

Article

Enhanced Slag–Metal Separation for Preparation of Al–Si Alloys from Crystalline Silicon Cutting Waste by a CaO–Al₂O₃–CaF₂ Slag Treatment

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Abstract

Crystalline silicon cutting waste (SCW) is a promising secondary silicon resource for Al–Si alloy production, but high-melting Al₂O₃ generated during aluminothermic reduction hinders alloy droplet coalescence and slag–metal separation. In this study, a CaO–Al₂O₃–CaF₂ slag treatment strategy was developed to regulate in situ formed Al₂O₃ and improve Al–Si alloy recovery from SCW. The effects of slag composition, smelting temperature, and holding time on separation behavior, massive alloy yield, and Si recovery were investigated. Increasing CaF₂ content decreased the liquidus temperature and calculated the viscosity of the slag, thereby improving slag fluidity and promoting the migration and coalescence of Al–Si droplets. The optimal conditions were a smelting temperature of 1400 °C, a holding time of 10 min, and a slag composition of 20 wt.% Al₂O₃–20 wt.% CaO–60 wt.% CaF₂. Under these conditions, the massive alloy yield and Si recovery reached 89.32% and 83.43%, respectively. Mechanistic analysis indicated that the process involved alloying, slagging, and slag–metal separation. CaF₂ promoted the formation of a low-melting, low-viscosity liquid slag, which facilitated slag aggregation, droplet migration, and efficient slag–metal separation. This work provides a low-cost and efficient technical approach for the high-value recycling of SCW, showing potential for future industrial application.

Keywords: photovoltaic solid waste; silicon cutting waste; Al–Si alloy; CaO–Al₂O₃–CaF₂ slag; slag–metal separation; high-value recycling



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1. Introduction

At present, diamond wire slicing has become the mainstream manufacturing technology for crystalline silicon wafers [1,2]. Nevertheless, approximately 30%–35% of the bulk silicon feedstock is pulverized into fine particles during cutting and eventually forms silicon cutting waste (SCW) [3,4]. Driven by the rapid expansion of the photovoltaic (PV) sector, the annual output of SCW will keep growing sharply in the foreseeable future [5,6]. Moreover, SCW particles generally exhibit micrometer-scale sizes, leading to potential environmental concerns during storage and handling [7,8]. Therefore, it is imperative to develop efficient recycling strategies for SCW, which can not only prevent the loss of valuable silicon resources but also mitigate the environmental impacts associated with waste accumulation [9,10].

SCW mainly consists of elemental Si, amorphous SiO₂ and trace metallic impurities. Benefiting from its high silicon content, SCW is recognized as a high-value secondary silicon resource instead of ordinary industrial solid waste [11,12]. In recent years, numerous recycling approaches have been developed for SCW, which can be categorized into three branches: pyrometallurgical routes, hydrometallurgical purification, and fabrication of silicon-based functional materials. Representative pyrometallurgical technologies include induction smelting [13–15], alloying [16–19], slag refining [20–22] and directional solidification [23,24], while hydrometallurgical approaches are dominated by acid leaching for impurity removal [25–29]. As for functional material synthesis, researchers have successfully fabricated silicon carbide (SiC) [4,30], silicon nitride (Si₃N₄) [31–34], composite ceramics and lithium-ion battery anodes from SCW [35–38]. Among all existing technologies, induction smelting stands as the most mature commercialized route to extract metallurgical-grade silicon (MG-Si) from SCW. The obtained MG-Si is further adopted as the feedstock for Al-Si alloy manufacturing via a separate secondary melting procedure. However, silicon has an extremely high melting point of 1693 K, rendering standalone induction smelting highly energy-intensive.

To reduce energy consumption and simplify the recycling process, our previous study proposed a one-step Al-Si alloying route, in which SCW was directly mixed with Al powder and smelted to recover Si into Al-Si alloys [39]. The feasibility of this route was demonstrated, and Al-Si alloys were successfully obtained. However, the direct Al-Si alloying process is still restricted by the formation and distribution of Al₂O₃ during smelting. The SiO₂ layer on SCW particles reacts with Al through aluminothermic reduction, generating Si and high-melting Al₂O₃. Although the generated Si can dissolve into molten Al and contribute to Al-Si alloy formation, the in situ formed Al₂O₃ tends to remain on the surface of Al-Si alloy droplets. This Al₂O₃-rich layer hinders the contact, migration, and coalescence of alloy droplets, thereby limiting slag–metal separation and reducing the recovery efficiency of a massive Al-Si alloy. Therefore, the key challenge in the one-step preparation of Al-Si alloys from SCW is not only to promote Si dissolution into molten Al, but also to regulate the in situ generated Al₂O₃. Similar thermochemical regulation strategies have been reported to modify reaction processes and enhance resource recovery from solid wastes [40].

To address this critical limitation, a composite flux system composed of CaO and CaF₂ is proposed in this study. The two additives react with in situ generated Al₂O₃ to form low-melting, low-viscosity CaO-CaF₂-Al₂O₃ ternary molten slag throughout the alloying process. The effects of CaO addition, slag composition, smelting temperature, and holding time on alloy recovery and slag–metal separation were systematically investigated. The microstructure and phase distribution of slag-containing products were characterized to clarify the role of the slag phase in alloy droplet migration and coalescence. Based on these results, the mechanism of Al-Si alloy recovery from SCW under CaO-Al₂O₃-CaF₂ slag treatment was revealed.

2. Experimental

2.1. Materials

The SCW used in this research was supplied by Haobo Co., Ltd. in Jiangsu, China. The SCW mainly consists of Si, SiO₂, carbonaceous impurities, and minor metallic impurities. The mass fractions of Si, SiO₂, C, and metallic impurities with their oxides were 79.79 wt.%, 15.43 wt.%, 2.13 wt.%, and 2.65 wt.%, respectively. The microscopic characteristics of SCW particles were observed by SEM and TEM, as shown in Figure 1. The SCW particles exhibited a thin flake-like morphology and were highly agglomerated. The TEM image further reveals that a thin amorphous SiO₂ layer was present on the surface of crystalline

Si particles. The SCW exhibited a fine particle size distribution with a median particle size (D_{50}) of 1.34 μm , while the Al powder used in this study had a median particle size (D_{50}) of 10.95 μm .

