Rare Metal Materials and Engineering
Volume 54, Issue 2, February 2025
Available online at www.rmme.ac.cn

Science Press

Cite this article as: Huang Sen, Long Weimin, Shan Jiguo, et al. Phase Formation Mechanism of Al-Si-Ge Filler Metals Based on Thermodynamics Calculation[J]. Rare Metal Materials and Engineering, 2025, 54(02): 293-300. https://doi.org/10.12442/j.issn.1002-185X.20240431.

ARTICLE

Phase Formation Mechanism of Al-Si-Ge Filler Metals Based on Thermodynamics Calculation

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Abstract: A series of Al-*x*Si-*y*Ge filler metals (x=4 – 12 and y=10 – 40, wt%) were prepared, and the effect of Si and Ge on microstructure and melting characteristics of filler metals was studied. The thermodynamic model of Al-Si-Ge ternary alloy was established to analyze the phase formation mechanism of filler metals based on Miedema model, Tanaka model, and Toop equation. This research provided a basis for the composition optimization of filler metals and the analysis of metallurgical reaction process between filler metals and base materials. Results show that Al-Si-Ge alloy is composed of Al-Ge eutectic phase, Al-Si eutectic phase, and primary Si. Ge addition promotes the precipitation of primary Si. Ge is the main melting point depressant element of filler metals. With the increase in Ge content from 10wt% to 40wt%, the solid phase line of filler metals remains unchanged, whereas the liquidus temperature decreases from 567.65 °C to 499.96 °C. With the increase in Ge content of filler metal, Ge content in eutectic Si phase is increased, the endothermic peak of Al-Si eutectic reaction according to thermogravimetry curve becomes smoother, and Al-Si eutectic temperature is decreased. Ge addition can reduce the free energy of Al-Si alloy system. The lowest point of free energy is located on Al-Ge side. The eutectic Ge phase with the composition similar to pure Ge composition is the most likely to appear in the microstructure of filler metals, whereas the eutectic Si phase with the composition similar to pure Si composition is the least likely to appear. The thermodynamic calculation results are consistent with the experiment results.

Key words: Al-Si-Ge filler metals; microstructure; thermodynamics; phase formation mechanism

Currently, large-scale Al-Si-Mg and Al-Zn-Mg-Cu alloy components in high-end equipment become complex, which improves the requirements for the strength, corrosion resistance, and quality of welded joints. Welding techniques, such as laser welding and friction stir welding, cannot meet the requirements for welding of aluminum alloy components with complex structures[1–2], particularly for the thin-walled components, which are prone to severe deformation during processing. Vacuum brazing is a clean efficient high-quality welding technique with unique advantages for the connection of large thin-walled components[3–7].

One of the problems for vacuum brazing of Al-Si-Mg and Al-Zn-Mg-Cu alloys is the selection of filler metals. The brazing temperature of Al-Si and Al-Si-Mg filler metals commonly used for brazing aluminums is 590–620 °C, which is higher than the melting temperature of Al-Si-Mg and Al-Zn-Mg-Cu alloys[5–6]. Therefore, ternary alloys (Al-Si-Ge, Al-Si-Zn, and Al-Si-Cu), quaternary alloys (Al-Si-Cu-Zn, Al-Si-Cu-Ge, and Al-Si-Cu-Mg), and quinary alloys (Al-Si-Cu-Ge-Mg) have been developed for brazing 6061 aluminum alloys[2]. However, Cu and Zn can reduce the corrosion resistance of joints, and Zn and Mg affect the surface cleanliness of the welded joint[1,5]. Therefore, further in-depth research on Al-Si-Ge filler metals is crucial in order to meet the high-quality brazing requirements[8–9].

Research on Al-Si-Ge filler metals mainly focuses on microstructure, mechanical properties, and melting characteristics. Liu et al[10] studied the multi-temperature state diagram of Al-Si-Ge system (the Al-rich region) by combining the thermal analysis and the alloy phases. The results indicated that the liquid phase of the ternary system was composed of two primary crystal planes of α-Al and Si-Ge

Received date: July 16, 2024
Foundation item: National Natural Science Foundation of China (U22A20191)
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solid solution phases. Hayes et al[11] investigated the thermodynamic properties of Al-Si-Ge filler metals based on the results from Ref.[12–14]. They compared the results with those in Ref.[15] and found that there were liquid phase, Al rich solid solution, and Si-Ge solid solution in the system, but no ternary phase existed. Zhang et al[16] investigated the influence of Ge content on microstructure and phase formation of Al-18Si alloy and found that a primary solid solution containing Si and Ge could appear in the alloy when Ge content was high, and the increase in Ge addition amount in Al-18Si-*x*Ge alloys led to an increase in Ge content of primary Si. Osintsev et al[17] analyzed the composition of Al-Si-Ge filler metals, and the results showed that there were aluminum-based α solid solution, silicon-based β solid solution, and germanium-based β_n solid solution in the alloy, and the higher the Ge content in alloy, the higher the appearance probability of nonequilibrium β_n phase crystals. Gurin et al[18] investigated the chemical composition of precipitates in Al-Si-Ge alloys solidified during centrifugation. The results indicated that the sharp increase in Ge content (correspondingly, the decrease in Si content) was observed near the borders of Si-Ge precipitates. The surface of the precipitates was covered by a thin Ge-rich layer. Schubert et al[19] prepared Al-Si-Ge filler metals by a combination method of melt-spinning and annealing and studied the phase transition process. The results showed that the foils were relatively brittle in the as-quenched alloy due to the occurrence of metastable phases, but after appropriate annealing treatments, the metastable phases were transformed into β-Ge(Si) particles within the α-Al matrix. Ivannikov et al[20] studied the thermodynamic characteristics and microstructure of Al-Si-Ge filler metals, and found that with the increase in Ge content from 28wt% to 40wt%, the liquidus temperature of filler alloys was decreased from 514.8 °C to 474.3 °C, and the alloy contained the solid solutions of (Al, Ge), (Ge, Si), (Al, Ge), and the one based on Ge.

