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Effects of germanium additions on microstructures and properties of Al−Si filler metals for brazing aluminum

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Abstract: A series of Al−Si−Ge filler metals were studied for brazing aluminum. The microstructures and properties of the filler metals were investigated systematically. The results show that the liquidus temperature of Al−Si−Ge filler metals drops from 592 to 519 ℃ as the content of Ge increases from 0 to 30% (mass fraction). As the content of Ge increases, bright eutectic Ge forms. However, as the Ge content exceeds 20%, the aggregation growth of the eutectic structure tends to happen and coarsened primary Si−Ge particle forms, which is detrimental to the properties of alloys. The Al−10.8Si−10Ge filler metal has good processability and wettability with the base metal Al. When this filler metal is used to braze 1060 aluminum, the complete joint can be achieved. Furthermore, the shear strength test results show that the fracture of brazed joint with Al−10.8Si−10Ge filler metal occurs in the base metal.

Key words: Al−Si−Ge filler; microstructure; brazed joint; shear strength; 1060 aluminum

1 Introduction

As always, the eutectic Al−12Si alloy (mass fraction, %) is recognized as the most popular filler metal [1−4]. However, the brazing temperature of this aluminum brazing alloy must be above 600 ℃ due to the high eutectic point of Al−12Si alloy, which can bring about the degradation of mechanical properties or even localized melting in some engineering aluminum alloys when brazed [5]. Therefore, the development of a low-melting-point filler metal with satisfactory bonding strength is an important task for the aluminum industry. Some authors have tried to add a third element, such as Cu, Zn and Ag, into the Al−Si binary system, and a series of Al−Si−Cu [6−9], Al−Si−Zn [10] and Al−Ag−Cu [11] filler metals were developed. The Al−Si−Cu filler metal plays an important role in the brazing of aluminum alloys, but the copper in the filler metal would form Al−Cu intermetallic compounds, which greatly deteriorate the ductility of the brazing alloy as well as the brazed joints [12]. SUZUKI et al [13] had introduced a eutectic Al−4.2Si−40Zn filler metal with a melting point of 535 ℃, which had good hot processability by the reason of no intermetallic compound. Nevertheless, its disadvantage was the high content of zinc, which caused the dissolution of the aluminum substrate.

Similar to Al−Si alloy, Al−Ge alloy has also been researched in recent years [14,15]. It shows a large spreading area on the surface of aluminum substrate by virtue of its low melting temperature and good wettability [16]. The phase diagram of Al−Ge binary alloy is a simple eutectic phase diagram with eutectic temperature of 420 ℃. However, the content of Ge in the eutectic composition is as high as 51.6% (mass fraction), making such filler metal excessively brittle and expensive for most applications. Researches have shown that Al−Si−Ge alloys with low concentrations of silicon and germanium have fine and densely-distributed precipitates of GeSi solid solution compared with the Al−Ge alloys [17]. In a previous study, KAYAMOTO et al [18] developed a series of Al−Si−Ge−Mg filler metals with high Ge content. When the Al−Si−35Ge−Mg alloy was applied to braze a 6061 aluminum alloy at 575 ℃ for 60 min, the brazed joint provided sufficient joint strength equal to that of the base alloy, and the bonding strength decreased to values lower than 100 MPa for brazing a 5052 aluminum alloy. SAITO et al [19] developed an Al−Si−45Ge−Cu filler metal with a low melting point. When this filler metal was used for

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brazing a 2017 aluminum alloy, the joint strength over 138 MPa was obtained after diffusion treatment. However, due to the high brittleness resulting from high content of Ge, these filler metals were difficult to be processed into wire or foil. The previous investigations were only feasibility study at an early stage, and involved only Al−Si−Ge alloys with high Ge content. Thus, new filler metals with low contents of Ge which can achieve good processability and high joint strength should be studied further. Besides, the systematic investigation of microstructures and mechanical properties of the Al−Si−Ge filler metals and brazing joints have never been reported.

Therefore, for the development of brazing technology of aluminum and its alloys, a deep understanding of the Al−Si−Ge filler metal is necessary. The aim of this study is focused on the microstructures and properties of Al−12Si-based filler metals such as Al−10.8Si−10Ge, Al−9.6Si−20Ge and Al−8.4Si−30Ge for brazing aluminum, and a traditional Al−12Si filler metal is also employed for comparison.