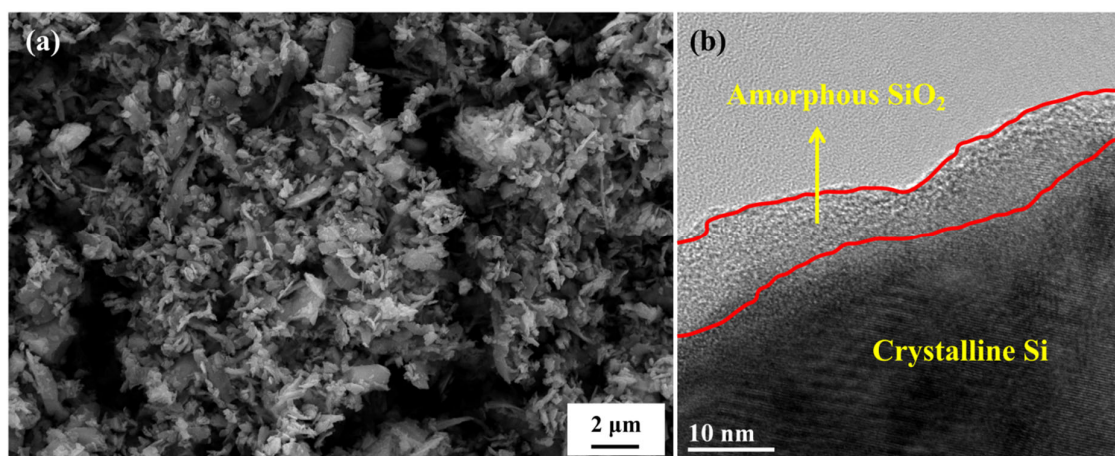


Figure 1. SEM (a) and TEM (b) images of SCW particles.

Commercial Al powder with a purity of 99.85 wt.% was purchased from the Boyu Metal Co., Ltd. in Shenyang, China. Analytical-grade CaO and CaF₂ were obtained from the Sinopharm Chemical Reagent Co., Ltd. in Shenyang, China.

Before the smelting experiments, the SCW was dried at 100 °C for 2 h to remove moisture. The dried SCW, Al powder, CaO, and CaF₂ were weighed according to the designed experimental conditions. The mass ratio of SCW to Al powder was fixed at 1:4 for all experiments. According to the reaction ($3\text{SiO}_2 + 4\text{Al} \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Si}$), 100 g of SCW containing 15.43 g SiO₂ requires only approximately 9.24 g Al for complete SiO₂ reduction. Therefore, the excess Al used in this study was not only intended for aluminothermic reduction, but also to provide sufficient molten Al for Si dissolution and Al-Si alloy formation.

2.2. Methods

The weighed raw materials were thoroughly mixed, and then charged into an alumina crucible, which was placed in the constant-temperature zone of a tube furnace. The furnace tube was sealed and purged with Ar gas to provide an inert atmosphere. The furnace was heated to the target temperature at a heating rate of 5 °C/min and held for the designed duration. After smelting, the furnace was cooled to room temperature, and the products were taken out for subsequent separation and characterization. To investigate the effects of slag composition and smelting temperature, smelting experiments were carried out using different CaO-CaF₂ additions at 1200, 1300, and 1400 °C. To further evaluate the effect of holding time, additional experiments were performed at 1400 °C for 10, 60, and 120 min.

2.3. Characterization and Calculation

After smelting, the macroscopic morphology of the products was recorded. The massive Al-Si alloy was mechanically separated from the slag-containing products and weighed. The microstructure and elemental distribution were examined using a field-emission scanning electron microscope (FE-SEM, ULTRA PLUS, Zeiss, Oberkochen, Germany) equipped with an energy-dispersive X-ray spectroscope (EDS). The chemical composition of the obtained Al-Si alloy was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Thermodynamic calculations were performed using FactSage 7.1. The Equilib module was used to calculate the melting temperatures of the designed slags. The Reaction module was applied to evaluate the Gibbs free energy changes of the proposed

reactions. The slag viscosities were calculated using the Viscosity module. The FToxid database was selected for all oxide slag-related calculations.

The smelting performance was evaluated using the massive alloy yield and Si recovery ratio. The massive alloy yield was calculated from the mass ratio of the collected massive alloy to the theoretical alloy mass:

$$Y_{alloys} = \frac{m_{alloys}}{m_0} \times 100\% \quad (1)$$

The Si recovery ratio was calculated according to the Si content in the collected alloy and the initial Si content in the SCW:

$$R_{Si} = \frac{m_{alloys} \times w_{Si,alloys}}{m_{SCW} \times w_{Si,SCW}} \times 100\% \quad (2)$$

where Y_{alloys} is the massive alloy yield, R_{Si} is the Si recovery, m_{alloys} is the mass of the collected massive alloy, m_0 is the theoretical alloy mass (calculated by considering the Si generated from SiO_2 reduction and the corresponding Al consumption), $w_{Si,alloy}$ is the Si mass fraction in the obtained alloy, m_{SCW} is the mass of SCW used in the experiment, and $w_{Si,SCW}$ is the Si mass fraction in the SCW.

3. Results and Discussion

3.1. Effect of CaO Addition and Design of CaO- Al_2O_3 -CaF₂ Slag Compositions

During the smelting of SCW with Al, the surface SiO_2 layer can be reduced by molten Al, producing Si and Al_2O_3 . The generated Si dissolves into molten Al to form Al-Si alloy droplets, whereas Al_2O_3 tends to remain around the alloy droplets. The presence of Al_2O_3 restricts the coalescence of alloy droplets because of its high melting point and poor fluidity. Therefore, CaO was first introduced as a basic slag-forming additive to react with the in situ generated Al_2O_3 and form a CaO- Al_2O_3 slag.

The CaO addition was designed according to the CaO- Al_2O_3 binary phase diagram, as shown in Figure 2. Based on the SiO_2 content in the SCW, 100 g of SCW can theoretically generate 17.49 g of Al_2O_3 when SiO_2 is completely reduced by Al. The CaO- Al_2O_3 phase diagram shows that the slag has a relatively low melting temperature when the mass fraction of CaO in the CaO- Al_2O_3 system is close to 50 wt.%. Therefore, the CaO addition was selected as 17.49 wt.% of the SCW mass to form a nominal 50 wt.% CaO-50 wt.% Al_2O_3 slag.

The macroscopic morphologies of the products obtained by smelting with and without CaO addition are compared in Figure 3. Compared with direct smelting, CaO addition reduced the amount of dispersed fine granular products and promoted the release and local coalescence of metallic droplets. The massive alloy yield increased from 70.79% without CaO addition to 79.63% with 17.49 wt.% CaO addition, confirming the beneficial effect of CaO on alloy droplet separation. Several metallic spheres were observed in the product, indicating that CaO addition partly weakened the negative effect of Al_2O_3 on alloy droplet aggregation. However, the alloy phase still existed mainly as separated spherical particles mixed with slag-containing granular products, rather than gathering into a continuous alloy pool. This indicates that CaO addition alone can improve local alloy droplet coalescence, but it is still insufficient for complete slag-metal separation.

The SEM-EDS results in Figure 4 further confirm the phase distribution of the spherical product obtained with CaO addition. The elemental mappings show that the spherical particle was mainly composed of Al and Si, demonstrating that it was an Al-Si alloy particle. In contrast, Ca and O were mainly enriched in the surrounding regions and at the particle interface, indicating the formation of Ca-Al-O slag through the reaction between CaO and Al_2O_3 . The EDS point analysis of the Ca-Al-O-rich region also confirms the presence of

calcium aluminate slag. These results suggest that CaO reacted with Al_2O_3 and formed a slag phase around the Al-Si alloy particles.