However, the analysis of the phase formation mechanism of Al-Si-Ge filler metals is rarely reported. In this research, a series of Al-*x*Si-*y*Ge filler metals (*x*=4–12 and *y*=10–40, wt%) were prepared. The effect of Si and Ge on the microstructure and melting characteristics of filler metals was studied. The thermodynamic model of Al-Si-Ge ternary alloy was established to analyze the phase formation mechanism of the filler metals based on Miedema model, Tanaka model, and Toop equation. This research provided a basis to optimize the composition of filler metals and to analyze the metallurgical reaction process between the filler metals and the base materials.

1 Experiment

High purity aluminum (99.99wt%), high purity germanium (99.999wt%), and AlSi30 alloy were used as raw materials to prepare Al-Si-Ge filler metals. All raw materials were melted in a clean graphite crucible by medium frequency induction heating at 900 °C for 5 min, and then the melt was poured into a cast graphite mold.

The microstructure characteristics of the samples were analyzed by scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). The phases observed in the microstructure were identified by X-ray diffractometer (XRD). The melting temperatures of these alloys were determined by differential scanning calorimetry (DSC), and the alloy was heated from room temperature to 600 °C under nitrogen atmosphere at heating rate of 10 °C/min. MATLAB software was used to calculate the free energy of alloy with different composition.

2 Results and Discussion

2.1 Microstructure of filler metals

Microstructures of Al-*x*Si-*y*Ge (*x*=4, 6, 8, 10, 12; *y*=10, 20, 30, 40) filler metals are displayed in Fig. 1. Al-Si-Ge filler metals are composed of black phase, gray phase, and white phase. Table 1 presents EDS analysis results of the points marked in Fig.1. The composition of black phase is 98.61wt% Al+1.39wt% Ge (Point A); the composition of gray phase is 1.15wt% Al+61.67wt% Si+37.18wt% Ge (Point B); the composition of white phase is 1.01wt% Al+2.44wt% Si+96.55wt% Ge (Point C). Fig. 2 displays XRD patterns of different Al-6Si-*y*Ge filler metals. It can be seen that α-Al, Si, and Ge are major phases of filler metals. Therefore, the white phase, gray phase, and black phase are Ge, Si, and α-Al, respectively, based on the results of EDS and XRD analyses. Liu et al[10] noted that there was no ternary eutectic reaction in Al-Si-Ge phase diagram. Zhang et al[16] also supported this point of view. In this research, Al-Si eutectic and Al-Ge eutectic are marked by red line and white line in Fig. 1, respectively.

It can be observed from Fig. 1a–1d that Al-4Si-*y*Ge filler metals consist of α-Al, Al-Si eutectic phase, and Al-Ge eutectic phase. Al-Ge eutectic is increased with the increase in Ge addition amount. Grey block-shaped phase (marked by yellow line in Fig.1) appears when Si content exceeds 4wt%, as shown in Fig. 1e–1t. The chemical composition of block-shaped phase is 4.26wt% Al+63.93wt% Si+31.81wt% Ge (Point D). Zhang et al[16] believed that block-shaped Si phase was not eutectic Si but primary Si phase. According to Table 1, the Ge content of primary Si is the lowest. With the increase in Ge content, the size of primary Si is gradually increased, reaching 200 μm.

It can be seen from Table 1 and Fig. 1 that with the Si content as constant in filler metals, Ge content in eutectic Si is increased with the increase in Ge addition amount. With the Ge content as constant in filler metals, Ge content in eutectic Si and primary Si is decreased with the increase in Si addition amount. Si content in eutectic Ge is basically invariable with the addition of Ge or Si. Ge content of eutectic Si in Al-8Si-10Ge, Al-8Si-20Ge, Al-8Si-30Ge, and Al-8Si-40Ge is 34.52wt%, 47.54wt%, 51.08wt%, and 57.96wt%, respectively, as shown in Table 1, and Si content in eutectic Ge is basically constant (Point J, M, Q, and U). When Ge content is 30wt%, Ge content in eutectic Si and primary Si is decreased with the