2 Experimental

The compositions of filler metals are listed in Table 1. High purity aluminum (purity 99.99%), silicon (99.99%) and germanium (99.999%) were used as starting materials to prepare Al−Si−Ge alloys. At first, Al−Si−Ge filler metals were prepared by melting an Al−12Si (mass fraction, %) alloy at 700 ℃ in alumina crucibles within an air furnace. Afterward, the temperature was raised to 1000 ℃, followed by various amounts of germanium being added to the molten Al−12Si alloy and then stirred for 30 min for homogenization. The thermal analysis of the alloys was measured by differential thermal analysis (DTA) technique under high purity nitrogen. The microstructure characteristics of samples were analyzed by optical microscopy (OM) and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS). The phase observation in the microstructure was made by X-ray diffraction (XRD). Wetting and brazing experiments were carried out in the tube type resistance furnace, and the improved AlF_3−KF−CsF flux was used in the experiment, whose melting temperature ranged from 480 to 500 ℃. Wetting test was carried out at 600 ℃ with 0.1 g filler metals. Brazing experiment was performed at 580 ℃ for 5 min, and 0.15 g filler metals were used. The base metal was pure aluminum plates with dimensions of 40 mm × 40 mm × 2 mm for spearing test and 60 mm × 20 mm × 2 mm for tensile test (Fig. 1). To ensure the accuracy of results, five specimens were tested under the same conditions with each filler metals. After brazing, the shearing strengths were measured by shear testing using a tensile testing machine at a tensile speed of 1 mm/min.

Table 1 Chemical compositions of filler metals (mass fraction, %)

Alloy	Si	Ge	Al
Al−12Si	12	−	Bal.
Al−10.8Si−10Ge	10.8	10	Bal.
Al−9.6Si−20Ge	9.6	20	Bal.
Al−8.4Si−30Ge	8.4	30	Bal.

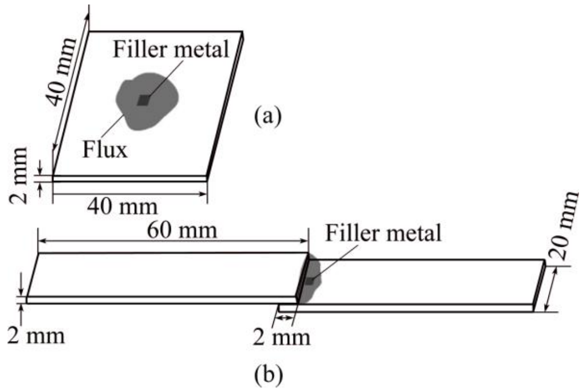

Fig. 1 Schematic illustration of brazing joint: (a) Spreading test; (b) Lap joint

3 Results and discussion

3.1 Melting characteristic of filler metals

Figure 2 shows the DTA curves of various filler metals. It can be seen that the solidus and liquids temperatures of the traditional Al−12Si filler metal decrease drastically from 561 to 504 ℃ and from 592 to 565 ℃ when 10% germanium is added into the alloy. In this case, the melting temperature interval of Al−10.8Si−10Ge alloy is narrow, which is favorable for the brazing process [20]. As the germanium content increases further

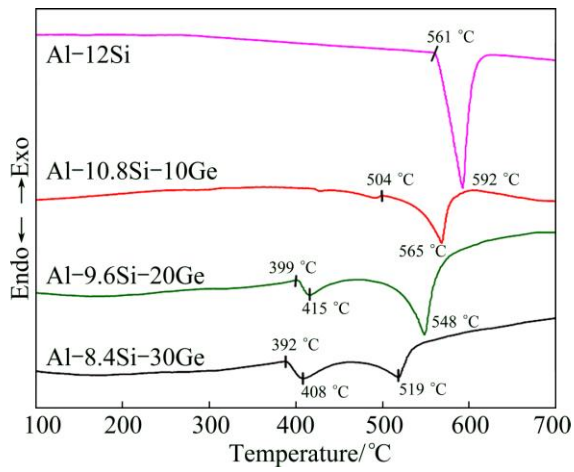

Fig. 2 DTA curves of Al−Si−Ge filler metals

to 20%, two endothermic peaks are found in the DTA curve of Al−9.6Si−20Ge ternary alloy, which corresponds to the Al−Ge eutectic process and Al−Si eutectic process, respectively. In this case, the temperature difference between the liquidus and solidus (ΔT) is wider, which is unfavorable for the brazing process. Increasing the germanium content up to 30% causes the two endothermic peaks to close each other, and the solidus temperature remains almost constant. However, the liquidus temperature of Al−Si−Ge ternary alloy decreases from 592 to 519 ℃ when up to 30% germanium was added.