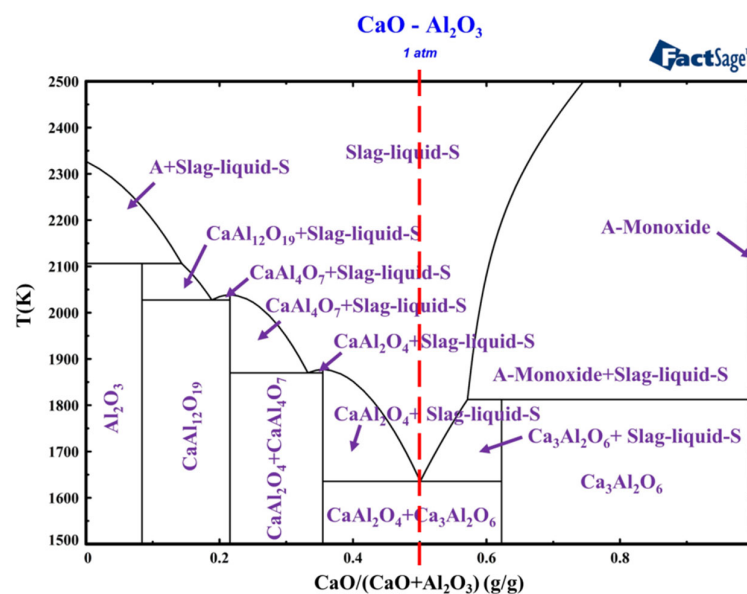


Figure 2. CaO- Al_2O_3 binary phase diagram used for determining the CaO addition.

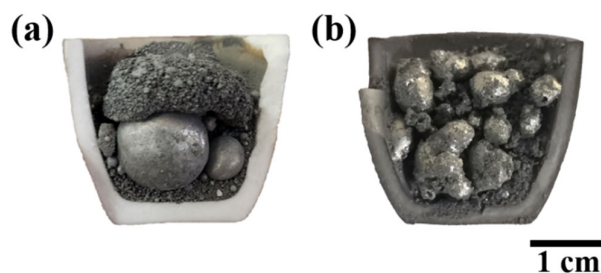


Figure 3. Macroscopic morphologies of products obtained by smelting SCW and Al at 1500 °C for 120 min: (a) without CaO addition; (b) with CaO addition.

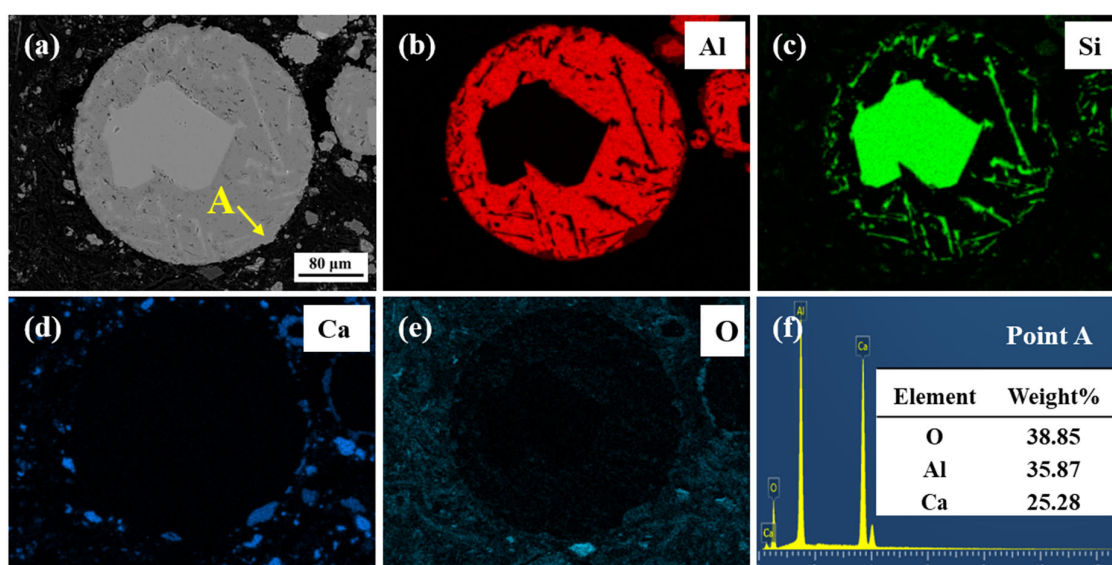


Figure 4. SEM/EDS analyzed results of the section of granular product obtained by smelting SCW and Al with CaO addition: (a) SEM micrograph; (b–e) EDS elemental mapping of Al, Si, Ca, O, respectively; (f) EDS spectrum of Point A.

Although CaO promoted the slagging of Al_2O_3 and the coalescence of Al-Si alloy droplets to some extent, the CaO- Al_2O_3 slag still exhibited limited fluidity under the smelting conditions. The relatively high viscosity of the slag hindered the continuous aggregation and shrinkage of the slag phase, so the alloy droplets could not be completely released from the slag-containing matrix. As a result, the product remained as multiple alloy spheres mixed with slag particles, and effective slag-metal separation was not achieved. These results demonstrate that CaO addition is effective in converting Al_2O_3 into calcium aluminate slag and promoting local alloy droplet coalescence, but the fluidity of the CaO- Al_2O_3 slag is still insufficient for complete alloy collection. Therefore, further slag regulation is required and CaF_2 was further introduced.

The CaO- Al_2O_3 - CaF_2 ternary phase diagram was used to determine the slag compositions. As shown in Figure 5, the low-liquidus-temperature region is located near the line where the mass ratio of CaO to Al_2O_3 is 1. Therefore, three slag compositions were selected along this region and denoted as points A, B, and C. Their compositions and melting temperatures are listed in Table 1. It should be noted that the slag compositions represent the nominal compositions of the final slag phase, which were calculated based on the in situ generated Al_2O_3 from SCW and the externally added CaO and CaF_2 . The actual amounts of slagging agents were determined according to the theoretical Al_2O_3 generation during the aluminothermic reduction of SiO_2 . With increasing CaF_2 content from point A to point C, the liquidus temperature decreased from 1503 to 1374 °C. Meanwhile, the calculated slag viscosities showed a continuous decrease with increasing temperature, as shown in Figure 6. At 1400 °C, the viscosities of slag A, B, and C were 0.148, 0.061, and 0.032 Pa·s, respectively. These results indicate that CaF_2 addition not only decreases the melting temperature of the slag but also improves its fluidity, which is beneficial for slag aggregation and subsequent slag-metal separation. These three CaO- Al_2O_3 - CaF_2 slag compositions were used in the following experiments to clarify the effect of CaF_2 content on slag formation, alloy droplet coalescence, and slag-metal separation.