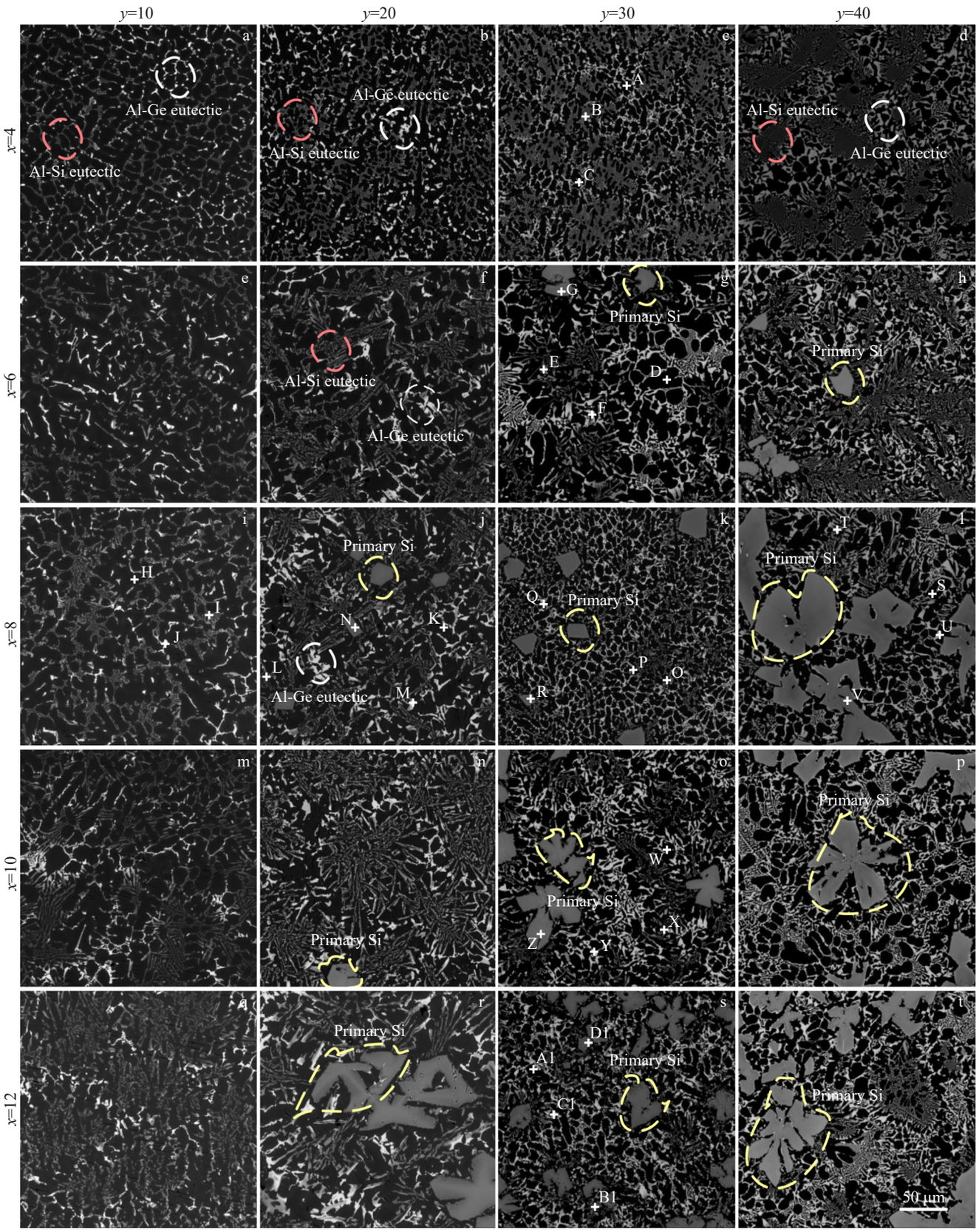

Fig.1 Microstructures of different Al-*x*Si-*y*Ge filler metals

increase in Si addition amount in filler metals, whereas the Si content in eutectic Ge remains unchanged, as shown in Table 1 (Point C, F, Q, Y, and C1). This result indicates that Ge addition has significant influence on the chemical composition of Si phase in filler metals, whereas Si addition cannot change the composition of eutectic Ge. Table 2 shows

Table 1 EDS analysis results of points marked in Fig.1 (wt%)

Point	Al	Si	Ge
A	98.61	0.00	1.39
B	1.15	37.18	61.67
C	1.01	2.44	96.55
D	97.79	0.00	2.21
E	1.58	40.02	58.40
F	1.90	1.53	96.57
G	0.87	51.61	47.52
H	97.11	0.00	2.89
I	6.71	58.77	34.52
J	1.78	0.99	97.23
K	96.07	0.00	3.93
L	1.26	51.2	47.54
M	0.91	2.28	96.81
N	1.48	53.99	44.53
O	96.97	0.00	3.03
P	1.89	47.03	51.08
Q	0.65	1.39	97.96
R	1.09	54.89	44.02
S	97.61	0.00	2.39
T	0.31	41.73	57.96
U	0.71	1.46	97.83
V	1.71	54.31	43.98
W	98.11	0.00	1.89
X	1.84	47.68	50.48
Y	1.99	0.50	97.51
Z	2.10	54.02	43.88
A1	97.74	0.00	2.26
B1	2.08	46.31	51.61
C1	1.53	1.68	96.79
D1	0.76	54.75	44.49