3.2 Microstructure of Al−Si−Ge filler metals

The microstructure of a traditional Al−12Si filler metal is shown in Fig. 3(a). It can be seen that the Al−12Si filler metal shows a nonequilibrium microstructure with a lamellar Al−Si eutectic phase and an α(Al) dendrite solid solution. When 10% Ge was added in the alloy, obvious changes can be found on the α(Al) solid solution and eutectic microstructure (Fig. 3(b)). Except for the grey Al−Si eutectic phase, bright Al−Ge eutectic also forms. Compared Al−12Si with Al−10.8Si−10Ge filler metals, it is seen that the eutectic microstructure in Fig. 3(b) is more dispersed than that in Fig. 3(a). Figure 3 shows that the Al−Si eutectic phase decreases considerably with the increase of Ge content in the Al−Si−Ge filler metal from 10% to 30%. When 20% Ge was added into the Al−Si alloy (shown in Fig. 3(c)), primary Si−Ge particle is exposed, and the amount of Al−Ge eutectic phase increases. Besides, the size of Al−Ge eutectic phase coarsens in the case of Al−9.6Si−20Ge in Fig. 3(c). Then, net-like Al−Ge eutectic phase assembles into blocks and the size of primary Si−Ge particle coarsens when the addition of Ge increases to 30%.

The XRD peaks shown in Fig. 4 confirm the phases observed in the microstructure of these Al−Si−Ge filler metals. The results indicate that the three alloys contain α(Al) solid solution, Ge and Si phases. The peaks of the phases in these patterns are found at the same positions and no significant difference is observed.

To further study the effect of Ge content on the microstructures of Al−Si−Ge filler metals, the scanning maps of typical areas in Al−10.8Si−10Ge and Al−9.6Si−20Ge filler metals were carried out. Figure 5 shows the scanning maps of eutectic areas in these alloys. It can be seen that the distributions of Ge correspond well to those of Si, indicating a uniform doping of Ge in Si phase. The distribution of eutectic phase of Al−10.8Si−10Ge is different from that of Al−9.6Si−20Ge, as shown in Fig. 5, and the eutectic Si and Ge phases in the Al−10.8Si−10Ge filler metal are more dispersed. Besides, the size of eutectic Ge coarsens and the eutectic structure

