-20Cu-2Ni filler metal with a melting temperature range between 518 and 538 °C. When this filler metal was applied to brazing a 3003 aluminum alloy, a shear strength over 75 MPa was obtained. Earlier, Suzuki et al. [7] had also studied a series of ternary eutectic Al-Si-Zn filler metals. They found that by increasing the zinc addition to the Al-12Si filler metal from 0 to 50 wt.%, the eutectic points of such ternary Al-Si-Zn alloys decreased linearly from 577 to 525 °C. In a previous study by the present authors [8], an Al-7Si-20Cu-2Sn-1Mg filler metal with a melting temperature range of 501-522 °C was developed. When this filler metal was used to braze a 6061-T6 aluminum alloy, an optimized bonding strength of 196 MPa was achieved. In the present study, a series of low-cost Al-Si-Cu-Zn filler metals with solidus temperatures lower than 500 °C has been further developed. Their microstructures in correspondence with the thermal properties have been studied.

#### 2. Experimental

A series of Al-Si-Cu-Zn filler metals with various compositions, as shown in Table 1, was prepared for the study. For this purpose, an Al-12 wt.% Si alloy was melted first at 700 °C in an air furnace, and then the temperature was raised to 1000

Table 1

Chemical compositions and thermal properties of Al-Si-Cu-Zn filler metals in this study

Samples	Chemical compositions (wt.%)				$T_{\rm S}^{\ a}$ (°C)	$T_{\rm L}^{a}$ (°C)	$\Delta T^{a}$ (°C)
	Si	Cu	Zn	Al			
1	12.0	0	0	Bal.	579	593	14
2	10.8	10	0	Bal.	518	565	47
3	9.6	10	10	Bal.	495	546	51
4	8.4	10	20	Bal.	468	535	67
5	7.2	10	30	Bal.	446	519	73
6	10.2	15	0	Bal.	523	548	25
7	7.0	15	15	Bal.	473	526	53
8	9.6	20	0	Bal.	524	543	19
9	8.4	20	10	Bal.	486	524	38
10	7.2	20	20	Bal.	456	496	40
11	6.0	20	30	Bal.	429	482	53
12	8.4	30	0	Bal.	523	534	11
13	7.2	30	10	Bal.	477	532	55
14	6.0	30	20	Bal.	434	520	86

<sup>a</sup>  $T_{\rm S}$  indicates the solidus temperatures of the filler metals.  $T_{\rm L}$  indicates the liquidus temperatures of the filler metals.  $\Delta T = T_{\rm L} - T_{\rm S}$ .



Fig. 1. DTA curve and microstructure of the traditional Al– 12Si filler metal.

°C when various amounts of copper (99.9 wt.%, 2 mm diameter slug) were added into the molten Al–12Si alloy. After the mixture was stirred for 30 min for homogenization, various amounts of zinc were added into the Al–Si–Cu alloys. They were then cast in a stainless steel mold. The solidus and liquidus temperatures of these Al–Si–Cu–Zn filler metals were measured through differential thermal analysis (DTA). The specimens were heated from room temperature to 600 °C at a heating rate of 10 °C/min under an argon atmosphere. The microstructure was observed by means of optical microscopy after metallographic preparation and etching in 10 vol.% H<sub>3</sub>PO<sub>4</sub> at 50 °C for 60 s.

### 3. Results and discussion

The DTA curve and the corresponding microstructure of a traditional Al–12Si filler metal are shown in Fig. 1a and 1b respectively. During the heating process of the DTA analysis, the Al–12Si filler metal shows a nonequilibrium microstructure with a lamellar Al–Si eutectic phase and an  $\alpha$ -Al



Fig. 2. Effects of Zn addition on the decrease of solidus and liquidus temperatures for the A1-Si-10Cu filler metal.

dendrite solid solution. Figs. 2–4 show the DTA curves of various Al–Si–Cu–Zn filler metals. The solidi ( $T_{\rm S}$ ) and liquidi ( $T_{\rm L}$ ) of these filler metals obtained from the DTA analyses are summarized in Table 1. It can be seen that the solidus and liquidus temperatures of the traditional Al–12Si filler metal decrease drastically from 579 to 518 °C and from 593 to 565 °C, respectively, when 10% copper is added into the alloy. Further addition of zinc into



Fig. 3. Effects of Zn addition on the decrease of solidus and liquidus temperatures for the Al–Si–15Cu filler metal.