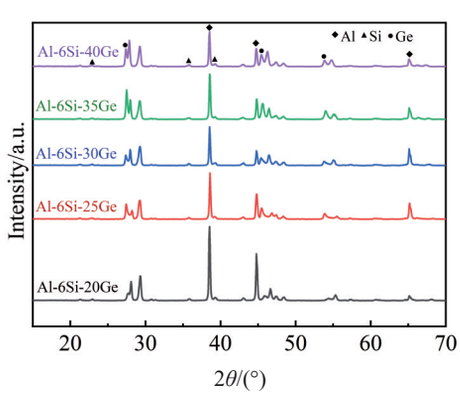

Fig.2 XRD patterns of Al-6Si-*y*Ge filler metals

the Ge content in different filler metals. When Ge content in filler metals increases from 1wt% to 10wt%, Ge content in eutectic Si is increased from 1.3wt% to 10.7wt%, whereas Si content in eutectic Ge is 1.4wt%–3.2wt% when Si content in filler metals increases from 7.5wt% to 12.5wt%.

Table 2 Ge content in different filler metals (wt%) [16–17]

Filler metal	Ge content in eutectic Si	Ge content in eutectic Ge	Ref.
Al-18Si-1Ge	1.31	-	[16]
Al-18Si-3Ge	3.31	-	[16]
Al-18Si-5Ge	5.67	-	[16]
Al-18Si-10Ge	10.7	-	[16]
Al-11.5Si-2Ge	4.8	-	[17]
Al-11.4Si-3.8Ge	17.5	-	[17]
Al-9.6Si-7.7Ge	24.2	98.3	[17]
Al-8.4Si-12.7Ge	37.8	98.6	[17]
Al-7.5Si-21Ge	59.5	96.8	[17]
Al-7Si-24Ge	64.4	92.8	[17]
Al-8Si-7.6Ge	32.8	97.6	[17]
Al-12Si-8.5Ge	32.4	97.2	[17]

Therefore, it can be concluded that when Ge content is low, Al-Si-Ge filler metals are composed of Al-Si eutectic phase and Al-Ge eutectic phase. With the increase in Ge content, the composition of Ge eutectic phase does not change significantly, but Ge content of Si eutectic phase is increased significantly. The filler metals composed of Al-Ge eutectic phase and Al-Si eutectic phase have higher Ge content. With the increase in Ge content, the primary Si phase, whose Ge content is lower than that of Si eutectic phase, is precipitated in the microstructure of filler metals.

2.2 Melting characteristics of filler metals

Fig. 3 shows DSC curves of different Al-*x*Si-*y*Ge filler metals. There are two endothermic peaks in DSC curves. The peak located at 490 – 560 °C represents the Al-Si eutectic reaction, and the peak located at 420–450 °C represents Al-Ge eutectic reaction. When Ge content increases from 10wt % to 40wt%, Al-Si eutectic reaction temperature decreases from 558.39 °C to 487.44 °C, and the shape of eutectic peak becomes smoother. These phenomena indicate that increasing Ge addition amount leads to the decrease in Al-Si eutectic reaction. Moreover, due to the inconsistent Ge content in Si phase of different regions of filler metals, the endothermic peak of Al-Si eutectic phase becomes wider and smoother. Table 3 displays the melting point (liquidus temperature) of different Al-*x*Si-*y*Ge filler metals. When Ge content increases from 10wt% to 40wt%, melting point decreases from 567.65 °C to 499.96 °C. The melting point of filler metals shows a downward trend with the increase in Si content, but the downward trend is not significant. When Si content increases from 4wt% to 12wt%, the melting point decreases from 518.50 °C to 514.25 °C. Hence, Si has little effect on the melting point of filler metals, and Ge is the melting point depressant element in filler metals.

2.3 Developed free energy prediction model

The formation mechanism of phase in filler metals was analyzed through the free energy model. The real solution free