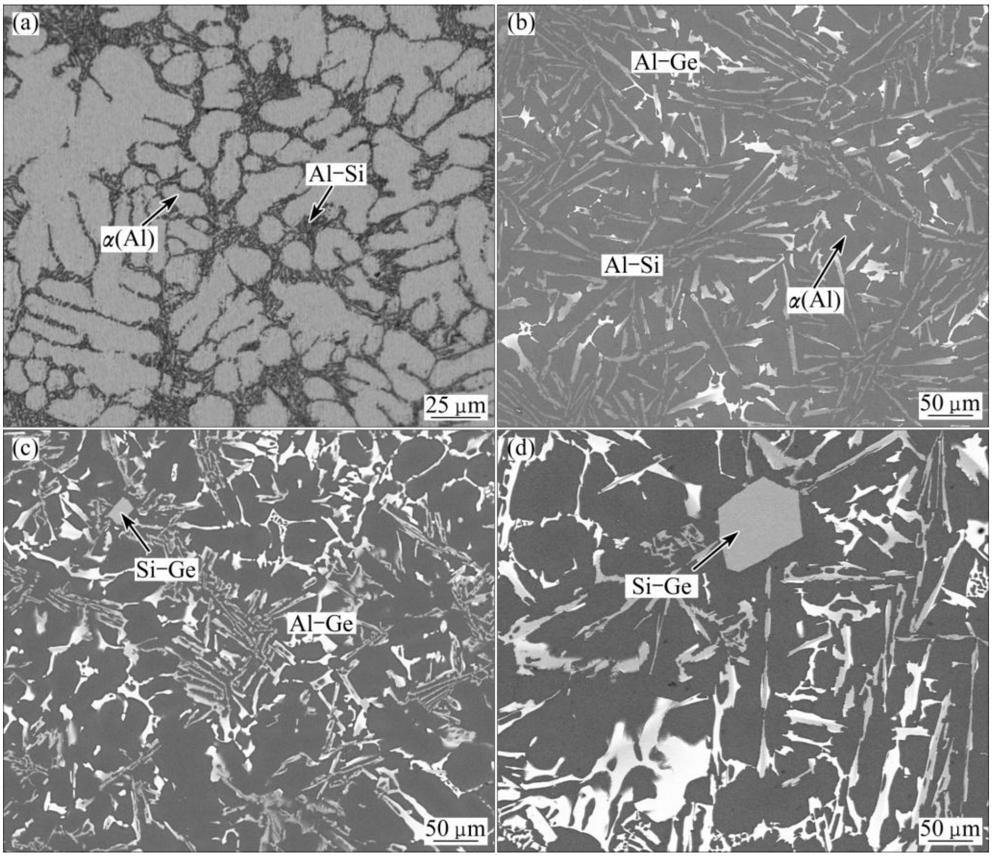

Fig. 3 OM (a) and SEM (b−d) images of filler metals: (a) Al−12Si; (b) Al−10.8Si−10Ge; (c) Al−9.6Si−20Ge; (d) Al−8.4Si−30Ge

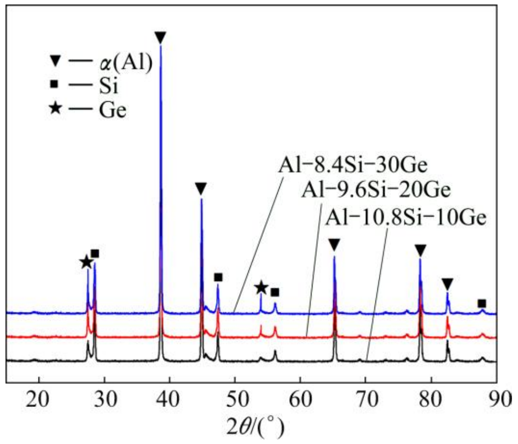

Fig. 4 XRD patterns of Al−Si−Ge filler metals

assembles into big blocks when the content of Ge increases.

The compositions of typical phases in both brazing alloys are listed in Table 2. It is believed that Al−Si−Ge filler metals mainly contain *α*(Al) solid solution, Al−Si eutectic phase, Al−Ge eutectic phase and some primary Si−Ge phase. Three typical particles are marked as *E*, *F* and *G* in Fig. 5(b_1). It can be obviously seen that the deep gray particle *E* mainly contains Si and extremely small amounts of Ge, the bright white particle *F* mainly contains Ge and small amounts of Si, and the dark white particle *G* contains almost the same amount of Ge and Si. It shows that a composition transition region that contains Si and Ge forms in the Al−Si−Ge ternary alloy. Figure 6 shows the line scanning results of the composition transition region in Al−9.6Si−10Ge alloy. From the element distribution map, it can be seen that Si occupies the center of the composition transition region and Ge distributes surrounding Si.

3.3 Brazeability of aluminum with Al−Si−Ge filler matels

Before brazing, wetting experiments were performed to determine the fluidity and wettability of the brazing alloys. The test results of wettability are shown in Fig. 7. In the tests, with the increase of Ge content, the spreading area increases first and then decreases. The average wetting area of Al−10.8Si−10Ge filler metal is 170 mm^2 at 600 ℃, which implies fine wetting of the brazing alloy. This improvement in wettability is due to the narrow melting temperature interval of Al−10.8Si−10Ge alloy. Moreover, the spreading of brazing alloy may be enhanced if it possesses a highly refined grain size and discrete phase [21,22]. Accordingly, wide temperature range, aggregated phase and coarsened structure affect the wettability of Al−9.6Si−20Ge and Al−8.4Si−30Ge filler metals.

