

Article

Vacuum Brazing of 6061 Aluminum Using Al-Si-Ge Filler Metals with Different Si Contents

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Abstract

Al-xSi-35Ge ($x = 4, 6, 8, 10, 12$, wt.%) filler metals were prepared to vacuum braise 6061 aluminum alloy. The wettability of filler metals was studied. A thermodynamics model of the Al-Si-Ge ternary alloy was established to analyze the mechanism and impact of Si in the microstructure of the brazed joint. The findings indicated that Si addition had a slight effect on the melting point of Al-xSi-35Ge filler metals. Great molten temperature region of fillers was responsible for the loss of Ge during the wetting process, making residual filler metal difficult to melt. The microstructure of the joint was characterized by a multilayer structure that was primarily composed of three zones: two transition regions (Zone I) and a filler residual region (Zone II). There was liquidation of filler metal for Al-Si-35Ge filler metals during brazing, resulting in holes and cracks in joints. Increasing the Si content in fillers could alleviate the liquidation of filler metal, owing to diminishing difference of chemical potential of Ge (μ_{Ge}) in fillers and 6061 substrates, hindering the diffusion of Ge from filler metal to substrates.

Keywords: vacuum brazing; 6061 aluminum alloy; Al-Si-Ge filler metals; microstructure; thermodynamics



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1. Introduction

The 6061 aluminum alloy was extensively used in fields such as electronic packaging, aerospace, and automotive manufacturing owing to its superior mechanical properties, formability, and corrosion resistance [1,2]. Currently, large-sized 6061 aluminum alloy components in high-end equipment were becoming increasingly complex in structure, causing higher requirements including joint strength, corrosion resistance, and weld forming quality. Welding techniques like laser welding and friction stir welding fall short in meeting the demands of joining 6061 aluminum alloy components with intricate structures [3,4]. This was especially true for thin-walled components, which were prone to developing substantial deformations during these processes [5]. Vacuum brazing, a clean, efficient, and high-quality welding technology, has unique advantages in achieving the connection of thin-walled and large components. It has been widely used in honeycomb panels, aerospace heat exchangers, and other fields [6–9].

Schwartz et al. connected 6061 aluminum alloy by vacuum brazing by using Al-Si brazing filler metal [10]. Zhang et al. and Tian et al. connected 6061 aluminum alloy by vacuum brazing by using Al-Si-Mg brazing filler metal around 580 °C [11,12]. However, the brazing temperatures of Al-Si and Al-Si-Mg filler metals were relatively high and close

to the melting temperature of the 6061 alloy. Such a narrow brazing process window might induce substantial residual stresses, overall deformation, and even instances of overburning [13,14]. In recent years, in order to broaden the 6061 brazing process window, scholars have added elements such as Cu and Ge to Al-Si filler metal to reduce the melting point [15,16]. Al-Si-Cu filler metal could meet the brazing requirements, owing to its lower eutectic temperature (525 °C) [17]. However, there was an intermetallic compound such as CuAl_2 and Cu_4Al_9 in the microstructure of Al-Cu-Si filler metal, resulting in reduced processability of the brazing filler metal. In addition, the large electrode potential difference between Cu and Al deteriorated the corrosion resistance of joints [18]. Ge had similar physical and chemical properties to Si, and the melting point of the Al-Ge alloy could reach 425 °C. Moreover, Ge could improve the spreadability of Al-Si alloy [19]. Thus, the study on Al-Si-Ge filler metal was one of the research hotspots in the vacuum brazing of 6061 aluminum alloy.

In recent years, research on Al-Si-Ge filler metal mainly focused on the lower melting point of fillers in order to reduce the brazing temperature. Werner et al. used amorphous Al-5Si-60Ge brazing filler metal for the vacuum brazing of 6061 aluminum alloy at 549 °C [20]. Kayamoto et al. prepared the brazing ribbons of Al-Si-Ge-Cu-Mg by rapid solidification technique and achieved vacuum brazing of 6061 aluminum alloy at 525 °C and 575 °C [21,22]. Fedorov et al. brazed 6082 aluminum alloy to 304 AISI using amorphous Al-40Ge-3.4Si brazing filler metals at 530 °C and 540 °C, respectively. Results showed that the microstructure in the joint was fine and homogeneous, but the shear strength of the joint was 20 MPa, which was lower than that of the induction brazing joint (53 MPa) [23]. Ivanikov et al. brazed 6082 aluminum alloy with amorphous Al-40Ge-3.4Si brazing filler metals at 520 °C and 540 °C, respectively, and the shear strength of the joint was 42 MPa [24].

In this paper, Al-xSi-35Ge ($x = 4, 6, 8, 10, 12$, wt.%) filler metals were designed to vacuum braze 6061 aluminum alloy. The melting characteristics and microstructure of filler metals were studied. The wettability of filler metals was analyzed. The influence of Si on microstructure in brazed joints was investigated.

2. Materials and Methods

The 6061 aluminum alloy (Al-0.8Si-1.2Mg, wt.%) rolling sheet produced by Mingtai Aluminum Industry (Zhengzhou, China) was employed as base metal. The base metal was cut into 10 mm × 10 mm × 10 mm blocks by wire electrical machining (DK7730). Before brazing, the surface of base metals was polished with 400 grit SiC sandpaper and then cleaned by ultrasonic.

High purity aluminum (99.99%, all compositions quoted in this work were in wt.% unless otherwise stated) and AlSi30 alloy produced by Mingtai Aluminum Industry (Zhengzhou, China) and germanium (99.999%) produced by Yunnan Germanium Industry (Kunming, China) were used as raw materials to prepare Al-xSi-35Ge alloys ($x = 4, 6, 8, 10, 12$). All raw materials were melted in a clean graphite crucible by medium-frequency induction heating at 900 °C, holding for 5 min, and then the melt was poured into a cast graphite mold. The alloy ingots were cut into foils with a thickness of 0.2 mm by wire electrical machining.

The base metals and filler metals were assembled into a sandwich-type structure, as shown in Figure 1a. The vacuum degree of the vacuum brazing furnace (BK3-515) was controlled at less than 5×10^{-3} Pa. The brazing temperature was usually set to 30 °C higher than the liquidus of the filler metal. The brazing temperature in this work was set as 550 °C, and the holding time was 4 min. The detailed brazing process is shown in Figure 1c. The brazed 6061 joint was subjected to shear tests using a universal testing apparatus (DNS-100). The shear rate was 1 mm/min according to GB/T 11363-2008 [25],

and the test was conducted using a self-designed fixture in Figure 1b. The average shear strength of three identical joints was calculated.