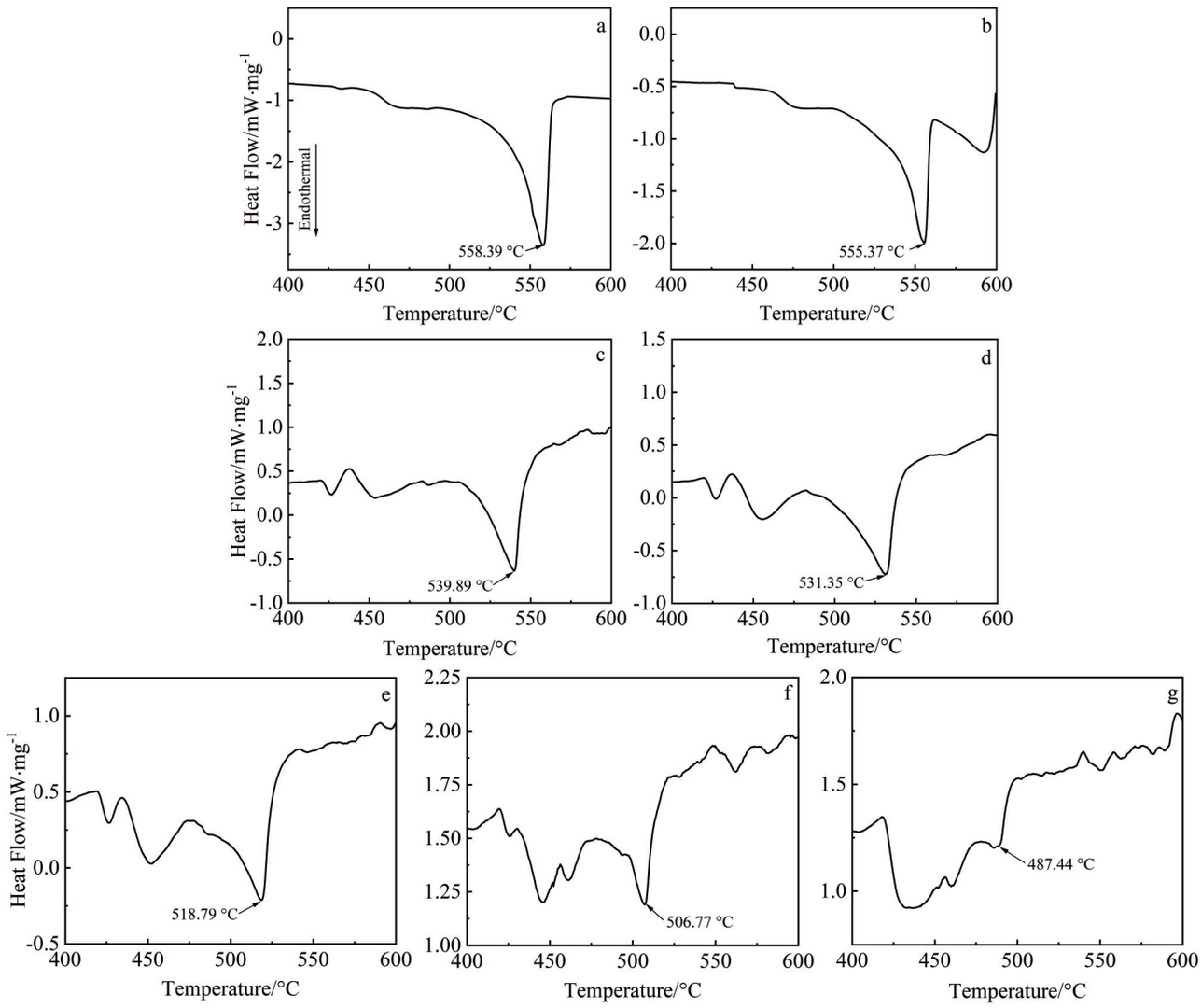

Fig.3 DSC curves of Al-*x*Si-*y*Ge filler metals: (a) Al-8Si-10Ge; (b) Al-8Si-15Ge; (c) Al-8Si-20Ge; (d) Al-8Si-25Ge; (e) Al-8Si-30Ge; (f) Al-8Si-35Ge; (g) Al-8Si-40Ge

Table 3 Liquidus temperature of Al-*x*Si-*y*Ge filler metals

Filler metal	Liquidus temperature, T_L/°C
Al-4Si-35Ge	518.50
Al-6Si-35Ge	516.79
Al-8Si-35Ge	515.07
Al-10Si-35Ge	515.22
Al-12Si-35Ge	514.25
Al-8Si-10Ge	567.65
Al-8Si-15Ge	560.95
Al-8Si-20Ge	552.02
Al-8Si-25Ge	541.06
Al-8Si-30Ge	528.36
Al-8Si-40Ge	499.96

energy G is the summation of the excessive molar free energy G^E and the ideal solution molar free energy G^I, as follows:

$$G = G^I + G^E \quad (1)$$

G^I can be expressed, as follows:

$$G^I = G^0 + \Delta G^I = x_i G_i^* + x_j G_j^* + x_k G_k^* + RT(x_i \ln x_i + x_j \ln x_j + x_k \ln x_k) \quad (2)$$

where G^0 is the standard molar free energy; ΔG^I is the increment of G^I resulting from atomic interaction; 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 can 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[21]. 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.

$$G^E = \frac{x_j}{1-x_i} G_{ij}^E(x_i, 1-x_i) + \frac{1-x_i-x_j}{1-x_i} G_{ik}^E(x_i, 1-x_i) + G_{jk}^E\left(\frac{x_j}{1-x_i}, \frac{1-x_i-x_j}{1-x_i}\right) \quad (3)$$

The excessive molar free energy of the binary system can be expressed, as follows:

$$G_{ij}^{E} = \Delta H_{ij} - T\Delta S_{m}^{E} \quad (4)$$

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.

Dybkov et al[22] proposed the relationship between ΔS_{m}^{E} and ΔH_{ij}, which can be described by Eq.(5), as follows:

$$\Delta S_{m}^{E} = \Delta H_{ij}\left(\frac{1}{T_i} + \frac{1}{T_j}\right)/14 \quad (5)$$

where T_i and T_j are the melting points of component i and j, respectively.