The brazing alloy is usually processed into foils and wires for the convenience of brazing, which requires excellent forming performance of the brazing alloy. All of the three filler metals are melted and processed into cylinders with 6 cm in diameter and 8 cm in height to test the plastic deformation ability by means of the compression experiments. The cylinder, protected by hydrogen, is hot-compressed into flat ingot with the thickness reduction of 50%. After compression, significant cracking destruction can be seen at the edge of Al−9.6Si−20Ge and Al−8.4Si−30Ge flat ingots, and there is an angle of 45° between the crack propagation direction and vertical direction, which shows brittle fracture of both alloys. Instead, the Al−10.8Si−10Ge alloy flat ingot has good surface quality and is crack-free, which indicates that the filler metal has excellent processability.

Figure 8 shows the back scattered electron images of the interface of the aluminum joints with Al−Si−Ge filler metals after brazing at 580 ℃ for 5 min. The acicular eutectic structure can be seen in the Al−10.8Si−10Ge and Al−9.6Si−20Ge filler metals, and there also exists coarsened primary Si−Ge phase in the Al−8.4Si−30Ge alloy. The EDS line scanning results show that there is no obvious diffusion layer in the brazed joint of Al−10.8Si−10Ge filler metal, as shown in Fig. 8(b). The effect of different Ge contents on the tensile strength of brazed joint is shown in Table 3. Since the traditional Al−12Si filler metal possesses a eutectic point at about 577 ℃ (DTA-analyzed melting range, 561−592 ℃), any brazing process for this filler metal carried out at around this temperature is destined for failure. When the Al−10.8Si−10Ge filler metals are used to braze aluminum at 580 ℃, the fracture occurs in the aluminum matrix, which shows that the shear strength in this case is high compared with that of the base metal Al. The joint strength of aluminum brazed with Al−9.6Si−20Ge filler metal reaches average shear strength of 79 MPa. It is worth mentioning that fracture occurs in the base metal at some of the tensile tests, which shows that the shear strength of brazed joint with Al−9.6Si−20Ge brazing alloy approaches to that of the base metal. The shear strength of about 67 MPa is obtained in the aluminum joint with Al−8.4Si−30Ge filler metal, which is related to the coarsened structure of this alloy.

The typical fracture morphologies of Al brazed joints with Al−9.6Si−20Ge and Al−8.4Si−30Ge filler metals are shown in Fig. 9. Fractures occur in the brazed seam and a complex fracture behavior exhibits. Some brittle rupture steps can be observed in the Al−9.6Si−20Ge fracture due to the brittle Si−Ge phase, and a large number of dimples are shown in Fig. 9(a), which reveals a mixture of brittle fracture and ductile fracture. Figure 9(b) shows the fracture graph of the Al joint brazed with Al−8.4Si−30Ge filler metal. Coarsened Si−Ge particles are