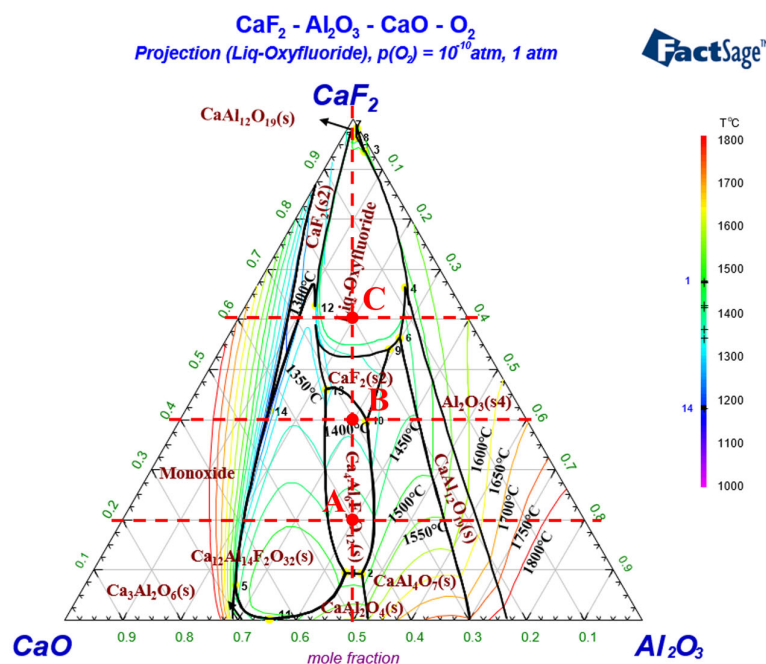
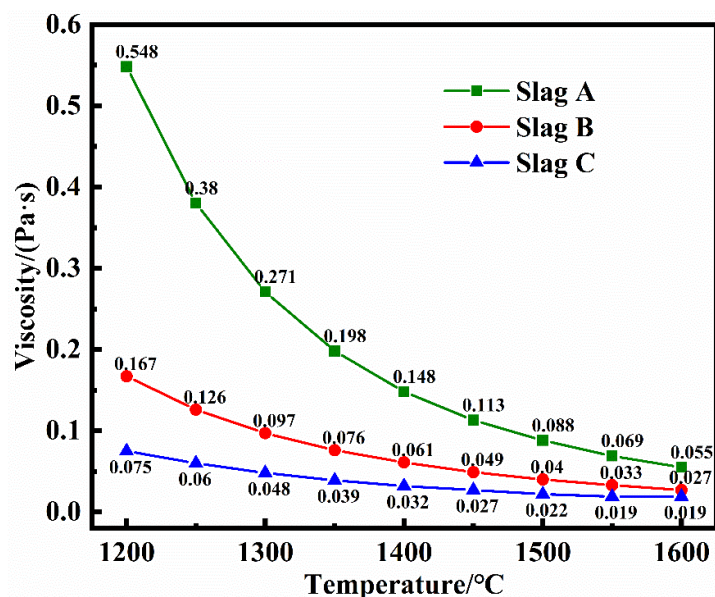


Figure 5. Phase diagram of the CaO- Al_2O_3 - CaF_2 ternary slag system and selected slag compositions.

Table 1. Designed compositions and melting temperatures of CaO-Al₂O₃-CaF₂ slags.

Point	Al ₂ O ₃ /wt. %	CaO/wt. %	CaF ₂ /wt. %	Solidus Temperature/°C	Liquidus Temperature/°C
A	40	40	20	1197	1503
B	30	30	40	1197	1395
C	20	20	60	1197	1374

**Figure 6.** Calculated viscosity variations of designed CaO-Al₂O₃-CaF₂ slags at different temperatures.

3.2. Effect of Slag Composition and Smelting Temperature on Al-Si Alloy Recovery

The effects of slag composition and smelting temperature on Al-Si alloy recovery were investigated using the three designed CaO-Al₂O₃-CaF₂ slag compositions. The smelting temperature was varied from 1200 to 1400 °C with the holding time fixed at 120 min, while the slag composition was changed from point A to point C. The macroscopic morphologies of the products obtained under different conditions are shown in Figure 7.

**Figure 7.** Macroscopic morphologies of products obtained at different smelting temperatures and CaO-Al₂O₃-CaF₂ slag compositions.

At 1200 and 1300 °C, the products were mainly composed of granular products and massive alloy particles, indicating incomplete slag–metal separation. In these cases, the alloy droplets were not sufficiently released from the slag-containing phase, and only part of them coalesced into massive alloy. When the smelting temperature was increased to 1400 °C, the morphology of the smelting products changed significantly. The Al–Si alloy gathered at the bottom of the crucible and formed a crescent-shaped alloy pool, while the slag phase, together with a small amount of entrapped alloy, aggregated into a relatively dense cylindrical block on one side of the alloy. This clear spatial separation between the alloy pool and slag-containing phase indicates that effective slag–metal separation was achieved at 1400 °C.

The massive alloy yield was used to quantitatively evaluate the recovery behavior, as shown in Figure 8a. For a fixed slag composition, the massive alloy yield increased with increasing smelting temperature. When the temperature increased from 1200 to 1400 °C, the massive alloy yields for slag compositions A, B, and C increased from 69.17%, 61.97%, and 53.92% to 77.09%, 84.63%, and 91.92%, respectively. The elevated temperature facilitates the formation of a low-viscosity liquid slag phase, thereby improving slag fluidity and promoting the migration and coalescence of Al–Si alloy droplets.

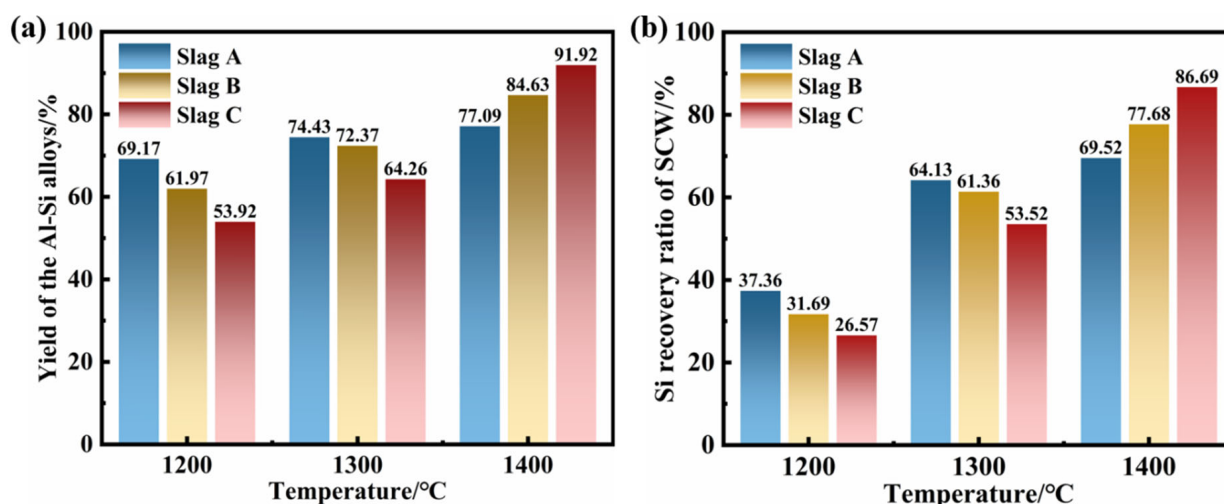


Figure 8. Effects of slag composition and smelting temperature on (a) massive alloy yield and (b) Si recovery ratio.