The excessive molar free energy of binary system can be replaced by Eq.(6), as follows:

$$G_{ij}^{E} = \Delta H_{ij}\left[1 - T\left(\frac{1}{T_i} + \frac{1}{T_j}\right)/14\right] \quad (6)$$

ΔH_{ij} can be calculated by Miedema model[23], as follows:

$$\Delta H_{ij} = f_{ij}\frac{x_i\{1+\mu_i x_j(\phi_i-\phi_j)x_j[1+\mu_j x_i(\phi_j-\phi_i)]\}}{x_i V_i^{2/3}\{1+\mu_i x_j(\phi_i-\phi_j)+x_j V_j^{2/3}[1+\mu_j x_i(\phi_j-\phi_i)]\}} \quad (7)$$

$$f_{ij} = \frac{2pV_i^{2/3}V_j^{2/3}[q/p(\Delta n_{ws}^{1/3})^2 - (\Delta\varphi)^2 - b(r/p)]}{(n_{ws}^{1/3})_i^{-1} + (n_{ws}^{1/3})_j^{-1}} \quad (8)$$

where f_{ij} represents the solution enthalpy resulting from electronegativity of elements; ϕ stands for the electronegativity; V is the molar volume; n_{ws} represents the electron density; μ is experimental constant related to element i and j; φ, q, r, b, and p are experimental constants. These parameters are reported in Ref.[24–26].

2.4 Thermodynamics analysis

Fig. 4 displays the free energy contour maps of Al-Si-Ge ternary alloy system at 25, 400, and 600 ° C. When the temperature decreases, the free energy of Al-Si-Ge alloy increases, but all free energy values are negative, indicating