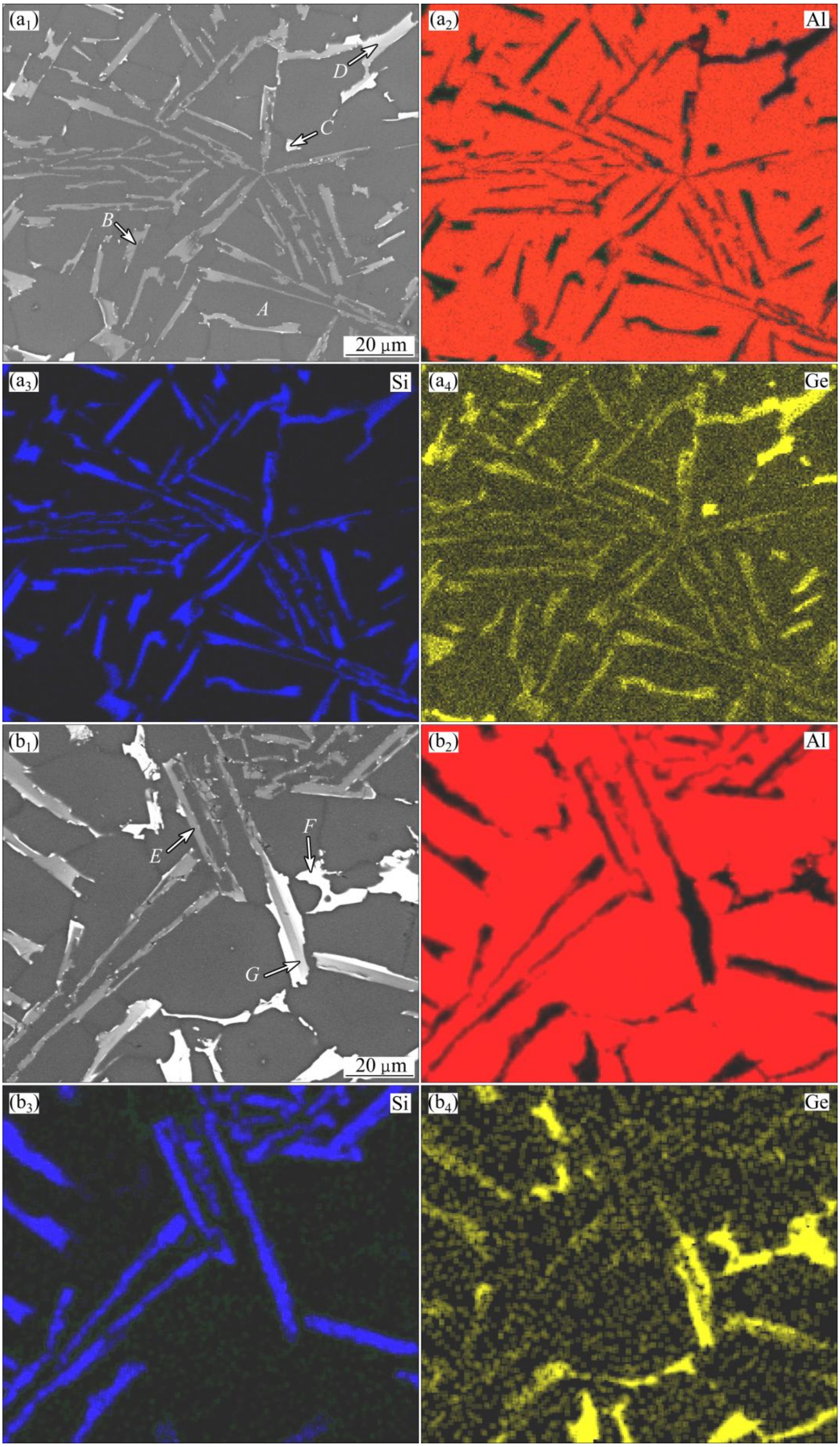

Fig. 5 SEM (a_1, b_1) images and EDS element mappings (a_2−a_4, b_2−b_4) of Al−10.8Si−10Ge (a_1−a_4) and Al−9.6Si−20Ge (b_1−b_4) filler metals

Table 2 EDS results of chemical compositions (mole fraction, %) of points marked in Figs. 5(a_1) and (b_1)

Point	Al	Si	Ge	Possible phase
A	98.91	0	01.09	*α*(Al)
B	0	99.59	0.41	Si
C	04.96	18.28	76.76	Si−Ge
D	0	76.57	23.43	Si−Ge
E	0	98.02	01.98	Si
F	0	04.26	95.74	Ge
G	0	66.67	33.33	Si−Ge

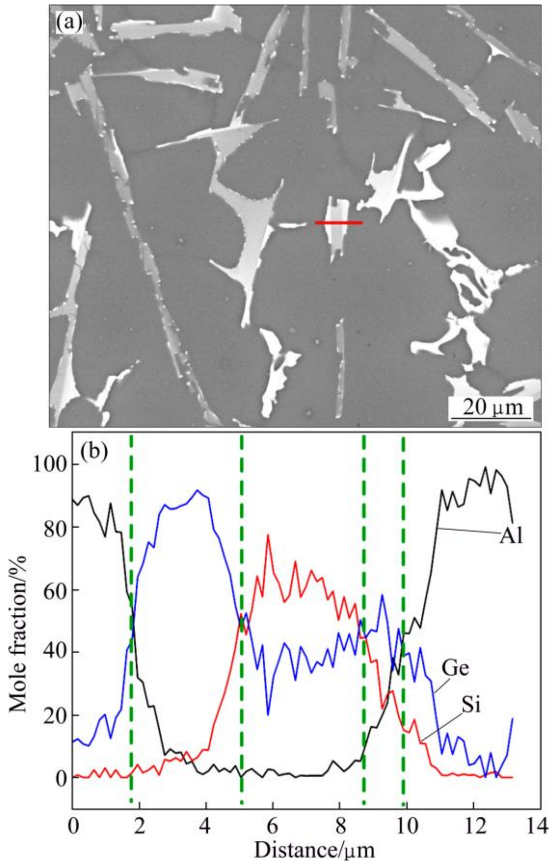

Fig. 6 SEM image (a) and major element content distribution of typical area (b) in Al−9.6Si−20Ge filler metal

