Effect of Different Reducing Agents on Silicon-Aluminum Alloy Prepared from Coal Fly Ash

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Abstract. The effect of charcoal and coke as reducing agents on the preparation of silicon-aluminium alloy from coal fly ash was studied. X-ray diffraction (XRD) analysis of the reduction products under the action of two reducing agents was carried out. The results showed that SiC and Al₂SiO₅ were formed in the reduction products with charcoal or coke as reducing agent at 2073K, and impurity Fe₂SiO₄ was formed in the products with coke as reducing agent. At 2173K, when charcoal or coke was used as reducing agent, the same kinds of reduction products were SiC, Si, Al, Al₂O₃ and Al₄.₅FeSi, and the intensity of diffraction peaks of Al and Si in reduction products by charcoal as reducing agent was higher than that of Al and Si in reduction products using coke as reducing agent. At 2273K and charcoal as reducing agent, the reduction products of coal fly ash were Al, Si, SiC and Al₄.₅FeSi. When coke was used as reducing agent, the products of reduction coal fly ash were Si, FeSi, SiC, Al and Al₄.₅FeSi. In this study, the reduction ability of charcoal is better than that of coke at different temperatures, and the reduction effect of silicon-aluminium alloy prepared by charcoal reduction coal fly ash is the best at 2273K for heating 30 minutes.

1. Introduction
Coal fly ash is a kind of solid particle waste generated by coal combustion in thermal power plants. Coal fly ash has become the largest single pollution source of industrial solid waste, and is also one of the largest discharge of industrial solid waste at present[1]. The open-air stacking of coal fly ash not only causes irreparable harm to the ecological environment and human health, but also increases the cost of treatment and storage of coal fly ash in thermal power plants. At present, coal fly ash is mainly used in building materials, road engineering, backfill engineering and other fields, but these applications belong to extensive low-value-added utilization, which can not fully realize the huge potential value of coal fly ash and is a waste of resource[2]. Coal fly ash is mainly composed of alumina and silicon oxide. Extracting silicon and aluminium alloy from carbon reduction coal fly ash can not only improve the high value-added application of coal fly ash, improve the pollution of coal fly ash to the environment and harm to human life, but also reduce the cost of producing silicon and aluminium alloy[3]. Therefore, it is urgent to study the efficient and high value-added resource utilization of coal fly ash, and a resource-saving and environment-friendly society can be established.

2. Test materials and methods
The raw material coal fly ash was taken from the Liupanshui a power plant, two kinds of reducing agents, one was charcoal with 85% fixed carbon content, the other was coke with fixed carbon content of 82.95%, and calcium lignosulfonate was used as binder. The chemical composition of coal fly ash is
shown in Table 1. Theoretically, the ratio of carbon to coal fly ash required for carbon reduction coal fly ash was 3:10. The fixed carbon in the reducing agent of this experiment was 1.2 times of the theoretical carbon content. The coal fly ash was first placed in a dry box and kept at 110 °C for 2 hours for drying. The raw materials were coal fly ash and charcoal or coke, and the quality of calcium lignosulfonate was 8% of the total amount of raw materials. The weighed coal fly ash, reducing agent, calcium lignosulfonate and appropriate amount of water were mixed uniformly, and 50 g was placed in a self-made mold, and pressed into a dough under a 10 Mpa single-arm hydraulic press. The pressed sample was placed in a constant temperature drying oven and dried at 120 °C.

Table 1 Chemical composition of Coal fly ash (wt.%)  
| Composition | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | TiO₂ | MgO | Others |
|-------------|------|-------|-------|-----|------|-----|--------|
| Content(wt.%) | 43.24 | 25.59 | 12.06 | 4.6 | 3.05 | 1.62 | 9.84 |

In this experiment, infrared temperature controlled HT-25AB high frequency induction melting furnace was used. The prepared sample was placed in a graphite crucible and the temperature of the melting furnace was set. The sample was reduced by induction smelting furnace at high temperature. The reduced product was characterized by a TD-2500 X-ray diffractometer.

