

Preparation of primary Al-Si alloy from bauxite tailings by carbothermal reduction process

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Abstract: Effects of various reaction parameters such as atmospheric pressure, treating temperature, sintering time and bituminite content on the preparation of primary Al-Si alloy by carbothermal reduction of bauxite tailings were investigated by XRD, XRF, infrared absorption carbon-sulfur analysis unit and SEM coupled with EDS. Meanwhile, the mechanism of carbothermal reduction of Al_2O_3 and SiO_2 was discussed. It is found that pressure and temperature are major factors that influence the carbothermal reduction of bauxite tailings. The appropriate conditions for preparation of primary Al-Si alloy are as follows: atmospheric pressure of 0.1 MPa, heating temperature of 1 900 °C, bituminite content of 95% (mass fraction) of theoretic bituminite content and sintering time of 1 h. Among four mechanisms of carbothermal reduction of Al_2O_3 and SiO_2 , the theory of the formation and decomposition of carbides might be the best one to interpret the reaction process.

Key words: primary Al-Si alloy; bauxite tailings; carbothermal reduction process; reduction mechanism

1 Introduction

Al-Si alloy has been widely used in many fields such as automotive, aerospace and military industries, owing to its excellent castability, weldability, thermal conductivity and corrosion resistance[1–3]. Furthermore, according to Ref.[4], of all the Al-based alloys, the consumption of Al-Si alloy is the largest. At present, production of Al-Si alloy includes mainly fusion and carbothermal reduction methods. Compared with fusion method, carbothermal reduction method owns lots of merits such as more simple process, lower price equipments, higher energy usage ratio, and lower requirement of raw materials[5]. Bauxite tailing, generated during the flotation-Bayer process, is a kind of waste product. At present, most of them are deposited on land surface, which not only occupies mass land but also pollutes environments[6]. On the other hand, the bauxite tailings, whose Al/Si(A/S) ratio is about 1.5, is a kind of secondary resources[7]. Therefore, preparation of Al-Si alloy by carbothermal reduction of bauxite tailings is both environmentally necessary and economically feasible.

In recent years, much attention has been paid to

using bauxite tailings to produce refractory, building and luminescent materials[8–11]. There are less literatures, however, published on the application of them in preparation of primary Al-Si alloy. Therefore, in this study, effects of reaction parameters on carbothermal reduction of bauxite tailings to prepare primary Al-Si alloy, which was used as deoxidant in steel-making process or to make cast Al-Si alloy, were investigated. Meanwhile, the mechanism of carbothermal reduction of Al_2O_3 and SiO_2 was discussed.

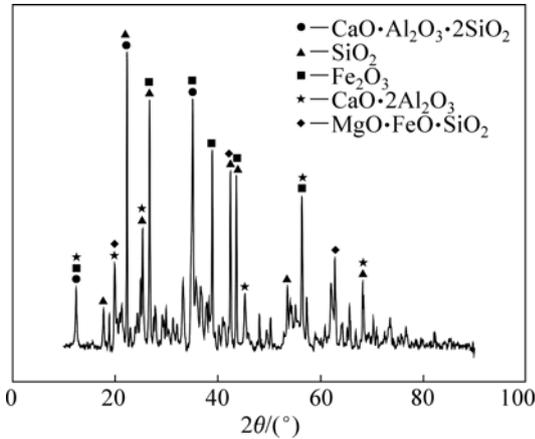
2 Experimental

2.1 Materials

In the present work, the floated bauxite tailings (Zhengzhou, Henan Province, China) and industrial grade alumina were chosen as raw materials. Table 1 gives a chemical composition of tailings, while Fig.1 shows its X-ray diffraction pattern. It is observed that this mineral was well crystallized, and Al_2O_3 , SiO_2 and Fe_2O_3 constituted the major components in the mineral. The quality bituminite (Shenfu, Shannxi Province, China) and sulphite pulp liquor were used as reductive agent and binder, respectively.

Table 1 Chemical composition of bauxite tailings (mass fraction, %)

Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO	MgO	K ₂ O	Others
43.8	26.33	10.52	3.08	2.8	0.42	0.14	12.91

**Fig.1** XRD pattern of bauxite tailings

2.2 Pelleting and heating treatment

The predetermined amounts of the above-mentioned materials were mixed uniformly and pressed into pellets of 20 mm in diameter and 25–30 mm in height under 22.5 MPa. Then, the pellets were dried in bake oven at 120 °C for 8 h to remove the moisture completely. After that, the green pellets were loaded into graphite crucible and heated in a vacuum graphite furnace with argon as the protective atmosphere to temperatures of 1 600–2 000 °C and then soaked for 0.5–1.5 h. The heating rate was 20 °C/min from room temperature to 1 200 °C and 5 °C/min from 1 200 °C to 2 000 °C.