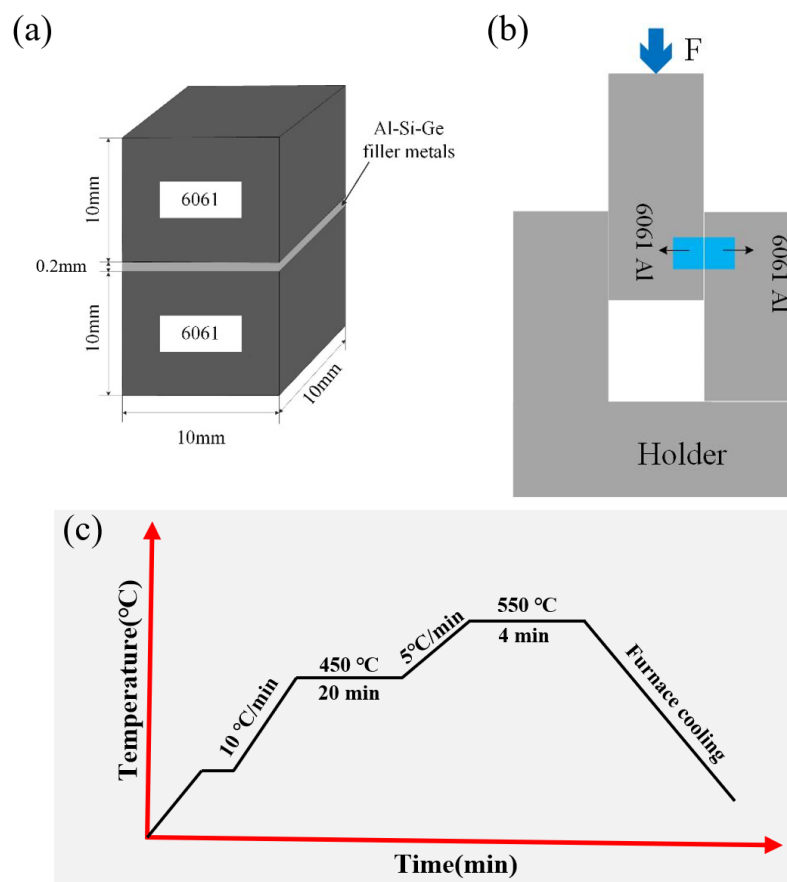


Figure 1. (a) Assembly of the 6061 alloy joint; (b) brazing progress; and (c) assembly schematic of shear test.

The brazed joints were sectioned perpendicular to the bonded interface and the microstructure of the braze zone, and the microstructure characteristics of the samples were analyzed by scanning electron microscopy (SEM, Sigma300, produced by Carl Zeiss AG in Oberkochen, Germany) equipped with an energy dispersive spectrometer (EDS, OXFORD Ultim MAX 40, produced by OXFORD Instruments in Oxford, UK). The phases observed in the microstructure were identified with an X-ray diffraction (XRD, Bruker D8, produced by Bruker in Karlsruhe, Germany). The melting points of these alloys were determined by differential thermal analysis (DTA, STA2500, produced by METTLER TOLEDO in Zurich, Switzerland), which was heated from room temperature to 600 °C under a nitrogen atmosphere at a heating rate of 10 °C/min.

3. Results and Discussion

3.1. Microstructures of Al-Si-Ge Filler Metals

The microstructure and EDS analysis results of Al-6Si-35Ge filler metal are shown in Figure 2 and Table 1. It can be seen from Figure 2a that the white phase, gray phase, and black phase were observed in the microstructure of the filler metal. According to the EDS results as shown in Figure 2b–d, the black phase mostly included Al, and it was presented by phase A. The white phase and gray phase mainly included Si and Ge, which were presented by the phases of B, C, and D. It can be seen from Table 1 that the chemical composition of phase A was 0.62 wt.% Al + 1.31 wt.% Si + 98.7 wt.% Ge, the chemical composition of phase B was 97.96 wt.% Al + 2.04 wt.% Ge, and the chemical composition of

phase C was 4.26 wt.% Al + 63.93 wt.% Si + 31.81 wt.% Ge. The XRD patterns of Al-xSi-35Ge filler metals are presented in Figure 3. All filler metals were composed of α -Al, Ge, and Si. Combining XRD and EDS analysis results, it can be confirmed that phase A, phase B, and phase C were α -Al, Ge-rich phase (Ge), and Si-rich phase (Si(Ge)), respectively. The chemical composition of lumpy phase D was similar to phase C, yet with higher Ge content and a bigger size. According to Ref. [13], phase C and phase D were primary Si(Ge) and eutectic Si(Ge). Figure 4 displays the microstructure of Al-xSi-35Ge filler metals. It could be seen from Figure 4 that there was no primary Si(Ge) in the microstructure of the Al-4Si-35Ge filler metal. When the Si content of the filler metal was 6 wt.%, primary Si(Ge) appeared. As Si content increased to 6 wt.%, the size of primary Si(Ge) increased. Therefore, Si promoted the formation of primary Si(Ge). Moreover, according to the Al-Si-Ge ternary alloy phase diagram [26], the Al-Si-Ge filler metal mostly consisted of the Al-Si eutectic phase and the Al-Ge eutectic phase, which were marked using a yellow circle and a red circle in Figure 4a. It can be seen that as the Si content increased, the Al-Si eutectic phase in the filler metal increased, and block-shaped Si(Ge) appeared in the filler metal. According to the research of Zhang et al. [13], the block-shaped Si phase was the primary Si(Ge) rather than the eutectic Si(Ge), and the block-shaped Si(Ge) increased when the Si content increased.