The effect of slag composition exhibited different trends at different temperatures. At 1200 and 1300 °C, the massive alloy yield decreased with increasing CaF_2 content from point A to point C. This can be attributed to the larger total amount of slag-forming additives introduced at higher CaF_2 contents. At relatively low temperatures, the slag was not completely melted, and the remaining solid slag-forming components could hinder the movement and coalescence of alloy droplets. Therefore, increasing CaF_2 content did not improve the alloy recovery under insufficient smelting temperature. In contrast, at 1400 °C, the massive alloy yield increased markedly with increasing CaF_2 content. Among the three slag compositions, point C, corresponding to 20 wt.% Al_2O_3 –20 wt.% CaO –60 wt.% CaF_2 , exhibited the best recovery performance, with a massive alloy yield of 91.92%. This improvement is closely related to the lower liquidus temperature and lower viscosity of the CaF_2 -rich slag. As shown in Figure 6, the calculated viscosity at 1400 °C decreased from 0.148 Pa·s for slag A to 0.032 Pa·s for slag C with increasing CaF_2 content. The lower viscosity allowed the liquid slag to flow, aggregate, and shrink more readily, thereby promoting the migration and coalescence of Al–Si droplets.

Based on the Si contents of the obtained alloys listed in Table 2 and the corresponding massive alloy yields, the Si recovery ratios were calculated, as shown in Figure 8b. The Si recovery ratio showed a similar tendency. At 1200 °C, the Si recovery ratios for slag compositions A, B, and C were only 37.36%, 31.69%, and 26.57%, respectively. When the temperature increased to 1300 °C, the Si recoveries increased to 64.13%, 61.36%, and 53.52%, respectively. At 1400 °C, the Si recovery further increased, reaching 69.52%, 77.68%, and 86.69% for slag compositions A, B, and C, respectively. The highest Si recovery ratio obtained with slag composition C at 1400 °C further demonstrates that a CaF₂-rich CaO-Al₂O₃-CaF₂ slag is favorable for recovering Si into the Al-Si alloy phase when sufficient thermal energy is supplied. Based on the above results, slag composition C and a smelting temperature of 1400 °C were selected as the preferred conditions for subsequent experiments.

Table 2. Si content of the alloys obtained at different smelting temperatures and compositions of slag (%).

Temperature/°C	Composition A	Composition B	Composition C
1200	9.02	8.54	8.23
1300	14.39	14.16	13.91
1400	15.06	15.33	15.75

3.3. The Influence of Holding Time on Al-Si Alloy Recovery

The effect of holding time on Al-Si alloy recovery was further investigated. The smelting experiments were carried out at 1400 °C for 10, 60, and 120 min using the three designed CaO-Al₂O₃-CaF₂ slag compositions. The variation in massive alloy yield with holding time is shown in Figure 9.

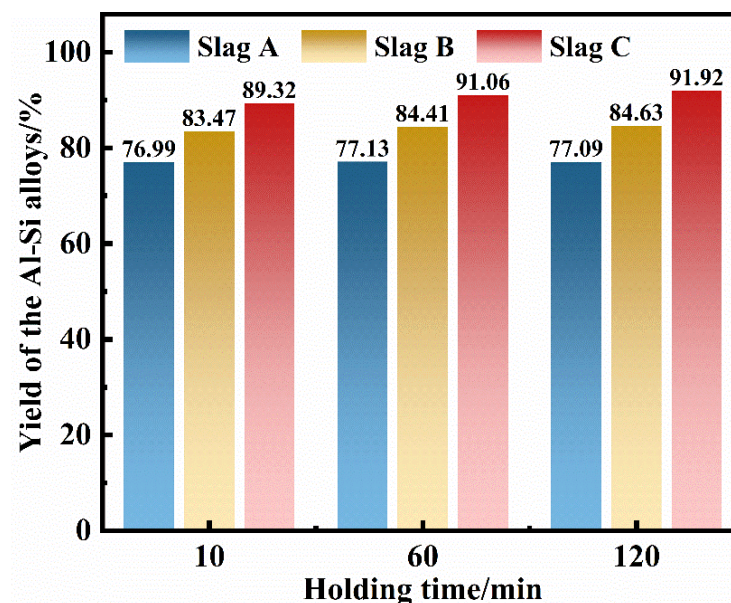


Figure 9. Effect of holding time on the massive alloy yield at 1400 °C.

For all slag compositions, the massive alloy yield increased slightly with increasing holding time. When the holding time was extended from 10 to 120 min, the massive alloy yields for slag compositions A, B, and C increased from 76.99%, 83.47%, and 89.32% to 77.09%, 84.63%, and 91.92%, respectively. This indicates that slag-metal separation continued during the holding process. With prolonged holding time, the liquid slag and Al-Si alloy droplets had more time to migrate, aggregate, and separate, leading to a gradual increase in the amount of collected massive alloy. However, the increase in massive alloy

yield was limited when the holding time was prolonged. For slag composition C, the massive alloy yield increased by only 2.60 percentage points when the holding time was extended from 10 to 120 min. This result suggests that the slag–metal separation process proceeded rapidly in the CaF_2 -rich $\text{CaO-Al}_2\text{O}_3\text{-CaF}_2$ slag system. A relatively complete separation between the liquid slag and Al-Si alloy could already be achieved within 10 min at 1400 °C.