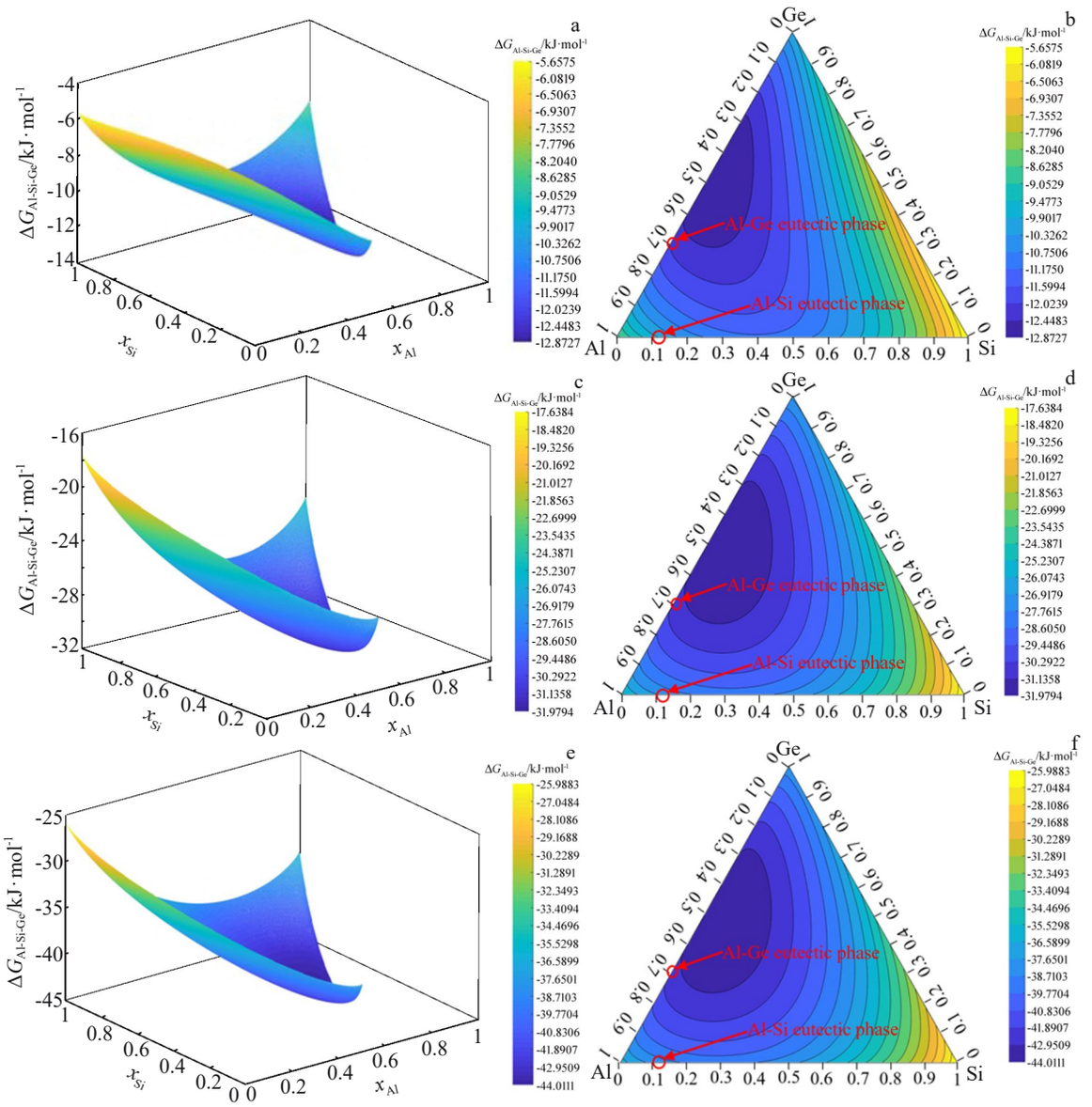

Fig.4 3D (a, c, e) and 2D (b, d, f) free energy contour maps of Al-Si-Ge ternary alloy system at different temperatures: (a–b) 25 °C; (c–d) 400 °C; (e–f) 600 °C

the existence of spontaneous reactions in the ternary alloy system. The trends of free energy change at different temperatures are similar, so the calculation results of the alloy system at 400 °C were analyzed to explain the formation mechanism of Al-Si-Ge filler metals.

Fig. 5 presents the effect of Ge addition on the free energy of Al-xSi (x=4, 8, 12, wt%) alloys. Within the appropriate composition range of filler metals, the free energy of all three alloys is decreased with the increase in Ge content, indicating that Ge addition can reduce the free energy of Al-Si binary alloy system. The lowest free energy is located on the Al-Ge side, demonstrating that Al is more inclined to undergo eutectic reaction with Ge to form Al-Ge eutectic phase. Eutectic Ge and eutectic Si in filler metals are both solid solutions. According to Table 1, it can be seen that Si content in (Ge, Si) solid solution phase of filler metals ranges from 1wt% to 60wt%. The free energy was calculated with different Si and Ge contents, and the results are shown in Fig. 6. It can be seen that with the increase in the content of SixGe(100−x), the change trends of free energy are similar: firstly decreasing and then increasing. When Ge content is 1wt%, the free energy is the highest. As Ge content increases, the free energy of the alloy decreases. When Ge content increases to 95wt%, the free energy is the lowest. When Ge content further increases to 99wt%, the free energy increases, indicating that the free energy order of Al-Si-Ge alloys is $Al_x(Si5Ge99)_{1-x}$ > $Al_x(Si1Ge99)_{1-x}$ > $Al_x(Si50Ge50)_{1-x}$ > $Al_x(Si70Ge30)_{1-x}$ > $Al_x(Si95Ge5)_{1-x}$ > $Al_x(Si99Ge1)_{1-x}$. Therefore, the Ge eutectic phase with the composition similar to pure Ge composition is the most likely to appear in the Al-Si-Ge ternary alloy system, whereas the Si eutectic phase with the composition similar to pure Si composition is the least likely to appear, which is consistent with the results in Section 2.1.

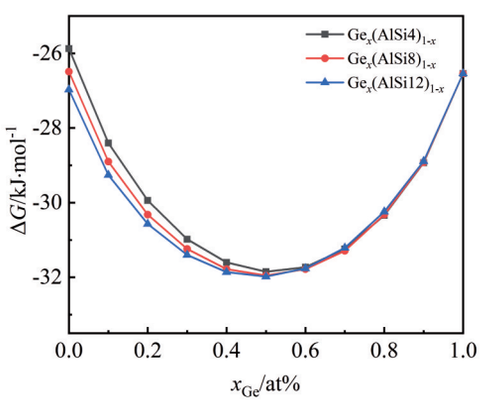

Fig.5 Influence of Ge addition on free energy of Al-Si binary system

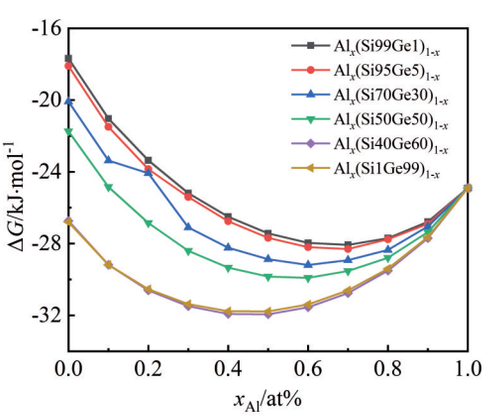

Fig.6 Influence of Si and Ge contents on free energy of Al-Si-Ge ternary system

3 Conclusions

1) Al-Si-Ge alloy is composed of Al-Ge eutectic phase, Al-Si eutectic phase, and primary Si, and the increasing Ge content promotes the precipitation of primary Si. With the increase in Ge addition amount in filler metals, Ge content in Si phase is increased. The Ge eutectic phase with the composition similar to pure Ge composition can be observed when the Si content in filler metals increases.

2) Ge is the melting point depressant element in filler metals. When Ge content increases from 10wt% to 40wt%, the solidus temperature of filler metals remains unchanged, while the liquidus temperature decreases from 567.65 °C to 499.96 °C. As Ge addition in filler metals increases, the endothermic peaks of Al-Si eutectic phase in DSC curves become smoother and the peak temperature decreases. As Si addition increases, the peak temperature of endothermic peak of Al-Ge eutectic phase remains unchanged.