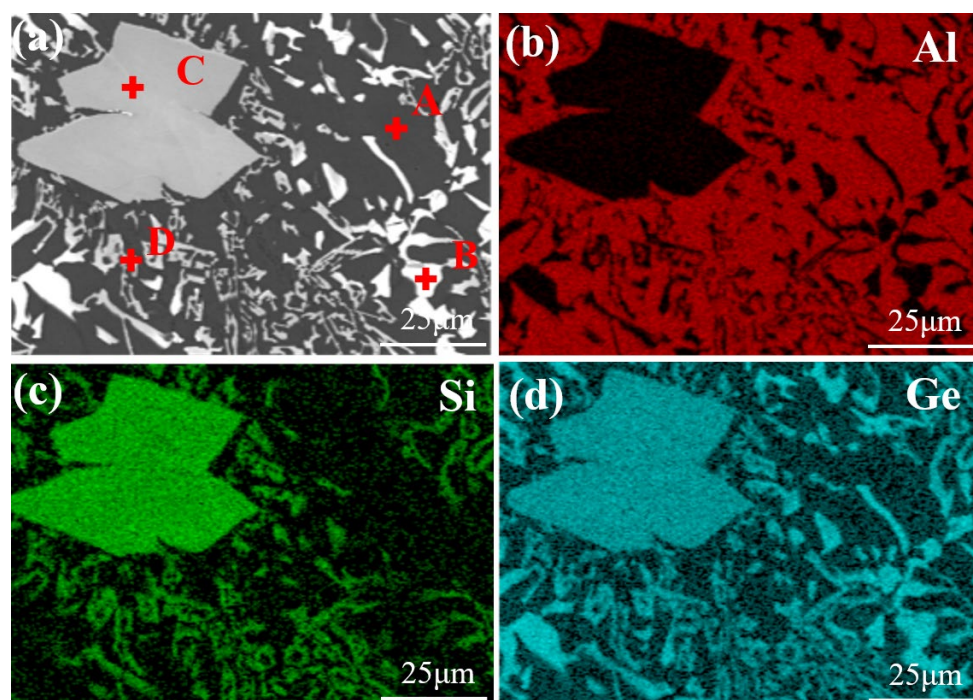


Figure 2. The microstructure and EDS analysis results of Al-6Si-35Ge filler metal: (a) microstructure of filler metals; (b) the distribution of Al; (c) the distribution of Si; and (d) the distribution of Ge.

Table 1. EDS analysis results marked in Figure 2a (wt.%).

Point	Al	Si	Ge	Possible Phase
A	97.96	0	2.04	α -Al
B	0.62	1.31	98.07	Ge
C	4.26	63.93	31.81	Si(Ge) _P
D	0	54.21	45.41	Si(Ge) _E

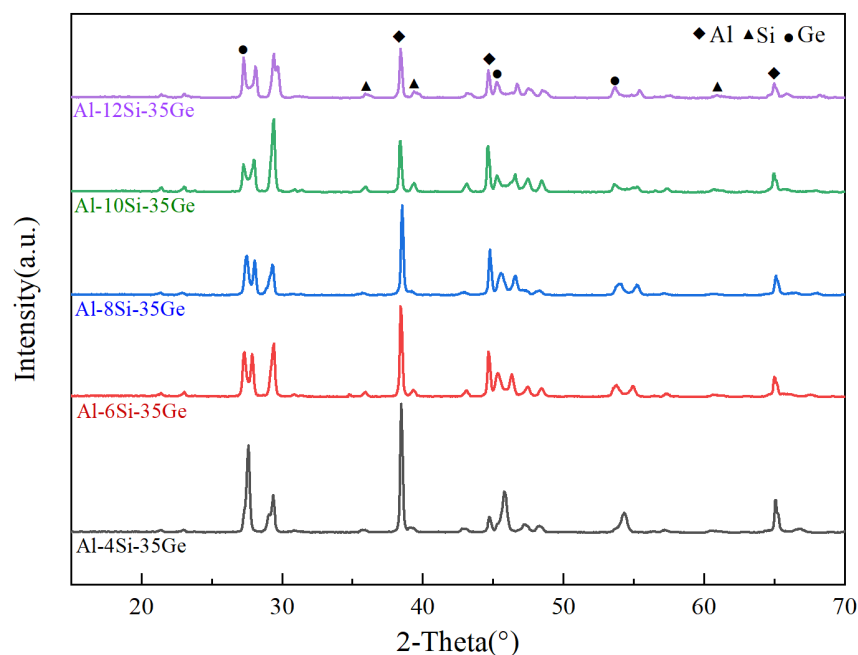


Figure 3. XRD patterns of Al-Si-35Ge filler metals.

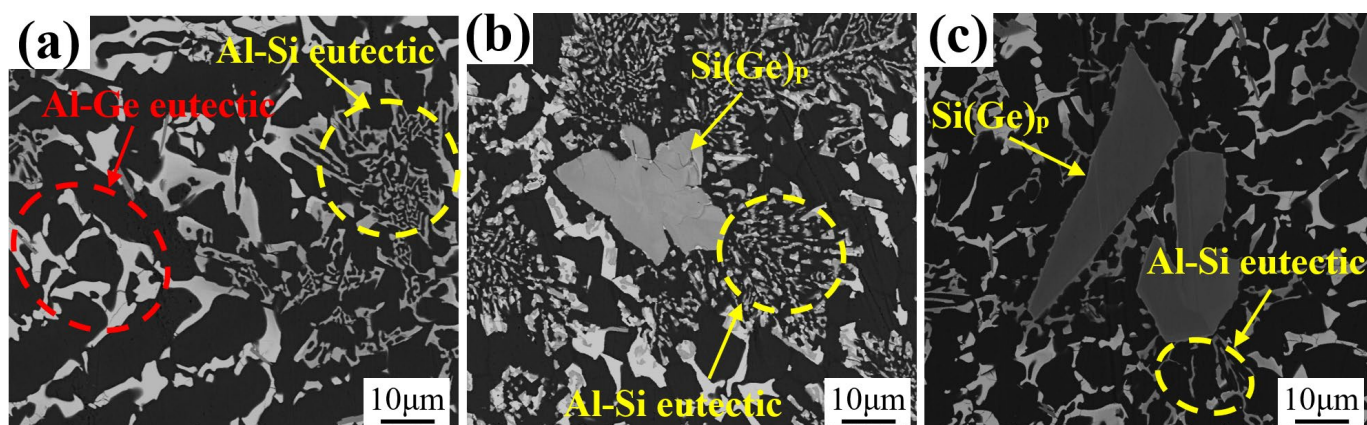


Figure 4. Microstructure of Al-xSi-35Ge filler metals: (a) Al-4Si-35Ge; (b) Al-8Si-35Ge; and (c) Al-12Si-35Ge.