3. Results and discussion

3.1. Phase analysis of coal fly ash reduced by charcoal or coke at 2073K

Figure 1 was the XRD pattern of carbon reduction coal fly ash product under the condition of reduction temperature of 2073K and heat preservation for 30 minutes. Figure 1a denoted that the reductant was charcoal; Figure 1b denoted that the reductant was coke. Figure 1a showed that when the charcoal was used as a reducing agent, the reduced coal fly ash products were SiC, Al₂SiO₅ and Al₂O₃ at the temperature of 2073K for heating 30 minutes. As shown from Figure 1b that under the condition of holding at 2073 K for 30 minutes, when the coke was a reducing agent, the reduced coal fly ash products were SiC, Fe₂SiO₄, Al₂SiO₅ and Al₂O₃. Under the reaction conditions of charcoal or coke as reducing agent at 2073K for heating 30 minutes, no aluminum, silicon or silicoalumino compounds were observed in the reduced products, indicating that the reduction temperature didn’t not reach the temperature at which the coal fly ash was reduced to prepare silicon aluminum. Compared with Figure 1a and Figure 1b, it was found that Al₂O₃ was present in the products of coal fly ash reduction with charcoal or coke as reducing agent at 2073K and holding for 30 minutes, indicating that alumina was not completely reacted. Silicon oxide reacts with carbon prior to alumina to form silicon carbide⁴.
Figure 1. The XRD pattern of coal fly ash reduced by different reducing agents at 2073K

![XRD pattern of coal fly ash reduced by different reducing agents at 2073K](image)

From Figure 1a and Figure 1b, it showed that SiC and Al$_2$SiO$_5$ were formed in the products of coal fly ash reduction by charcoal or coke as reducing agents at 2073K, and Figure 1b contained impurity Fe$_2$SiO$_4$, which indicated that at this temperature, coke produced more impurities than charcoal in reducing coal fly ash. The intensity of the diffraction peak of Al$_2$O$_3$ in Figure 1a was smaller than that of Al$_2$O$_3$ in Figure 1b, which indicated that the reaction between charcoal and alumina was more sufficient than that between coke and alumina. Under the condition of 2073K and holding for 30 minutes, the reduction effect of charcoal as reducing agent was better.

3.2. Phase analysis of coal fly ash reduced by charcoal or coke at 2173K

![XRD pattern of coal fly ash reduced by different reducing agents at 2173K](image)

Figure 2 showed the XRD pattern of the reduction products of coal fly ash at 2173K and heat preservation for 30 minutes, in which a was charcoal as reducing agent and b was coke as reducing agent. As shown in Figure 2a, it indicated that when the charcoal was a reducing agent, the reduced coal fly ash products were SiC, Si, Al, Al$_2$O$_3$, and Al$_{4.5}$FeSi. As Figure 2b showed that when coke was a reducing agent, the reduced coal fly ash products were Al, SiC, Al$_{4.5}$FeSi, Si and Al$_2$O$_3$. Aluminum,
silicon and Al\(_{4.5}\)FeSi were all target products. Compared with a and b in Figure 2, it was found that the products of coal fly ash reduction with charcoal or coke as reductant were all the same at 2173K and holding for 30 minutes, and all the products contained Al\(_2\)O\(_3\), indicating that alumina had not been completely reduced. No silicon oxide was found in the products, indicating that silicon oxide had completely reacted.

From Figure 2a and Figure 2b, it showed that SiC was formed in the products of coal fly ash reduced by charcoal or coke as reductant at 2173K, which might be the reaction of silicon oxide and carbon to form SiC. The intensity of the diffraction peaks of aluminum and silicon in Figure 2a was higher than that of aluminum and silicon in Figure 2b, indicating that charcoal was more effective as a reducing agent than coke as a reducing agent. The high temperature reactivity of charcoal is more reactive than other carbonaceous reducing agents\[^5\].