Among the three slag compositions, slag composition C consistently showed the highest massive alloy yield at each holding time. This further confirms that the CaF_2 -rich slag was more favorable for alloy droplet coalescence and slag–metal separation. The improved separation behavior can be attributed to the lower melting temperature and better fluidity of slag, which facilitated the migration and aggregation of Al-Si droplets during smelting. Considering both recovery efficiency and processing economy, the optimal conditions were identified as a smelting temperature of 1400 °C, a holding time of 10 min, and a slag composition of 20 wt.% Al_2O_3 -20 wt.% CaO -60 wt.% CaF_2 . Under these conditions, the massive alloy yield reached 89.32%, and the Si recovery reached 83.43%. And the chemical composition of the obtained Al-Si alloy under the optimal conditions was further analyzed by ICP-AES, as summarized in Table 3. The alloy product mainly consisted of Al and Si, with a Si content of 15.68 wt.%. In addition, minor amounts of impurity elements were detected, including Fe (0.457 wt.%), Ca (1.14 wt.%), Mn (0.002 wt.%), and Mg (0.003 wt.%). The presence of Ca in the alloy product was mainly attributed to the use of Ca-based fluxes, and the residual Ca was likely introduced through minor entrainment of Ca-containing slag during slag–metal separation.

Table 3. Chemical composition of the Al-Si alloy obtained under optimal conditions (wt.%).

Element	Si	Fe	Ca	Mn	Mg	Al
Content (wt.%)	15.68	0.457	1.14	0.002	0.003	Bal.

3.4. Microstructural Evidence for Slag Formation and Alloy Droplet Separation

To further clarify the slag formation and alloy droplet separation behavior, the microstructures and elemental distributions of the slag-containing products were analyzed by SEM-EDS. Since slag composition C exhibited the best recovery performance in the above experiments, the products obtained with slag composition C were selected for detailed microstructural observation. Figure 10 and Table 4 show the SEM-EDS results of the slag-containing products obtained with slag composition C at 1200 and 1300 °C.

At 1200 °C, the products mainly consisted of spherical Al-Si alloy droplets with small slag-related protrusions attached to their surfaces. The smooth regions were rich in Al and Si, while the protrusions contained Al, O, Ca, and F, indicating that alloying and initial slagging reactions had occurred. However, the slag phase was discontinuously distributed on the droplet surface, and the alloy droplets remained isolated.

When the smelting temperature increased to 1300 °C, the granular products still showed a mixed morphology of spherical and irregular particles. The surface of the irregular particles was covered with slag-related protrusions, while Al-Si alloy regions were also observed. Compared with the products obtained at 1200 °C, the slagging reaction was more pronounced at 1300 °C, but the slag phase still remained attached to the alloy droplets. This suggests that the slag was not sufficiently fluid to aggregate and separate from the alloy phase at 1300 °C.

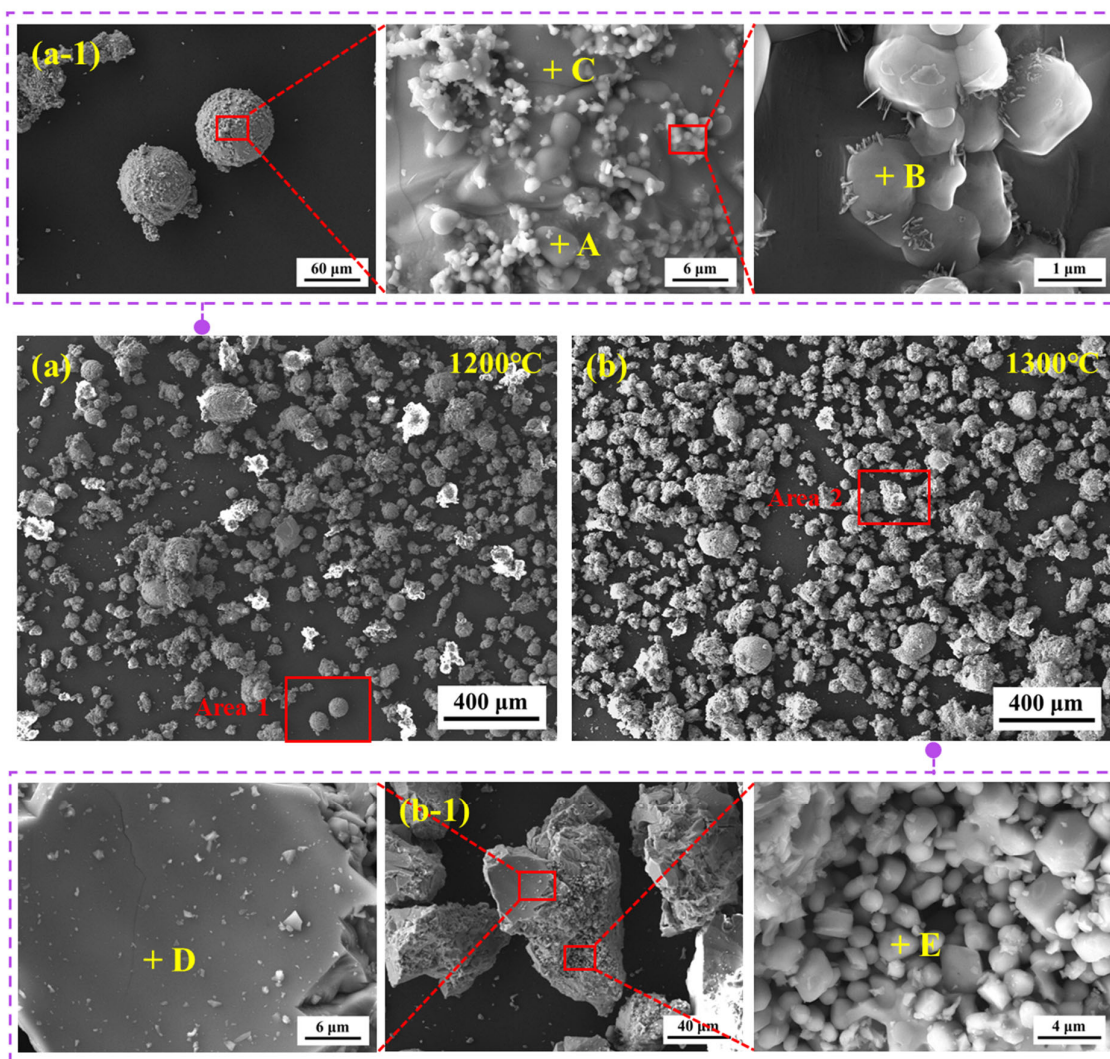


Figure 10. SEM analyzed results of granular products obtained at 1200 and 1300 °C with slag composition C: (a) SEM image of product obtained at 1200 °C; (a-1) magnified view of Area 1 in (a); (b) SEM image of product obtained at 1300 °C; (b-1) magnified view of Area 2 in (b).

Table 4. Elemental compositions of different regions in the granular product.