3.2. Melting Characteristics of Al-Si-Ge Filler Metals

Figure 5 shows the DTA curves of Al-xSi-35Ge filler metals with different Si contents. The solidus temperature (T_m) and liquids temperature (T_l) could be obtained by calculating the inflection point around the endothermic peak in the DTA curves. The peak at 500–510 °C represented the Al-Si(Ge) eutectic reaction, and the peak at 420–430 °C represented the Al-Ge eutectic reaction. It can be seen that peaks in DTA curves tend to shift to the right with increasing Si content. According to Figure 5, T_m of filler metals did not show a regular change as the Si content increased, while the T_l of filler metals showed a decreasing trend. The maximum T_l of the filler metal was 518.09 °C when the Si content was 4 wt.%, and the T_l decreased to 514.25 °C when the Si content was up to 12 wt.%.

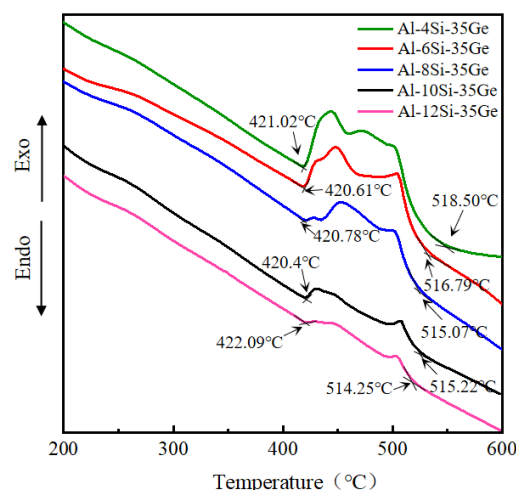


Figure 5. DTA curves of Al-xSi-35Ge filler metals.

3.3. The Wettability of Al-Si-Ge Filler Metals

Figure 6 shows the wetting morphology and EDS analysis results of Al-8Si-35Ge filler metals on the surface of 6061 substrates at a temperature of 550 °C and a holding time of 4 min. It can be seen that although the wetting area of filler metals was relatively large, the spreading of the main filler metal was not ideal, forming an alloy tumor. Cheng et al. believed that this was due to severe loss of melting-point depressant element in filler metal, resulting in higher melting point of residual filler metal [27]. The microstructure and EDS analysis results of the wetting area of the Al-8Si-35Ge filler metal are shown in Figure 6b,c. It can be seen that the chemical composition of the wetting area were mainly Al and Ge, indicating that wetting of Al-Si-Ge filler metals was mainly related to Ge diffusion on the surface of base metal. Figure 6d,e displays the microstructure and major element distribution of Al-8Si-35Ge filler metal and residual filler metal. It can be seen that the characteristics of the Al-Si(Ge) eutectic structure disappeared in the microstructure of the residual filler metal, and the lumpy Si(Ge) phase increased. Moreover, Al-Ge eutectic reduced, and Ge content of filler metal reduced from 34 wt.% to 24.1 wt.%, which was consistent with analysis results from Figure 6b,c. The residual filler metal was harder to melt due to the loss of Ge. Figure 7 illustrates the spreading area of filler metals with different Si content on 6061 substrates. It can be seen that the spreading area decreased with the increasing Si content, suggesting that Si could prevent the spread of Al-Si-Ge filler metal and hinder the loss of Ge.

3.4. Microstructure of Vacuum-Brazed 6061 Joints

Figure 8a shows the macroscopic morphology of 6061 joints at a brazing temperature of 550 °C and a holding time of 4 min, and the microstructure of the surface of 6061 substrates is displayed in Figure 8b. It can be seen from Figure 8b that the morphology of the base material surface was similar to the wetting morphology. In addition, it can be seen in Figure 8a that there was unmelted residual filler metal outside the brazing seam, which was the typical characteristic of the liquidation of filler metal [28]. The mechanism of filler metal liquation is shown in Figure 8c. According to Ref. [28], liquation of filler metal always occurred among the B–D segments in Figure 8c. When the filler metal composition was a (corresponding to the melting point T_2), the brazing temperature was set to T_3 to ensure the melting of filler metal during brazing. When the temperature rose to T_1 , the state of the brazing material was approximately composed of solid S and liquid L. According to the lever law, LC was the amount of solid phase, and CS was the amount of liquid phase. During the brazing process, the liquid phase flowed along the brazing seam, leaving only

solid (S), which would not melt at the brazing temperature T_3 and formed a filler metal overlap. Liquidation of filler metal was promoted by a large difference between solid–liquid phase lines (ΔT) of filler metals and a slow heating rate. According to Figure 5, the solid line of Al-Si-35Ge filler metal corresponding to the initial temperature of the extrapolated onset of Al-Ge eutectic was 420.4–422.09 °C, and the liquid line corresponding to the finishing temperature of the extrapolated onset of Al-Si(Ge) eutectic was 515.22–518.5 °C. The minimum ΔT can reach 92.16 °C. It could be seen from Figure 1c that the heating rate of vacuum brazing was 5–10 °C/min, so it needed at least 9 min to ensure the temperature increased from 421.02 °C (T_{eutectic}) to 518.5 °C (T_2). Therefore, both the great temperature difference and the long heating time cause the liquation of filler metals. The Al-Ge eutectic phase first melted and flowed along the surface of 6061, while the Al-Si(Ge) eutectic phase could not completely melt and formed filler metal overlap.