3.3. Phase analysis of coal fly ash reduced by charcoal or coke at 2273K

![Figure 3. The XRD pattern of coal fly ash reduced by different reducing agents at 2273K](image)

Figure 3 showed the XRD pattern of reduced coal fly ash product under the condition of reduction temperature 2273K and holding for 30 minutes, in which a was charcoal as reducing agent and b was coke as reducing agent. Figure 3a showed that when the charcoal was a reducing agent, the reduced coal fly ash products were aluminum, silicon, silicon carbide, and Al\(_{4.5}\)FeSi. As shown in Figure 3b, when the coke was a reducing agent, the reduced coal fly ash products were silicon, FeSi, silicon carbide, aluminum and Al\(_{4.5}\)FeSi. Aluminum, silicon and Al\(_{4.5}\)FeSi were all target products. Compared with a and b in Figure 3, it was found that under the reaction conditions of 2273K and 30 minutes heat preservation, the products of coal fly ash reduction with charcoal or coke as reductant were not identical, and there was no alumina in the products, indicating that alumina participated in the reaction completely.

From Figure 3a and Figure 3b, it showed that silicon carbide existed in the reduction products of charcoal and coke as reductant at 2273K, which reduced the formation rate of silicon; FeSi appeared in the products of coke as reductant, which reduced the yield of silicon. The intensity of the diffraction peak of aluminum in Figure 3a was greater than the intensity of the diffraction peak of aluminum in Figure 3b, and the products in Figure 3b had an impurity phase of FeSi, and the phase of the reaction of charcoal as a reducing agent was better, and there were more impurities in the products when coke was used as a reducing agent. It followed that in this experiment, under the same reaction conditions, the reduction ability of charcoal was better than that of coke.
4. Conclusion
SiC and Al_{4.5}SiO_{4} were formed in the reduction products with charcoal or coke as reductant at 2073K and 30 minutes holding time, and impurity Fe_{2}SiO_{4} was formed in the products with coke as reductant. At this temperature, coke produced more impurities than charcoal in reducing coal fly ash. Under the condition of 2173K and 30 minutes of heat preservation, the products of reducing fly ash using charcoal or coke as reducing agents were SiC, Si, Al, Al_{2}O_{3} and Al_{4.5}FeSi. The diffraction peak intensity of Al and Si in the reduction product XRD of charcoal as a reducing agent was greater than the diffraction peak intensity of Al and Si in the reduction product XRD of coke as a reducing agent, which indicated that charcoal was more effective as a reducing agent than coke as a reducing agent. Under the condition of 2273K and holding for 30 minutes, when charcoal was the reducing agent, the products of reduced coal fly ash were Al, Si, SiC and Al_{4.5}FeSi. When coke was used as reducing agent, the products of reduction coal fly ash were Si, FeSi, SiC, Al and Al_{4.5}FeSi. In this study, the reduction ability of charcoal was better than that of coke at different temperatures. Under the condition of 2273K and 30 minutes of heat preservation, the effect of preparing silicon-aluminium alloy with fly ash was the best.

Acknowledgments
This work was financially supported by the Guizhou Provincial Science and Technology Foundation (No.[2014]7460), the Liupanshui Normal University High-Level Talent Research Start Foundation (LPSSYKYJ201417), Guizhou provincial department of education fund project (Qianjiaohe KY Zi[2016]102), and Key supported discipline project of Guizhou province (Qianxuewei He Zi ZDXK [2016] 24).

References
[1] Pu Wei. Study on Preparation of Active Calcium Silicate from Fly Ash and High Filling Modification of Plastics[D]. GuiZhou University,2016.
[2] Zhang quanli. Study on resource utilization of DaFang fly ash[D]. GuiZhou University,2016.
[3] Chen xuan. The Research on Comprehensive Utilization of Fly Ash from a Power Plant of Shuicheng Iron and Steel[D]. Wuhan University of Science and Technology,2012.
[4] Li Ziyong, Wu Chunhan, Yu Qingchun, et al. Phase transformation of carbothermal reduction coal fly ash[J]. Journal of China coal society, 2016, 41(3):769-775.
[5] Chen Da. Choice of carbon reluctant for producing silicon metal[J]. Ferro Alloys, 2008, 33(4):15-19.