2.3 Analysis methods

The phase composition of the reaction products obtained was carried out by D/max-rB X-ray diffractometer (XRD). The microstructural study and energy dispersive analysis of X-ray (EDS) were performed by SSX-550 scanning electron microscope (SEM). Considering that Si plays an important role in the study and it is susceptible to oxidation, the reaction products were not subjected to decarburization in the XRD and SEM tests. XRF (100-E) and infrared absorption carbon-sulfur analysis unit (CS-244) were used to examine the reduction rate of Al₂O₃ and yield of SiC. The reaction products to be measured were washed with dilute hydrochloric acid to remove interfering materials such as metallic Al and aluminium carbide, and oxidized at 800 °C for 5 h in air to remove excess carbon.

3 Results and discussion

3.1 Effects of reaction parameters on carbothermal reduction process

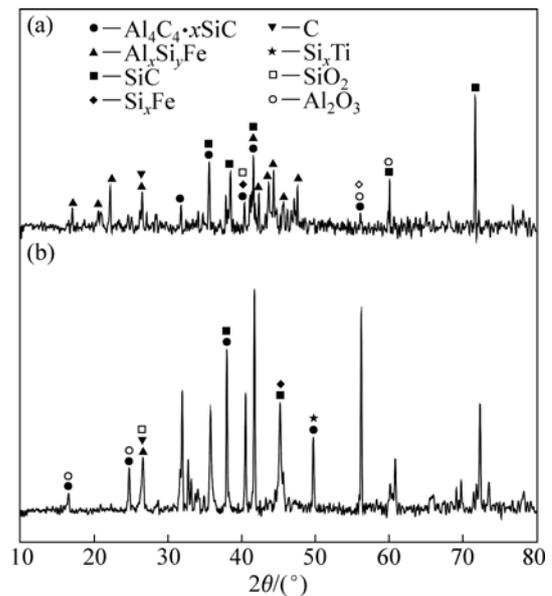
3.1.1 Effect of atmospheric pressure

In order to study the effect of atmospheric pressure on the carbothermal reduction of tailings, two reaction systems were designed. System 1 consisted of a graphite crucible without a lip. When the soaking temperature was achieved, the external atmospheric pressure was 0.03 MPa. System 2 consisted of a graphite crucible with a lip, and in the centre of the lip there were small holes for the pellets to communicate and equilibrate with the outside atmosphere at high temperature, and to keep the vapor products from escaping quickly. When the reaction proceeded, the external atmosphere was 0.1 MPa.

Figs.2(a) and (b) show the XRD patterns of the reacted products at 1 900 °C for 1 h through systems 1 and 2, respectively. It is observed that the phases constitute of System 1 is different distinctly from that of System 2. With the System 1, the products were Al₄C₃ and SiC, and the Al-Si-Fe alloy only accounted for marginal content; while with the System 2, the products composed mainly of Al-Si-Fe alloy, Al₄C₃ and SiC. These differences might be ascribed to the following reactions [11]:



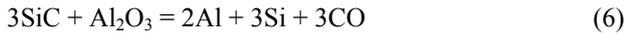
As can be seen in Eqs.(1) and (2), the gaseous products under low atmospheric pressure would push the reaction to move right constantly, resulting in the Si and Al loss. So, this indicates that low pressure is not good for the preparation of Al-Si alloy although it is favored in the case of thermodynamics view[12].

**Fig.2** XRD pattern of products by systems 1 (a) and 2 (b)

3.1.2 Effect of heating temperature

Fig.3 gives the XRD patterns of the products

prepared from bauxite tailings at 1 600, 1 700, 1 800, 1 900 and 2 000 °C, respectively. It is observed that the heating temperature has great effect on the phase composition of the products. Al₂O₃, SiO₂ and CaO were the major phase components when the treating temperature was 1 600 °C; and partial SiO₂ began to convert to SiC. When the temperature rose to 1 700 °C, there appeared peaks indexed as Al₄C₃·xSiC. According to the reaction: 2Al₂O₃+9C=Al₄C₃+6CO, the ΔG⁰, standard Gibbs free energy changes, turning to negative value at 1 991 °C, which was much higher than that at 1 700 °C. The main reason laid in the thermodynamic analysis on the assumption that all the pressure of gas phase was 0.1 MPa, while the actual pressure of CO was very low in the treating temperature. Meanwhile, with the temperature rising, the peaks of Al₄C₃·xSiC became weak, which may be due to the following reactions:



When being treated at 1 900 °C, the products obtained were composed mainly of Al-Si-Fe alloy (primary Al-Si alloy) and carbides. With the reaction temperature further rising, the change of components of reaction products was not pronounced. Thus, it is concluded that, for preparation of primary Al-Si alloy by carbothermal reduction of bauxite tailings, the optimal temperature is 1 900 °C. Furthermore, it is noteworthy that, from 1 600 °C to 2 000 °C, SiC always exists in the

products owing to the fact that it is prone to form and is difficult to decompose, which enhances the difficulties of preparation of primary Al-Si alloy by carbothermal reduction significantly.