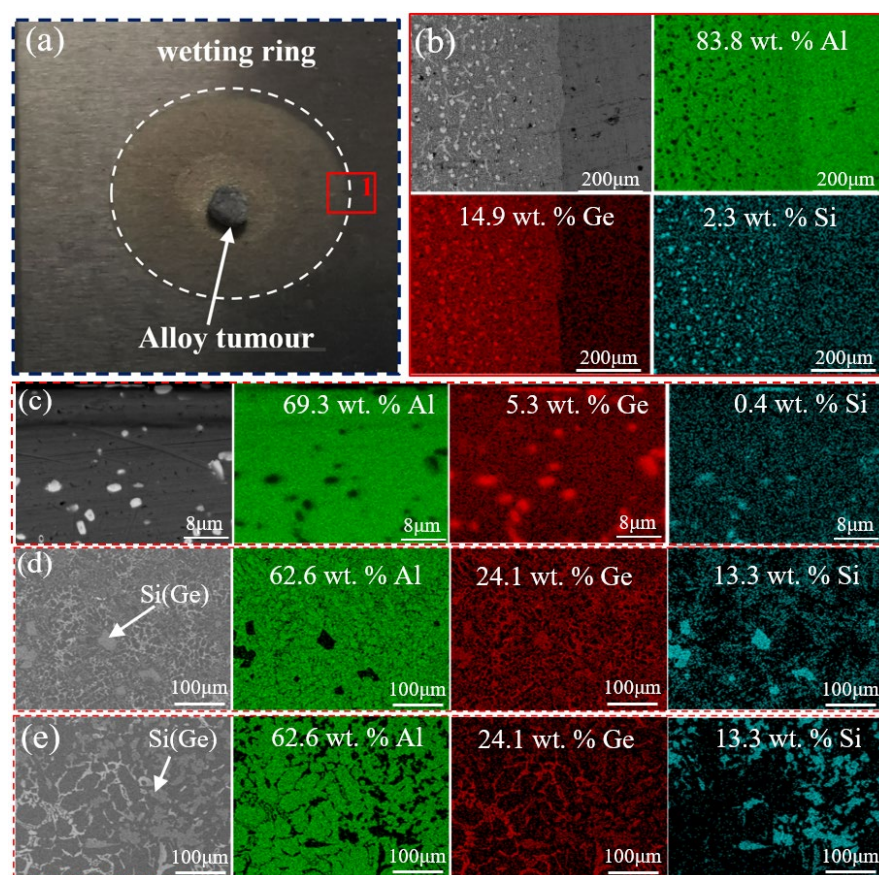


Figure 6. The wetting of Al-8Si-35Ge filler metal on the surface of the 6061 alloy: (a) wetting morphology; (b) the distribution of major elements of the wetting boundary marked with red line in (a); (c) the distribution of major elements of the cross-section of the wetting boundary; (d) original filler metal; and (e) residual filler metal.

As illustrated in Figure 9, the microstructure of 6061 brazed structures with Al-8Si-35Ge was investigated when the brazing temperature was 550 °C. It can be seen from Figure 9b that the brazed joint consisted of two solid diffusion reaction layers (Zone I) and a filler metal residual zone (Zone II). Zone I was close to the 6061 alloy substrate and was composed of black phase, gray particle phase, and gray–white particle phase, which were represented by phases of E, F, and G in Figure 9a. Zone II was composed of black phase, gray block phase, gray–white block phase, and white phase, which were represented by phases H, I, J, and K in Figure 9c. It can be seen from the chemical composition in Table 2. The chemical composition of phase E was 97.4 wt.% Al + 1.7 wt.% Si + 0.9 wt.% Ge. Phase E was α -Al according to the Al-Si-Ge phase diagram. Phase F had brighter contrast

when compared to the A phase. As indicated in Table 1, the chemical composition of phase F was 90 wt. % Al + 1.9 wt. % Si + 9.1 wt. % Ge. F phase was deduced to be Al-rich (Al, Ge) according to [15]. The contrast of the G phase was the lightest, compared to the phases of E and F. As indicated in Table 1, the chemical composition of phase G was 47.6 wt.% Al + 0.9 wt.% Si + 0.6 wt.% Si + 51.5 wt.% Ge. Phase G was deduced to be (Al, Ge) according to Ref. [23]. The chemical composition of phase H was close to phase E, and phase H was α -Al. The chemical composition of phase I was 1.2 wt.% Al + 59.2 wt.% Si + 39.6 wt.% Ge. Phase I was Si-rich Si(Ge) according to the Si-Ge phase diagram. As indicated in Table 1, the chemical composition of phase J was comparable to that of phase I, but Ge content at phase J was larger, being 55.6% (wt.%). Phase I was (Si, Ge). The chemical composition of phase K was 50.3 wt.% Al + 0.4 wt.% Si + 49.7 wt.% Ge. Phase K was (Al, Ge).

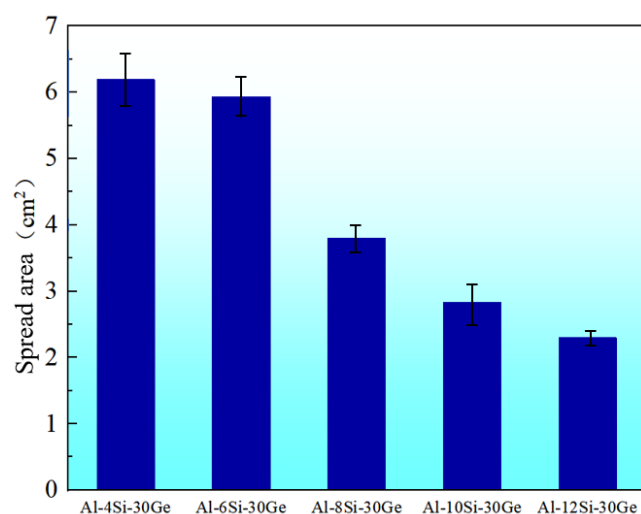


Figure 7. The spread area of different filler metals.

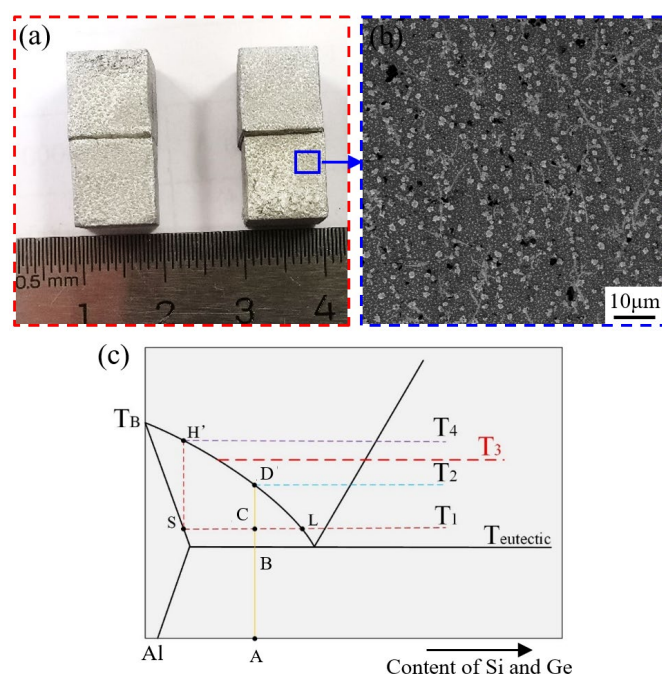


Figure 8. (a) Macroscopic morphology of the brazed joint; (b) microstructure of the 6061 surface; and (c) schematic diagram of the liquation of Al-Si-35Ge filler metals.