3) The thermodynamic calculation results of Al-Si-Ge ternary alloy show that Ge can reduce the free energy of Al-Si binary alloy system, and the lowest free energy is located on Al-Ge side. Ge eutectic phase with the composition similar to pure Ge composition is the most likely to appear in the filler metals, whereas the Si eutectic phase with the composition similar to pure Si composition is the least likely to appear.

References

1 Ivannikov A, Abramov A, Popov N *et al*. *Metals*[J], 2023, 13: 149

2 Long Weimin, Zhao Yue, Zhong Sujuan *et al*. *Rare Metal Materials and Engineering*[J], 2021, 50(1): 7

3 Long Weimin, Lu Quanbin, He Peng *et al*. *Journal of Materials Engineering*[J], 2016, 44(6): 17

4 Fedorov V, Uhlig T, Wagner G *et al*. *Metals*[J], 2023, 13(9): 1574

5 Niu Zhiwei, Huang Jihua, Yang Hao *et al*. *Applied Mechanics and Materials*[J], 2015, 751: 61

6 Zhang Jinfeng, Cheng Jianping, Gong Yingzhou. *Vacuum*[J], 2009, 46(1): 6

7 Tian Hui. *Modern Welding*[J], 2008(4): 23 (in Chinese)

8 Xia Hobo, Zhao Xiaoye, Tan Caiwang *et al*. *Journal of Materials Processing Technology*[J], 2018, 258: 9

9 Long Weimin, Zhang Guanxing, Zhang Qingke. *Scripta Materialia*[J], 2015, 110: 41

10 Liu Shuqi, Sun Guoping, Zhang Qiyun. *Acta Metallurgica*

Sinica[J], 1982, 18(4): 451
11 Hayes F, Longbottom R, Ahmad E *et al*. *Journal of Phase Equilibria*[J], 1993, 14(4): 425
12 Murray J, McAlister A. *Bulletin of Alloy Phase Diagrams*[J], 1984, 5(1): 74
13 McAlister A, Murray J. *Bulletin of Alloy Phase Diagrams*[J], 1984, 5(4): 341
14 Olesinski R, Abbaschian G. *Bulletin of Alloy Phase Diagrams*[J], 1984, 5(2): 180
15 Song H, Hellawell A. *Metallurgical Transactions A*[J], 1990, 21(2): 733
16 Zhang Yongrui, Gao Tong, Liu Xiangfa. *Journal of Alloys & Compounds*[J], 2014, 585: 442
17 Osintsev O, Betsofen S, Konkevich V *et al*. *Russian Metallurgy*[J], 2009, 2009(3): 231
18 Gurin V, Nikanorov S, Derkachenko L *et al*. *Materials Science & Engineering A*[J], 2008, 491(1–2): 343
19 Schubert T, Loser W, Teresiak A *et al*. *Journal of Materials Science*[J], 1997, 32(8): 2181
20 Ivannikov A, Fedorov V, Abramov A *et al*. *Metals*[J], 2021, 11(12): 1926
21 Tan Caiwang, Zang Chengwei, Xia Hongbo *et al*. *Journal of Manufacturing Processes*[J], 2018, 34: 251
22 Dybkov V I. *Material Science Foundations*[J], 2010, 68: 287
23 Buschow K, Bouten P, Miedema A. *Reports on Progress in Physics*[J], 1982, 45(9): 937
24 Ding Z Y, Hu Q D, Lu W Q *et al*. *Scripta Materialia*[J], 2017, 130: 214
25 Miedema A. *Journal of Physics F: Metal Physics*[J], 1974, 4(1): 120
26 Miedema A, Gingerich K. *Journal of Physics B: Atomic & Molecular Physics*[J], 2001, 12(13): 2081

基于热力学计算的Al-Si-Ge钎料相形成机理

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摘　要：制备了不同成分的Al-*x*Si-*y*Ge三元钎料合金（*x*=4~12，*y*=10~40，质量分数），研究了Si和Ge对钎料微观结构和熔化特性的影响。基于二元合金生成焓模型（Miedema model）、熵焓模型（Tanaka model）和Toop方程建立了热力学计算模型，分析钎料的相形成机理，为钎料成分优化和分析钎料与母材的冶金反应过程提供基础。结果表明，Al-Si-Ge主要由Al-Ge共晶相、Al-Si共晶相和初晶Si组成，Ge的增加会促进初晶Si的析出。Ge为钎料的主要降熔元素，随着Ge含量从10%增加至40%，变化钎料固相线保持不变，液相线从567.65 ℃降低至499.96 ℃。随着钎料中Ge添加量的增加，共晶Si相中的Ge含量增加，热重分析曲线中Al-Si共晶反应的吸热峰变得更平滑，Al-Si共晶温度降低。添加Ge可以降低Al-Si合金体系的自由能，自由能的最低点位于Al-Ge侧。成分接近纯Ge的共晶Ge相最有可能出现在钎料中，而成分接近纯Si的共晶Si相最不可能出现。热力学计算结果与实验结果一致。

关键词：Al-Si-Ge钎料；微观组织；热力学；相形成机理

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