Fig. 4. Effects of Zn addition on the decrease of solidus and liquidus temperatures for the Al-Si-20Cu filler metal.

such an Al–Si–10Cu filler metal causes its solidus and liquidus to plunge further as shown in Fig. 2. From Table 1, it can be estimated that the addition of about 10% zinc into the Al–Si–10Cu filler metal results in a decrease of solidus and liquidus temperatures of about 25 and 15 °C, respectively. The declining of solidi and liquidi for the Al–Si–Cu filler metals due to the addition of zinc can be attributed to the low melting point of the zinc element (420 °C), which dissolved with a high solubility in the Al–Si–Cu alloys.

When the copper content of the Al–Si–Cu filler metals is increased from 10% to 20%, Figs. 3 and 4 show that the solidus temperatures have remained almost constant in the range between 518 and 524 °C. However, the liquidus temperatures still drop sharply to 543 °C when copper is added up to 20%. Here, the declining phenomenon of solidus and liquidus due to the addition of zinc to the Al–Si–20Cu filler metal is much more conspicuous than the case of the Al–Si–10Cu filler metal. In this situation, the addition of about 10% zinc into the Al–Si–20Cu filler metal has caused the declination of solidus and liquidus by about 35 and 20 °C, respectively.

As the copper content of the Al–Si–Cu filler metal is further increased from 20% to 30%, Fig. 5 shows that the solidus temperature has remained constant and the liquidus temperature decreased slightly. An increase in the zinc content of the Al–



Fig. 5. Effects of Zn addition on the decrease of solidus and liquidus temperatures for the A1–Si–30Cu filler metal.

Si-30Cu filler metal results in an obvious declination of the solidus temperature, and, a slight decrease of the liquidus temperature. In this case, the temperature difference between the liquidus and solidus ( $\Delta T$ ) is wider, which is unfavorable for the brazing process.

The microstructure of the Al-10.8Si-10Cu filler metal (Fig. 6a) consists of an Al-Cu-Si ternary



Fig. 6. Microstructures of (a) Al-10.8Si-10Cu and (b) Al-8.4Si-10Cu-20Zn filler metals.

eutectic phase, a dendrite  $\alpha$ -Al solid solution, the  $CuAl_2$  ( $\theta$ ) intermetallic compound and some silicon particles with an Al-Si eutectic phase surrounding them. Since zinc is highly soluble in aluminum, the addition of zinc to this Al-Si-10Cu filler metal has not changed of its microstructure much (Fig. 6b). However, it is still noticeable that the amounts of the  $CuAl_2(\theta)$  intermetallic compound and the Al-Cu-Si ternary eutectic phase have decreased in the Al-Si-10Cu-Zn alloys. The microstructures of the Al-Si-15Cu and Al-Si-15Cu-Zn filler metals as shown in Fig. 7a and b, respectively, are similar to those found in the Al-Si-10Cu and Al-Si-10Cu-10Zn alloys. Fig. 8a shows that the Al-Si eutectic phase and the dendrite  $\alpha$ -Al solid solution decrease considerably along with the increasing of the copper content in the Al-Si-Cu filler metal up to 20%. When 10% zinc is added into the Al-Si-20Cu filler metal, the Al-Si eutectic phase disappears. Fig. 8b shows that the Al-Cu eutectic structure, the Al-Cu-Si ternary eutectic structure and the CuAl<sub>2</sub> intermetallic compound have stayed in the Al-Si-20Cu-10Zn alloy. As the zinc content is increased up to 20%, all of the eutectic phases (Al-Si, Al-Cu and Al-Cu-Si) are replaced by a mixture of the CuAl2 intermetallic compound, an  $\alpha$ -Al solid solution and silicon particles as shown in Fig. 8c. Fig. 8 also indicates that the size of silicon particles has expanded with the increasing of zinc



Fig. 7. Microstructures of (a) Al-10.8Si-15Cu and (b) Al-8.4Si-15Cu-25Zn filler metals.