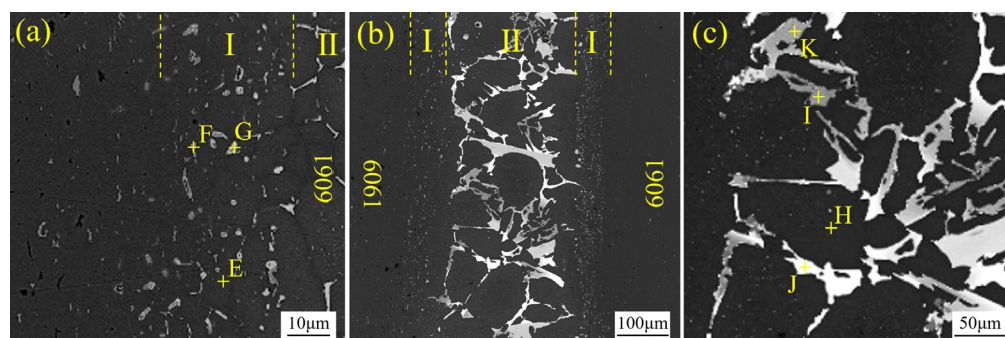


Figure 9. Typical microstructure of a 6061 joint brazed with Al-8Si-35Ge filler metal (a) and (c) magnified images of Zone I and Zone II in (b).

Table 2. EDS analysis results marked in Figure 9 (wt.%).

Point	Al	Si	Ge	Possible Phase
E	97.4	1.7	0.9	α -Al
F	90	1.9	9.1	(Al, Ge)
G	46.1	0.6	53.3	(Al, Ge)
H	96.9	0	3.1	α -Al
I	1.2	59.2	39.6	Si(Ge)
J	5.2	43.9	50.9	Si(Ge)
K	50.3	0.4	49.7	(Al, Ge)

Figure 10 shows the microstructure of 6061 joints with Al-xSi-35Ge filler metals with different Si contents. The microstructure of joints with different filler metals was similar. Holes and cracks were found in the brazed joints, and it was reduced with the increasing Si addition. The causes of defects were closely related to the liquidation of filler metal. The Al-Ge eutectic phase began to melt at 420 °C, and the Al-Si eutectic phase completely melted above 514 °C. The Al-Ge eutectic with a low melting point melted and flowed along the surface of 6061 substrates, resulting in changes in the chemical composition of the residual filler metal. The melting point of residual filler metal increased, and it was difficult to melt at the predetermined brazing temperature due to the decreasing Ge content. The increase in melting point deteriorated the metallurgical bonding between residual filler metal and 6061 substrates and resulted in the formation of defects.

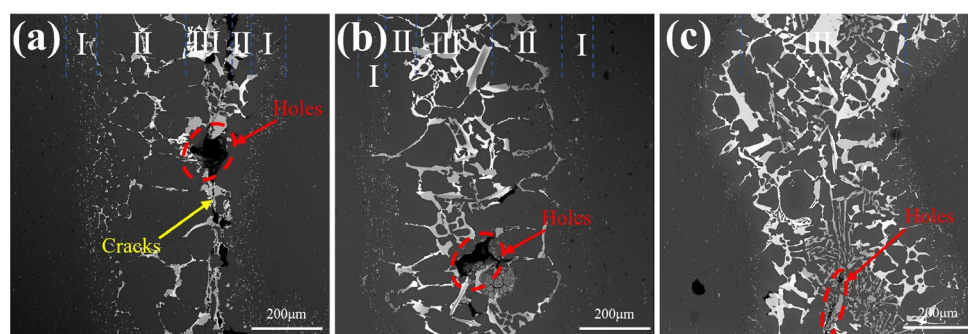


Figure 10. Interfacial microstructure of 6061 joints with Al-xSi-35Ge filler metals: (a) Al-4Si-35Ge; (b) Al-8Si-35Ge; and (c) Al-12Si-35Ge.

3.5. The Mechanism and Influence of Si in the Microstructure of Brazed Joint

3.5.1. Thermodynamics Model

The metallurgical bonding between residual filler metal and 6061 substrates was realized through the diffusion of elements in the filler metals and substrates. According to

the thermodynamic principle, element diffusion was dependent on the chemical potential. The chemical potential (namely, partial molar free energy) could be expressed by the following equation:

$$\mu_i = \frac{\partial G}{\partial x_i} \quad (1)$$

where μ_i is the chemical potential of element i , G represents the free energy of alloy systems, and x_i represents the mole fraction of element i . G was always the summation of the excessive molar free energy G^E and the ideal solution molar free energy G^I .

Therefore, it could be expressed as follows:

$$G = G^I + G^E \quad (2)$$

G^I could be expressed as follows:

$$G^I = G^0 + \Delta G^I = x_i G_i^* + x_j G_j^* + x_k G_k^* + RT(x_i \ln x_i + x_j \ln x_j + x_k \ln x_k) \quad (3)$$

where G^0 is the standard molar free energy; ΔG^I is the increment of G^I resulted from atomic interaction; and G_i^* , G_j^* , and G_k^* represent the molar free energies of pure components i , j , and k , respectively. x is the mole fraction of the corresponding component. R is the gas constant. T is the temperature.

G^E is calculated with the Toop model [29]. G^E could be calculated according to the values of G_{ij}^E , G_{ik}^E , and G_{jk}^E in the binary system, using the Toop model. G_{ij}^E , G_{ik}^E , and G_{jk}^E stand for the excessive molar free energy in i - j , i - k , and j - k binary systems, respectively.

$$G^E = \frac{x_j}{1-x_i} G_{ij}^E(x_i, 1-x_i) + \frac{1-x_i-x_j}{1-x_i} G_{ik}^E(x_i, 1-x_i) + G_{jk}^E\left(\frac{x_j}{1-x_i}, \frac{1-x_i-x_j}{1-x_i}\right) \quad (4)$$

G_{ij}^E could be expressed as follows:

$$G_{ij}^E = \Delta H_{ij} - T \Delta S_m^E \quad (5)$$

where ΔH_{ij} stands for the solution enthalpy (formation enthalpy) in the binary system and ΔS_m^E represents the excessive entropy in the binary system.