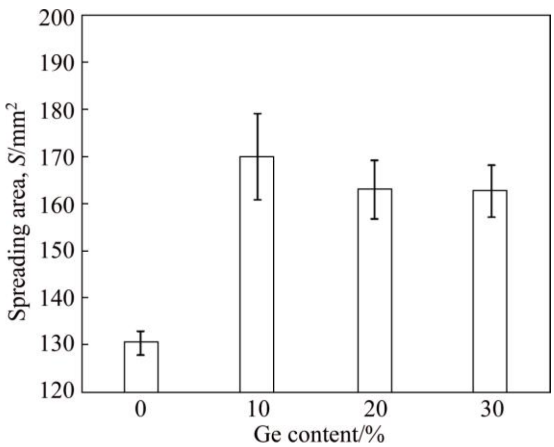

Fig. 7 Spreading area of Al−Si−Ge filler metals on Al plate

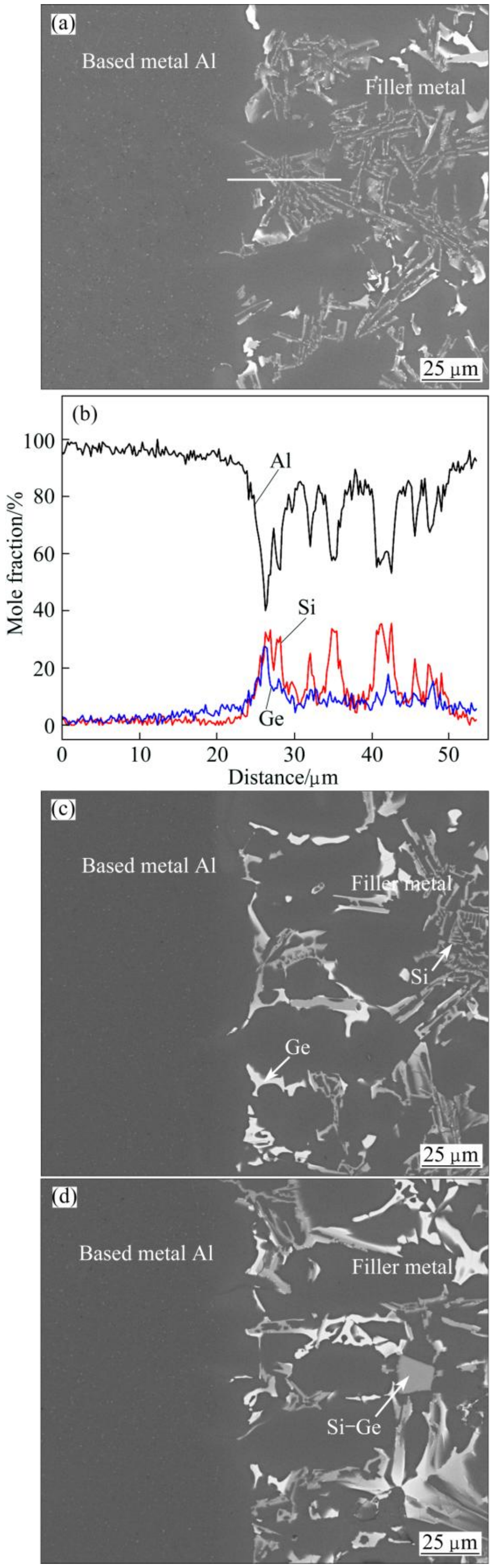

Fig. 8 SEM images (a, c, d) and element line scanning pattern (b) of joints brazed at 580 ℃ for 5 min: (a, b) Al−10.8Si−10Ge; (c) Al−9.6Si−20Ge; (d) Al−8.4Si−30Ge