3.1.3 Effects of soaking time and bituminite content

The reduction rate of Al₂O₃ (mass ratio of reacted Al₂O₃ to total Al₂O₃) and the yield of SiC (mass ratio of Si ion in SiC to Si ion in total SiO₂) are the important indexes of carbothermal reduction process of tailings. The high reduction rate of Al₂O₃ means the high recovery rate of metal and the reduction reaction proceeding relatively completely; while the high yield of SiC does not favor the preparation of primary Al-Si alloy, owing to too much SiC content leading to the hearth of electric arc rising up, and even the production breaking off[13].

Table 2 shows the reduction rate of Al₂O₃ and yield of SiC with soaking time of 0.5, 1 and 1.5 h. With prolonging soaking time, the reduction rate of Al₂O₃ increased, but the increasing ratio was not pronounced. On the other hand, the SiC content decreased constantly, meaning that SiC was decomposed. And when the soaking time exceeds 1 h, the decreasing ratio became small. Based on these, it is concluded that too long soaking time is not necessary, and 1 h is appropriate.

Table 2 Effect of soaking time on reduction rate of Al₂O₃ and yield of SiC

Soaking time/h	Reduction rate of Al ₂ O ₃ /%	Yield of SiC/%
0.5	70.70	66.7
1	72.52	56.5
1.5	73.54	52.3

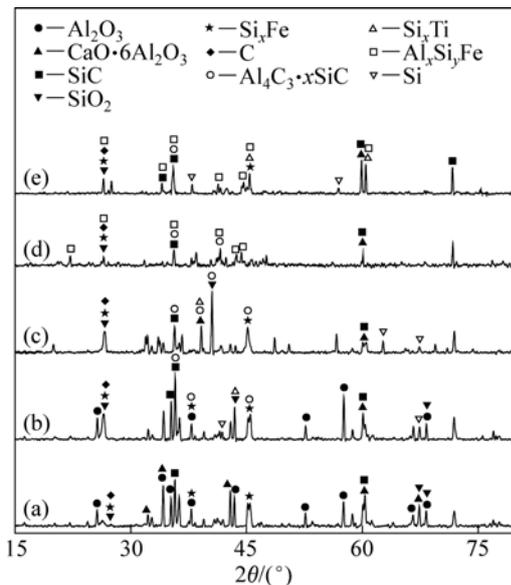


Fig.3 XRD patterns of products prepared from bauxite tailings at various temperature: (a) 1 600 °C; (b) 1 700 °C; (c) 1 800 °C; (d) 1 900 °C; (e) 2 000 °C

Fig.4 shows the effect of the different relative content of bituminite (the percentage of bituminite content of theoretic one) on the reduction rate of Al₂O₃ and yield of SiC. It is observed that, the reduction rate of Al₂O₃ increased firstly with increasing bituminite content up to

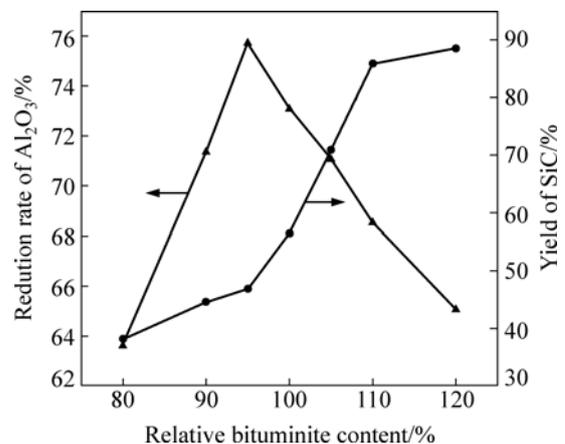


Fig.4 Effect of bituminite content on reduction rate of Al₂O₃ and yield of SiC

95% and decreased with further increasing bituminite content. The yield of SiC increasing firstly was not obvious; while when the bituminite content increased over 95% of theoretic one, the yield of SiC increased apparently. Thus, it is concluded that the best bituminite content is 95% of theoretic one. This may be due to the fact that carbothermal reduction of SiO₂ is much easier than Al₂O₃. A little larger C amount is good for production of SiC owing to the reaction: SiO₂+3C=SiC+2CO. The SiC produced needed to consume lots of C, resulting in the phenomenon that the C content used to reduce Al₂O₃ was deficient[13]. Therefore, when the bituminite content is larger than 95% of theoretic one, the reduction rate of Al₂O₃ decreased inversely.