Tanaka et al. propose that the relationship between the excessive entropy ΔS_m^E and the solution enthalpy ΔH_{ij} could be described as follows [30]:

$$\Delta S_m^E = \Delta H_{ij}(1/T_i + 1/T_j)/14 \quad (6)$$

In this equation, T_i and T_j are the melting points of components i and j , respectively.

The excessive molar free energy of the binary system could be replaced by the following expression:

$$G_{ij}^E = \Delta H_{ij}[1 - T(1/T_i + 1/T_j)/14] \quad (7)$$

ΔH_{ij} could be calculated using the Miedema model of solution enthalpy, which is developed by Miedema et al. [31]:

$$\Delta H_{ij} = f_{ij} \frac{x_i[1 + \mu_i x_j(\varnothing_i - \varnothing_j)]x_j[1 + \mu_j x_i(\varnothing_j - \varnothing_i)]}{x_i V_i^{2/3}[1 + \mu_i x_j(\varnothing_i - \varnothing_j)] + x_j V_j^{2/3}[1 + \mu_j x_i(\varnothing_j - \varnothing_i)]} \quad (8)$$

$$f_{ij} = \frac{2pV_i^{2/3}V_j^{2/3} \left[q/p \left(\Delta n_{ws}^{1/3} \right)^2 - (\Delta \phi)^2 - b(r/p) \right]}{\left(n_{ws}^{1/3} \right)_i^{-1} + \left(n_{ws}^{1/3} \right)_j^{-1}} \quad (9)$$

where x represents the molar fraction of elements. ϕ stands for electronegativity. V is the molar volume. n_{ws} represents the electron density. q , r , μ , a , p , and b are experimental constants. These parameters and values could refer to the research results reported by Miedema et al. [32,33].

3.5.2. Thermodynamics Analysis

Figure 11 shows the calculation results of the free energy of the Al-Si-Ge ternary system ($G_{\text{Al-Si-Ge}}$) at 550 °C. It can be seen that $G_{\text{Al-Si-Ge}}$ was always negative, indicating spontaneous metallurgical reactions in the Al-Si-Ge ternary system. The position $G_{\text{Al-Si-Ge}}$ was on the Al-Ge side, indicating the existence of an Al-Ge eutectic phase in the alloy system. Figure 12 shows the calculated chemical potential of Ge (μ_{Ge}) in the Al-Si-Ge ternary system at 550 °C. The μ_{Ge} was -44.8 kJ/mol when the Al content was 98 wt.% (corresponding to the Al content of 6061). The μ_{Ge} was higher than -10 kJ/mol when the Al content was 60 wt.% (corresponding to the Al content of Al-Si-Ge filler metals). Therefore, the driving force for Ge diffusion to regions with high Al content was higher, namely the trend of Ge diffusion from the filler metals to the 6061 substrates was higher. The reaction between the filler metal and 6061 substrates was achieved through the diffusion of Ge from the filler metals to the 6061 substrates, which was consistent with the EDS analysis results. The loss of Ge led to a decrease in residual solder activity and an increase in joint defects. According to the calculation results, the μ_{Ge} in 6061 substrates was -24.5 kJ/mol. The μ_{Ge} in Al-4Si-35Ge filler metal was greater than -1.5 kJ/mol, but it significantly decreased to -8.4 kJ/mol when the Si content was up to 12 wt.%. Obviously, Si addition could narrow the difference of μ_{Ge} in the filler metals and 6061 substrates. The lower difference of μ_{Ge} mean that weak trend of Ge diffusion from filler metals to 6061 substrates.

According to Sections 3.3 and 3.4, the formation of brazing defects in the microstructure of joints resulted from the premature melting and flowing of the Al-Ge phase, which was related to the diffusion of Ge from filler metal to base metal. At this time, the larger the spread area was, the more severe the loss of melting-point depressant element Ge in the residual filler metals, resulting in the formation of defects in the brazed joints due to the increasing melting point of residual filler metal. According to the calculation results, Si addition can hinder the diffusion of Ge from filler metal to base metal, meaning that Si can reduce the loss of melting-point depressant element Ge in the residual filler metals. Hence, the spread area of filler metal was decreased, and defects in the brazed joint were reduced with increasing Si content in the filler metal, which was consistent with experimental results.

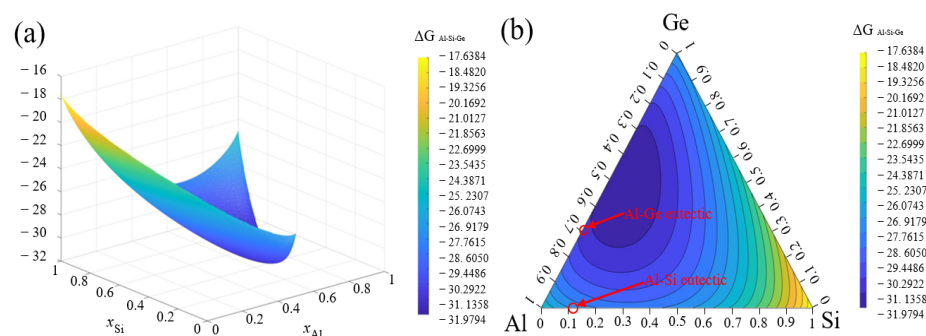


Figure 11. (a) Three-dimensional graphs and (b) corresponding contour maps for calculated free energy of Al-Si-Ge ternary system ($\Delta G_{\text{Al-Si-Ge}}$) at 550 °C.

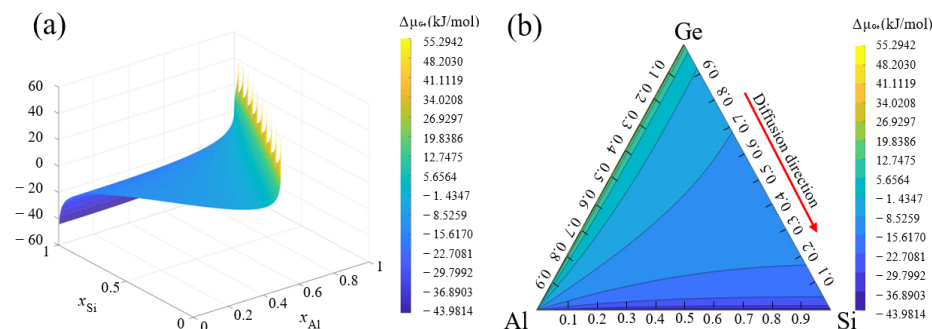


Figure 12. (a) Three-dimensional graphs and (b) corresponding contour maps for calculated chemical potential of Ge (μ_{Ge}) at 550 °C.