Element	Elemental Compositions/%				
	Point A	Point B	Point C	Point D	Point E
Al	34.71	33.57	37.66	25.90	31.2
Si	0.73	5.06	34.01	--	0.1
O	52.62	42.64	2.48	40.98	39.4
Ca	11.94	17.67	25.84	23.39	28.7
F	--	1.06	--	9.73	0.6

When the temperature increased to 1400 °C, the product morphology changed significantly. Instead of dispersed particles, the slag-containing phase aggregated into a dense cylindrical block, which was spatially separated from the crescent-shaped massive Al-Si alloy. As shown in Figure 11, the cylindrical product mainly consisted of a continuous matrix with a small number of embedded spherical particles and Si-rich regions. EDS analysis results shown in Table 5 indicated that the continuous matrix was mainly composed of Al, O, Ca, and F, confirming the formation of a CaO-Al₂O₃-CaF₂ slag phase. The embedded spherical particles were rich in Al and Si, corresponding to residual Al-Si alloy

droplets trapped in the slag. In addition, a few Si-rich regions were detected, which may be attributed to incompletely alloyed SCW particles that were isolated by the slag phase during smelting. These microstructural features indicate that, at 1400 °C, the slag phase became sufficiently fluid to aggregate into a continuous slag body, allowing most Al-Si droplets to migrate out of the slag phase and coalesce into the massive alloy pool. Only a small amount of alloy remained entrapped in the slag.

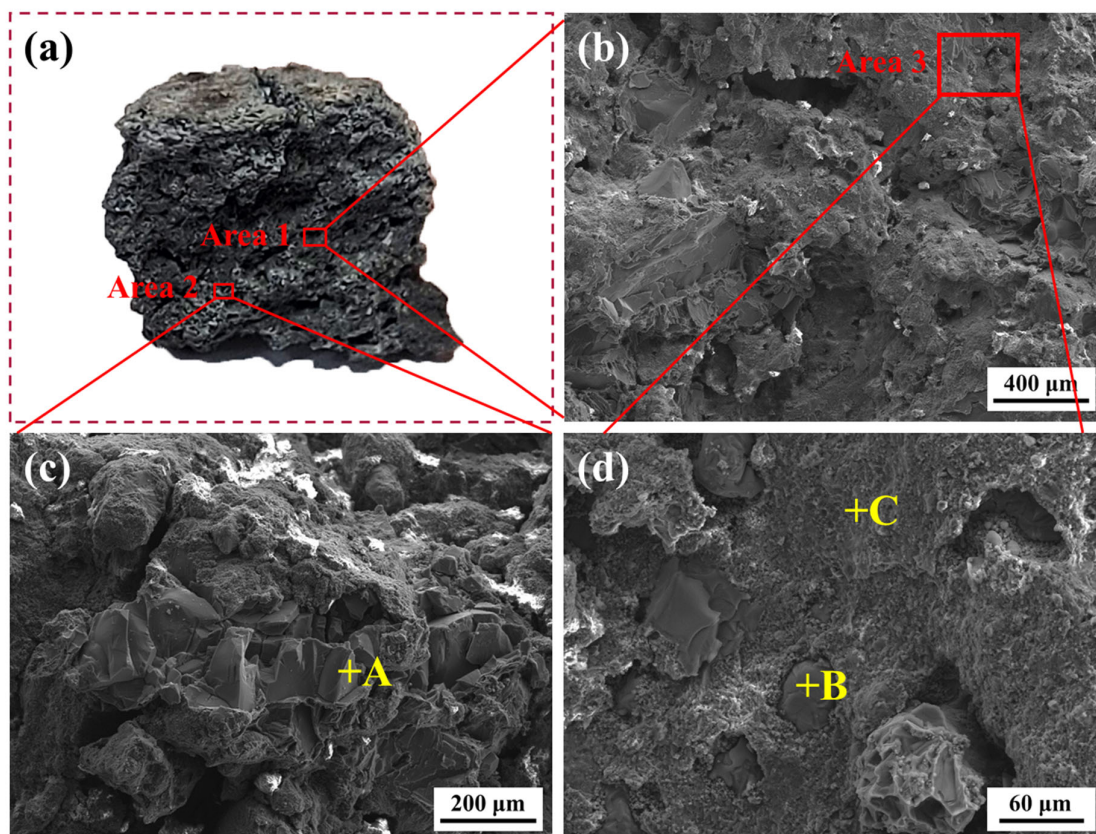


Figure 11. SEM analyzed results of the cylindrical slag-containing product obtained at 1400 °C with slag composition C: (a) Macroscopic morphology of the product; (b) magnified view of Area 1; (c) magnified view of Area 2; (d) magnified view of Area 3.

Table 5. Elemental compositions of different regions in the cylindrical product obtained at 1400 °C.

Element	Elemental Compositions/%		
	Point A	Point B	Point C
Al	3.75	54.42	26.3
Si	96.25	41.05	2.6
O	--	4.53	35.9
Ca	--	--	23.8
F	--	--	11.4

3.5. Mechanism of Al-Si Alloying Process from SCW Under the Action of CaO-Al₂O₃-CaF₂ Slag

To further clarify the smelting process and separation mechanism during the Al-Si alloying process from SCW, interrupted experiments were carried out under slag composition C, and the material states during the heating stage were sampled at 1320, 1330, 1340, and 1350 °C. The corresponding macroscopic morphologies and schematic illustrations are presented in Figure 12. As shown in Figure 12, when the temperature reached 1320 °C, the product was mainly composed of grey granular materials, in which only a few Al-Si alloy spheres were locally observed. At this stage, the newly formed alloy was still completely

mixed with the slag-containing phase, indicating that the alloying reaction had occurred, whereas no obvious slag–metal separation had yet taken place. When the temperature increased to 1330 °C, the number of Al–Si alloy spheres in the product increased significantly, suggesting that the alloy droplets gradually coalesced and local slag–metal separation began to occur. However, the alloy droplets were still largely dispersed in the slag-containing matrix. With a further increase in temperature to 1340 °C, the granular products became bonded together and the overall volume of the material shrank markedly, forming a relatively dense and hard cylindrical block. Meanwhile, several large Al–Si alloy spheres appeared on the surface of the block. This morphology indicates that a liquid slag phase had formed and started to aggregate, thereby promoting the extrusion of alloy droplets from the slag-containing matrix. When the temperature reached 1350 °C, the cylindrical block became even denser and more compact, while the alloy phase accumulated around it. This result demonstrates that the liquid slag continued to aggregate and contract, causing the surrounding Al–Si alloy to overflow from the slag network and further coalesce into an alloy pool.