Table 3 Shear strength of aluminum brazed joints with Al−Si−Ge filler metals

Brazing method	Filler metals	Brazing temperature/℃	Holding time/min	Average shear strength/MPa	Fracture location
Furnace brazing	Al−12Si	580	5	Failed	Lap joint
	Al−10.8Si−10Ge	580	5		Matrix
	Al−9.6Si−20Ge	580	5	79	Lap joint
	Al−8.4Si−30Ge	580	5	67	Lap joint

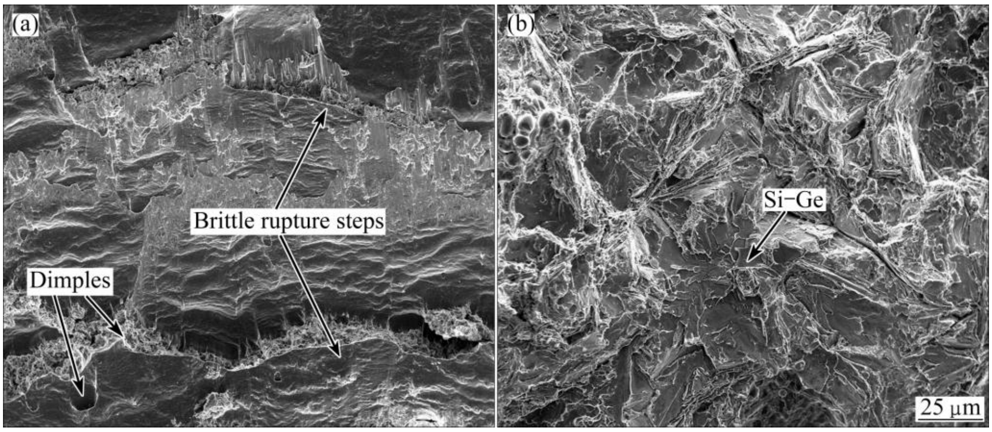

Fig. 9 Fractographs of aluminum joints brazed with Al−Si−Ge filler metals at 580 ℃ for 5 min: (a) Al−9.6Si−20Ge; (b) Al−8.4Si−30Ge

observed in the fracture surface, which shows that the fracture changes from a ductile one to a brittle one with the increase of Ge content.

4 Conclusions

1) With the addition of germanium increasing from 0 to 30%, the liquidus temperature of Al−Si−Ge filler metals falls from 592 to 519 ℃. The melting temperature interval of Al−10.8Si−10Ge alloy is narrow, which is favorable for the brazing process.

2) The main microstructures of Al−Si−Ge filler metals contain α(Al) solid solution, eutectic Si, eutectic Ge and some Si−Ge phase. When 10% Ge is added into the alloy, the eutectic microstructure changes to be more dispersed. As the Ge content reaches further to 20%, the eutectic structure becomes coarsened gradually and large primary Si−Ge particle forms.

3) The average wetting area of Al−10.8Si−10Ge filler metal is 170 mm^2, which implies fine wettability. As the Ge content continuously increases, the spreading areas reduce.

4) The Al−10.8Si−10Ge filler metal has good processability. When this filler metal is employed to braze aluminum, it possesses a high shear strength capping the Al matrix. When brazed with the Al−9.6Si−20Ge and Al−8.4Si−30Ge filler metals which contain more Ge, the joints become brittle and the shear strengths of brazed joints decrease.

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Ge 添加对 Al−Si 系钎料合金显微组织和性能的影响

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摘 要：研究一系列 Al−Si−Ge 钎料用于铝钎焊，并对钎料合金的显微组织和性能进行分析。结果表明：Al−12Si 共晶合金中添加从 0 到 30%(质量分数)的 Ge，可使 Al−Si−Ge 钎料合金的液相线温度由 592 ℃ 下降到 519 ℃。随着 Ge 含量的增加，形成了 Al−Ge 共晶组织。然而，当 Ge 含量超过 20%时，共晶组织趋于聚集长大，钎料合金中形成粗大颗粒状的初生 Si−Ge 相，这些粗大组织的形成极大地降低了钎料合金的性能。Al−10.8Si−10Ge 钎料具有优良的加工性能和铺展润湿性，当采用此钎料钎焊 1060 纯铝时，可以获得完整的钎焊接头，剪切测试结果表明此钎料钎焊接头的断裂位置发生在母材。

关键词：Al−Si−Ge 钎料；显微组织；钎焊接头；抗剪强度；1060 纯铝

(Edited by Mu-lan QIN)