3.6. Mechanical Properties

The shear strength of 6061 joints is demonstrated in Figure 13. The shear strength with Al-4Si-35Ge filler metal was 19.6 MPa. When the Si content was up to 8 wt.%, the shear strength reached the maximum (57.3 MPa), but it decreased to 31.2 MPa with the further addition of Si. The fracture morphology of 6061 joints brazed with Al-Si-35Ge filler metals is shown in Figure 14. The chemical composition in the marked positions on the fracture surface is displayed in Table 3. The α -Al (positions 1, 4, 7), Ge (positions 2, 5, 8), and Si(Ge) (positions 3, 6, 9) were detected on the fracture surfaces. According to Figure 14a, there were a large number of cleavage steps and planes on Ge (position 2) and Si(Ge) (position 3) phases. The existence of the cleavage plane indicated cleavage fracture. However, no fracture characteristic on α -Al was observed, suggesting the existence of defects in the joint. Hence, the fracture mode of joints was “cleavage fracture + cleavage fracture”, and the joint shear strength was 19.6 MPa. It could be seen from Figure 14b that dimples on α -Al were observed (position 4) when using Al-8Si-35Ge filler metal. The existence of the dimples indicated ductile fracture. Similarly, cleavage steps and planes on Ge (position 5) and Si(Ge) (position 6) phases. Therefore, the fracture mode of joints was “ductile fracture + cleavage fracture”, and the shear strength was increased to 57.3 MPa. The fracture morphology of the joint with Al-12Si-35Ge filler metal is presented in Figure 14c. Ge (position 8) and Si(Ge) (positions 7, 9) were characterized by a lamellar cleavage plane, suggesting that the fracture mode of joints was “cleavage fracture”. It can be seen from Figure 10 that Si(Ge) and Ge in the brazed joints increased and coarsened when Ge content in filler metals rose from 4 wt.% to 12 wt.%. Moreover, the indentation hardness of Al, Ge, and Si(Ge) was 0.7 GPa, 10.2 GPa, and 11.5 GPa, respectively [24]. The coarse brittle phase reduces the toughness of the joint, leading to local stress concentration and cracking when the joint was subjected to shear force, thereby reducing the shear strength of the joint. Hence, the shear strength decreased to 31.2 MPa when Si content in the filler metals was 12 wt.%.

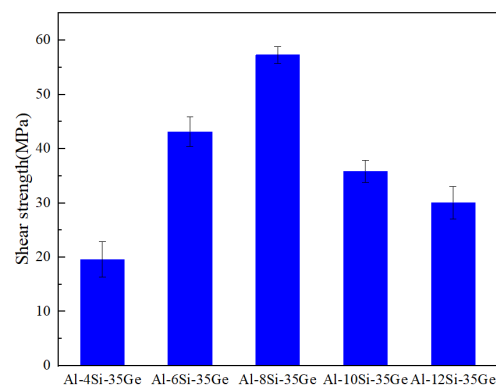


Figure 13. Shear strength of 6061 joints.

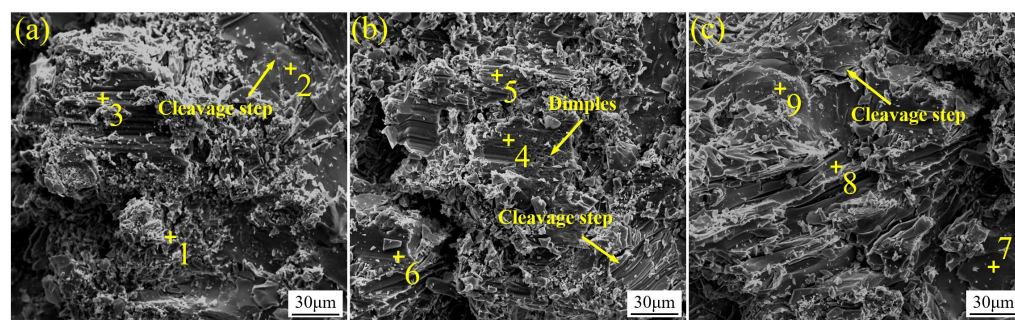


Figure 14. The fracture morphology of 6061 joints: (a) Al-4Si-35Ge; (b) Al-8Si-35Ge; and (c) Al-12Si-35Ge.

Table 3. Chemical composition (wt.%) of the marked spots in Figure 14.

Point	Al	Si	Ge	O	Possible Phase
1	76.8	7.5	1.6	14.1	α -Al
2	1.9	0.8	91.3	6	Ge
3	0.3	52.5	46.1	1.1	Si(Ge)
4	95.4	0.8	1.4	2.4	α -Al
5	1.6	0	97.1	1.3	Ge
6	0	56.1	42.3	1.6	Si(Ge)
7	1.2	40.4	55.3	3.1	Si(Ge)
8	2.8	0.7	93.8	2.5	Ge
9	0	48	50.1	1.9	Si(Ge)

4. Conclusions

In the present work, five Al- x Si-35Ge ($x = 4, 6, 8, 10, 12$, wt.%) filler metals with different Si contents were prepared to braze 6061 alloy. The influence of Si content on the microstructure and melting characteristics of Al- x Si-35Ge filler metals was discussed. The influence of Si on the microstructure and shear strength of brazed joints was analyzed. The main conclusions were drawn as follows:

- (1) The melting point of Al- x Si-35Ge filler metals decreased from 518.5 °C to 515.22 °C when the Si content increased from 4 wt.% to 12 wt.%. The primary Si phase appeared in the microstructure of filler metals when the Si content was 6 wt.%.
- (2) The microstructure of the joint was characterized by a multilayer structure that was primarily composed of three zones: two transition regions (Zone I) and a filler residual region (Zone II).
- (3) Liquidation of filler metal occurred during brazing, resulting in the formation of defects such as holes and cracks in the microstructure of 6061 joints. Si can hinder this phenomenon by reducing the difference of μ_{Ge} in fillers and 6061 substrates.
- (4) The maximum shear strength of the joint was 57.3 MPa, using Al-8Si-35Ge filler metal. Lower Si content in fillers resulted in defects in joints, and higher Si content introduced much more brittle Si(Ge).

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