3.1.4 SEM study

Fig.5(a) shows the back scattered electron image of sintered products by carbothermal reduction under argon atmosphere at 1 900 °C for 1 h. As seen in Fig.5(a), six phases were found from the contrast of the back scattered electron image. EDS analysis was preformed to get the chemical composition of each phase and the results are represented in Fig.5(b) and Table 3, respectively. It can be known that the white phase consists mainly of Al-Si-Fe-Ti alloy, including small amounts of C and P.

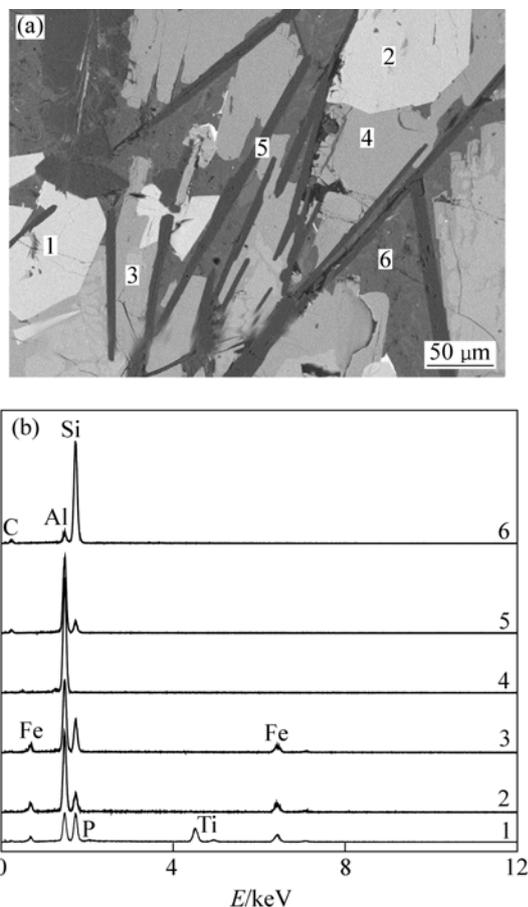


Fig.5 Backscattered electron image and EDS spectra of sample treated at 1 900 °C for 1 h

Both the gray white and the gray phases are the intermetallic Al-Si-Fe alloys, and the diversity between them is the different elements content. The gray black phase is constituted mainly of Al and the O content is marginal. This means that there is free Al, but is not detected by XRD, which might be due to its content not high enough. The dark gray strip-like and the dark plate-like phases are the Al-Si-C alloys. From Table 3 and XRD results, one could learn that, the both phases are Al₄C₃·SiC and Al₄C₃·46SiC.

Table 3 EDS results of sintering products

Alloy No.	Phase	x/%
1	White	Al24.2Si23.5Ti17.8Fe17.9-C15.2P1.4
2	Gray white	Al60.9Si18.6Fe20.5
3	Gray	Al52.3Si30.3Fe17.4
4	Gray black	Al88.1O11.9
5	Dark gray strip-like	Al41.8Si10.3C47.9
6	Dark plate-like	Al4.2Si46.2C49.6

It is noteworthy that the carbon content cannot be confirmed with great assurances (weak intensities of carbon's peak in spectra) because of EDS method limitations (The EDS scintillation detector is capable of identifying elements with atomic numbers equal to or greater than 5 but for those below 8 the quantification becomes very difficult).

3.2 Reduction mechanism

In terms of mechanism of carbothermal reduction of Al₂O₃ and SiO₂, there are mainly four theories[5, 11–12]: 1) silicothermic reduction; 2) two-step reduction; 3) the formation and decomposition of carbides; 4) the formation and decompose of Al-oxycarbides. Up to date, the reduction mechanism has not been clarified. So, in this work, the reduction mechanism of the carbothermal reduction of Al₂O₃ and SiO₂ was discussed.