content in the Al-Si-20Cu-Zn alloy. The observations of microstructures in these Al-Si-Cu-Zn filler metals are consistent with the results of the DTA analysis. On the DTA curves of Al-Si-10Cu-Zn (Fig. 2) and Al-Si-15Cu-Zn (Fig. 3), two endothermic peaks are observed, as they approach each other for the Al-Si-20Cu-Zn alloys (Fig. 4). As for the microstructure of the Al-8.4Si-30Cu filler metal shown in Fig. 9a, the Al-Si eutectic phases disappears and is replaced by the Al-Cu eutectic phase, the Al-Cu-Si ternary eutectic phase and the CuAl<sub>2</sub> intermetallic compound as in the case of the Al-Si-20Cu-10Zn filler metal (Fig. 8b). However, the addition of 20% zinc to such an Al-Si-30Cu alloy



Fig. 8. Microstructures of (a) A1-9.6Si-15Cu, (b) A1-7Si-20Cu-10Zn, and (c) A1-7.2Si-20Cu-20Zn filler metals.



Fig. 9. Microstructures of (a) A1-8.4Si-30Cu and (b) A1-6Si-30Cu-20Zn filler metals.

causes the reappearance of the Al–Si eutectic phase (Fig. 9c). The reappearance of the Al–Si eutectic phase due to the addition of 20% zinc to Al–Si–30Cu is also consistent with the results of the DTA analysis. It can be seen in Fig. 5 that the single endothermic peak on the DTA curve of the Al–8.4Si–30Cu alloy is split into two endothermic peaks on the DTA curve of the Al–6Si 30Cu–20Zn alloys.

To summarize the results of the thermal analysis and microstructure observations, an Al-7.2Si-20Cu-20Zn filler metal is suggested, which possesses a melting temperature range between 456 and 496 °C.

## 4. Conclusions

Al-Si-Cu filler metals with a Cu content between 10 and 30 wt.% will have solidus temperatures near 520 °C, but these temperatures can be further decreased to a value lower than 500 °C through the addition of zinc from 10 to 30 wt.%. By adding 20-30 wt.% zinc into the Al-Si-20Cu filler metals, their liquidus temperatures can be lowered to below 500 °C. The microstructures of the Al-Si-Cu filler metals contain eutectic phases (Al-Si, Al-Cu and Al-Si-Cu), a CuAl<sub>2</sub> intermetallic compound, an  $\alpha$ -Al solid solution and silicon particles. With the increase of zinc content in the Al–Si–Cu filler metals, the formation of eutectic phases (Al–Si, Al–Cu and Al–Si–Cu) will be restrained.

#### References

- Sugiyama Y. Brazing of aluminum alloys. Welding Int 1989;3(10):700-10.
- [2] Kawas H, Takemoto T, Asano M, Kawakatsu I, Liu K. Study of a method for evaluating the brazeability of aluminum sheet. Welding J 1989;68(10):396s-403s.
- [3] Hattori T, Sakai S, Sakamoto A, Fujiwara C. Brazeability of aluminum in vacuum—nitrogen partial-pressure atmosphere brazing. Welding J 1994;73(10):233s-40s.
- [4] Kayamoto T, Kim J-H, Saito S, Onzawa T. Brazing of

Al-Mg alloy and Al-Mg-Si alloy with Al-Ge based filler metals. Proc Workshop J Welding Soc 1994;12(10):495-501.

- [5] Humpston G, Sangha S-P-S, Jacobson D-M. New filler metals and process for fluxless brazing of aluminium engineering alloys. Mater Sci Technol 1995; 11(10):1161-7.
- [6] Jacobson D-M, Humpston G, Sangha S-P-S. A new low-melting-point aluminum braze. Welding J 1996; 75(8):243s-50s.
- [7] Suzuki K, Kagayama M, Takeuchi Y. Eutectic phase equilibrium of Al–Si–Zn system and its applicability for lower temperature brazing. J Jpn Inst Light Met 1993;43(10):533–8.
- [8] Yeh M-S, Tsao L-C, Tsai T-C, Wu C-S, Chuang T-H. Development of a low-melting-point filler metal for brazing aluminum alloys. Metal Mater Trans 2000; 31A(10):2239–45.