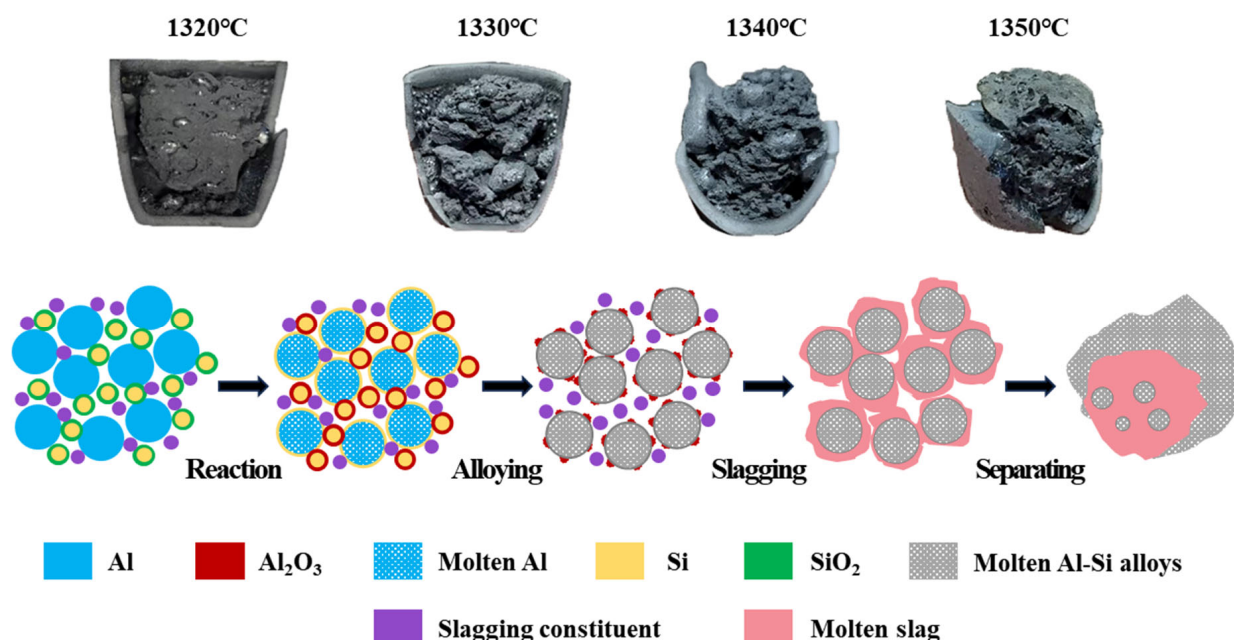


Figure 12. Macroscopic evolution and schematic illustration of the slag–metal separation process during the alloying process.

The above observations indicate that the formation and evolution of the slag phase play a crucial role in determining the final slag–metal separation behavior. During the alloying process, the surface SiO₂ layer on SCW particles was reduced to generated Al₂O₃. Therefore, the subsequent transformation of the generated Al₂O₃ into a fluid slag phase is essential for overcoming the separation barrier. The thermodynamic feasibility of the reactions between Al₂O₃ and CaO was evaluated by calculating the Gibbs free energy changes of calcium aluminate formation reactions (Equations (3) and (4)), as shown in Figure 13.



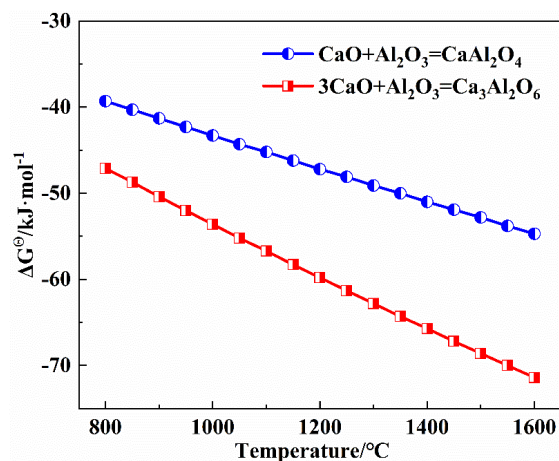


Figure 13. Thermodynamic analysis of calcium aluminate formation through reactions between CaO and Al₂O₃.

It can be observed that the calculated ΔG° values of both reactions remained negative over the investigated temperature range, indicating that the formation of calcium aluminate phases was thermodynamically favorable during the smelting process. Although CaO addition promoted the conversion of Al₂O₃ into calcium aluminate slag, the CaO-Al₂O₃ slag still exhibited relatively limited fluidity under the smelting conditions. The high viscosity of the slag restricted continuous aggregation and shrinkage of the slag phase, resulting in incomplete release of Al-Si alloy droplets from the slag-containing matrix. Therefore, CaF₂ was introduced to further regulate the slag properties. The decrease in slag viscosity induced by CaF₂ can be further understood from the structural modification of the aluminate melt. In the CaO-Al₂O₃ slag system, Al₂O₃ mainly acts as a network-forming component, and the polymerized aluminate structural units contribute to the high viscosity of the slag. According to previous studies, F⁻ ions can participate in the coordination environment of Al³⁺ and modify the local aluminate structure through the formation of Al-F-containing structural units, such as [AlO₃F] units [41,42]. This structural modification decreases the connectivity and polymerization degree of the aluminate network, thereby reducing slag viscosity and improving slag fluidity.

Based on the above observations, the recovery process under the action of the CaO-CaF₂ slag-forming agents can be divided into three consecutive stages, namely alloying, slagging, and slag-metal separation. During the alloying stage, SCW particles reacted with molten Al, where the SiO₂ layer on the particle surface was reduced by Al to generate Si and Al₂O₃. The generated Si dissolved into molten Al to form Al-Si alloy droplets, while Al₂O₃ accumulated around the droplet surface. During the slagging stage, the generated Al₂O₃ reacted with CaO-containing slag components and was incorporated into the CaO-Al₂O₃-CaF₂ slag phase. Meanwhile, CaF₂ modified the aluminate melt structure, reduced slag polymerization, and improved slag fluidity. During the final slag-metal separation stage, the low-viscosity liquid slag continuously aggregated and contracted, forcing Al-Si alloy droplets to migrate out of the slag network and coalesce into a continuous alloy pool. Consequently, the combined effects of Al₂O₃ slagging by CaO and structural regulation by CaF₂ enabled efficient slag-metal separation and high-value recovery of Al-Si alloys from SCW.

4. Conclusions

In this study, a CaO-Al₂O₃-CaF₂ slag regulation strategy was proposed to enhance the recovery of Al-Si alloy from crystalline silicon cutting waste. The main conclusions are as follows:

- (1) CaO addition promoted the conversion of in situ formed Al_2O_3 into calcium aluminate slag and improved the coalescence of Al-Si alloy droplets. However, the alloy still existed mainly as separated spherical particles, indicating that CaO- Al_2O_3 slag alone was insufficient for complete slag-metal separation.
- (2) Introducing CaF_2 into the CaO- Al_2O_3 slag system significantly improved slag-metal separation. The optimal conditions were a slag composition of 20 wt.% Al_2O_3 -20 wt.% CaO-60 wt.% CaF_2 , a smelting temperature of 1400 °C, and a holding time of 10 min. Under these conditions, the massive alloy yield reached 89.32% and the Si recovery reached 83.43%.
- (3) The smelting process mainly involved alloying, slagging, and slag-metal separation. CaF_2 promoted the formation of a low-melting and low-viscosity liquid slag, which enhanced slag aggregation and enabled Al-Si droplets to migrate out of the slag network and coalesce into an alloy pool.

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