The course of the reactions and the products formed at various stages could be followed through analysis of XRD patterns of products. Fig.6 shows the XRD patterns of the products prepared from industrially pure alumina and silica at 1 600, 1 700, 1 800, 1 900 and 2 000 °C for 1 h. XRD patterns of samples reacted at 1 600 and 1 700 °C contained peaks of SiC, Al₄C₃ and Si due to the fact that the following reactions began to perform:



The SiC and Al₄C₃ contents increased firstly with reaction temperature rising up to 1 800 °C and then

decreased with reaction temperature further rising, and at 2000 °C there were Al and Al-Si peaks emerged. It is ascribed to the phenomenon that Eqs.(3)–(7) began to proceed. Furthermore,

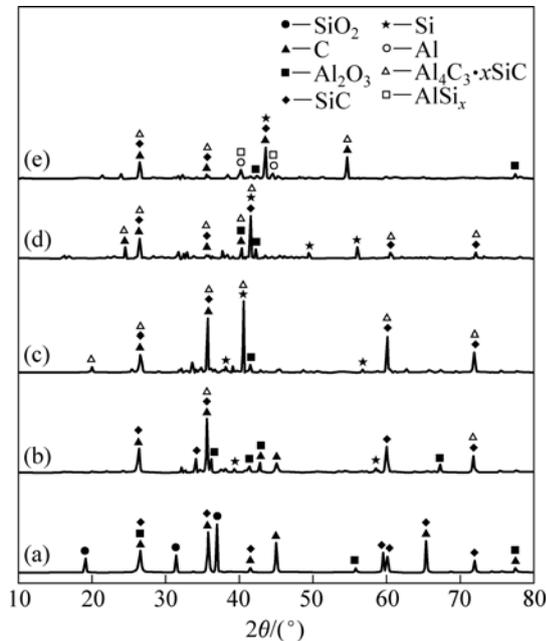


Fig.6 XRD patterns for samples prepared from industrially pure alumina and silica at different temperatures: (a) 1 600 °C; (b) 1 700 °C; (c) 1 800 °C; (d) 1 900 °C; (e) 2 000 °C

according to Ref.[14], Eqs.(5) and (7) were capable of proceeding which had been verified by experiment. Based on these, it is clear that the process of carbothermal reduction of Al_2O_3 and SiO_2 is accompanied by the formation and decomposition of carbides.

In the case of silicothermic reduction theory, the key step can be represented by



The initiative temperature of above-mentioned reaction is 2 128 °C; while according to Ref.[12], Al was capable of forming by Eq.(11) at 1 900 °C, which was also demonstrated by our experiment. However, using silicothermic reduction theory to interpret the carbothermal reduction of Al_2O_3 and SiO_2 may not be feasible. It is attributed to the yield of SiC of 65.9% and the residual ratio of SiO_2 of 24.7%, which were tested by infrared absorption carbon-sulfur analysis unit and XRF, resulting in the Si content used to reduce Al_2O_3 is very low. Besides, Eq.(3) is much easier to perform than Eq.(11), because Eq.(3) is spontaneous and exothermic at even much lower temperature.

As for two-step reduction theory, the initiative temperature of Eq.(12) is higher than that of Eq.(10) by almost 100 °C. So, the formation rate of Al_2O is very

low, and meanwhile, the formation rate of SiO is low because of the high formation rate of SiC and high residual ratio of SiO_2 . Therefore, the two-step reduction theory may not interpret carbothermal reduction of Al_2O_3 and SiO_2 process:



Considering that there are no $\text{Al}_4\text{O}_4\text{C}$ peaks from 1 600 to 2 000 °C, the process of carbothermal reduction of Al_2O_3 and SiO_2 may not be interpreted by the formation and decomposition of Al-oxycarbides theory.

In addition, according to Refs.[15–16], Fe_2O_3 plays an important role in carbothermal reduction of Al_2O_3 and SiO_2 , due to the fact that Fe could improve the reduction rate of Al_2O_3 and decompose the carbides such as Al_4C_3 and SiC at high temperature, resulting in the reduction reaction easier to perform. Therefore, from this point of view, it is also shown that using the theory of the formation and decomposition of carbides to interpret the process of carbothermal reduction of Al_2O_3 and SiO_2 may be feasible.

4 Conclusions

1) Atmospheric pressure and reaction temperature are major factors that influence the carbothermal reduction of bauxite tailings. The appropriate conditions for the preparation of primary Al-Si alloy are as follows: atmospheric pressure 0.1 MPa, heating temperature 1 900 °C, bituminite content of 95% of theoretic bituminite content, and sintering time 1 h.

2) The primary alloy obtained consists of six phases. Besides Al-Si-Fe alloy with high content of Al, there are some carbides in the alloy, which are not in favor of preparation of primary Al-Si alloy.

3) Among four mechanisms of carbothermal reduction of Al_2O_3 and SiO_2 , the theory of the formation and decomposition of carbides may be the most appropriate one to interpret the carbothermal reduction process.

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