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Preparation of β-SiC/Al_2O_3 composite from kaolinite gangue by carbothermal reduction

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Abstract

β-SiC/Al_2O_3 composite from kaolinite gangue and anthracite has been prepared by carbothermal reduction of kaolinite gangue at low cost. Carbon black and anthracite were chosen as the reducing agent. Phase evolution was studied in the temperature range 1500–1600 °C. XRD analysis shows that the relative intensity of Al_2O_3 and β-SiC increase at higher soaking temperature, soaking time and excess amount of carbon black or anthracite. The results also indicate that anthracite can replace the carbon black as the reductant to achieve the synthesis of β-SiC/Al_2O_3 composite using all materials from coal measures.

Keywords: B. Composites; D. Al_2O_3; D. SiC; D. Mullite

1. Introduction

PR China is the largest coal production country and the largest consumer, every year about 1–1.3 billion tonnes of coal waste was generated [1]. Only about 35% was utilized and some of the utilization yields second pollution. So the utilization of gangue is a serious problem and bottlenecked the economic development of local coal areas, especially for Shanxi, Henan and Liaoning province in the north of China. Many measures and polices have been taken to prompt the applications of gangue effectively. For example, the gangue, especially coal series kaolinite (tonstein) with little impurities was used in the manufacture of pottery, cement and other building products. Recently, kaolinite gangue was used to prepare mullite in the north of China.

Coal gangue is divided into two kinds, that is siliceous and kaolinite gangue (coal series kaolinite), which were widely distributed in Permian and Jura coal bed in the north of China. Li et al. [2,3] has synthesized β-SiC from siliceous gangue and superfine carbon black. Wang et al. [4,5] studied the preparation of β-SiC from siliceous gangue and anthracite or bituminous coal as the reductant. Siliceous waste was considered as an excellent raw material for synthesis of β-SiC. Han and Li [6] has prepared β-SiC/Al_2O_3 from kaolinite gangue and anthracite. It is an easier way to get cheap β-SiC/Al_2O_3 composite at low cost. SiC and corundum are the main components of the Al_2O_3–SiC–C castables, which has been widely used in blast furnace trough. Generally, SiC and corundum was introduced respectively. So theβ-SiC/Al_2O_3 composite may be has potential applications in Al_2O_3–SiC–C castables as a substitute of SiC and corundum.Similar works on the preparation of Al_2O_3/SiC from clay minerals, such as pyrophyllite, kaolinite and montmorillonite, have been reported [7–10].

In this paper, the synthesis of β-SiC/Al_2O_3 composite from kaolinite gangue by carbothermal reduction method using anthracite and carbon black as reductant has been studied.

2. Experimental procedures

The kaolinite gangue (from Jincheng City, Shanxi Province, PR China) was chosen as the raw material for

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Table 1
Chemical composition of kaolinite gangue

Composition	Mass %
SiO_2	61.10
Al_2O_3	28.25
Fe_2O_3	1.85
CaO	0.37
MgO	0.62
K_2O	3.00
Na_2O	0.83
IL	8.72

the present work. Among all the reducers anthracite is the cheapest. In order to reduce cost, in this study anthracite was used as reducer comparing to carbon black. The chemical composition of gangue is given in Table 1 and the industrial analysis's of anthracite and carbon black are listed in Table 2. The X-ray diffraction pattern of gangue was shown in Fig. 1. The result shows that the gangue is mainly composed of kaolinite and quartz.

The gangue and anthracite were separately crushed and ground together in a vibrating mill. The powder was screened and the powder under 200 mesh was used. The average particle size of the carbon black is about 22–26 μm.

The predetermined amounts of the material powders were mixed in an alumina ball mill and pressed into pellets of 10 mm diameter and 10–12 mm height under 10 MPa. Then the pellets were dried at 110 °C for 24h. The specimens were calcined at a $MoSi_2$ furnace under the protection of coke granules. The rising temperature rate was about 300 °C/h. Experimental variables investigated in the work were: (i) mixing ratio of the anthracite. Anthracite must exceed the theoretical content to make the reaction complete. The excess anthracite is 10, 15, 20 and 25%, respectively. (ii) Soaking temperature and soaking time. The samples were heated at 1500, 1550 and 1600 °C for 3 and 4 h, respectively. (iii) Particle size of the raw materials and (iv) carbon source. Carbon black and anthracite were chosen as the reducers.

The particle size of the raw material was measured by a GSL-101B laser particle size analyzer.

D/MAX-III X-ray diffractometry was used to identify the crystalline phase using copper Kα radiation. Zevin method, a half quantitative method was used to determine the silicon carbide, mullite and Al_2O_3 content.

Philips XL 30 TMP scan electron microscopy (SEM) was used to analyze the morphology of the silicon carbide and other products.

Table 2
Industrial analysis of anthracite and carbon black

Raw materials	M_{ad}	A_{ad}	V_{ad}	F_{ad}	$S_{t.ad}$
Anthracite	1.28	27.74	7.76	63.22	0.78
Carbon black	1.18	1.14	1.18	97.68	0.36

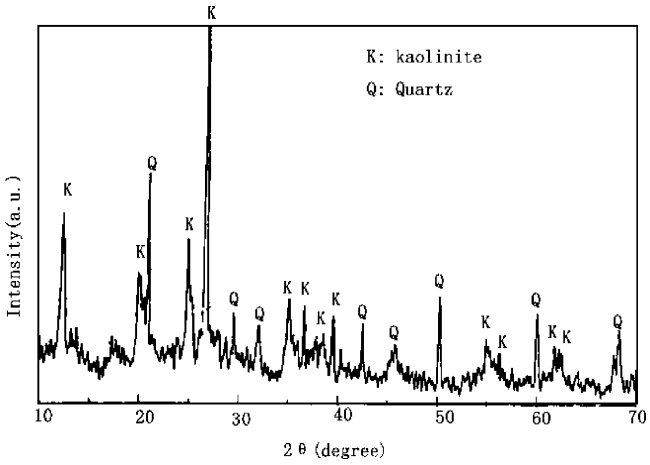

Fig. 1. XRD pattern of gangue.

3. Results and discussion

3.1. Effect of heating temperature

Fig. 2 gives the XRD patterns of the products prepared at 1500, 1550 and 1600 °C. Mullite, and β-SiC can be founded when the temperature is 1500 °C. Cristobalite has begun convert to β-SiC. There is a glassy hump at 15–30° which means the existence of amorphous phase SiO_2 and mullite primary crystal. After heated at 1500 °C, there is a considerable mullite content in the samples, but in the samples heated at 1600 °C, mullite is only a little. β-SiC and α-Al_2O_3 became the dominant phases.

3.2. Effect of the anthracite content

Fig. 3 gives the XRD patterns of the samples soaked at 1600 °C with various anthracite contents. Fig. 4 shows the relative content of the substances in the products with the anthracite content. The results show that when the anthracite is increased, the amount of β-SiC and α-Al_2O_3 were

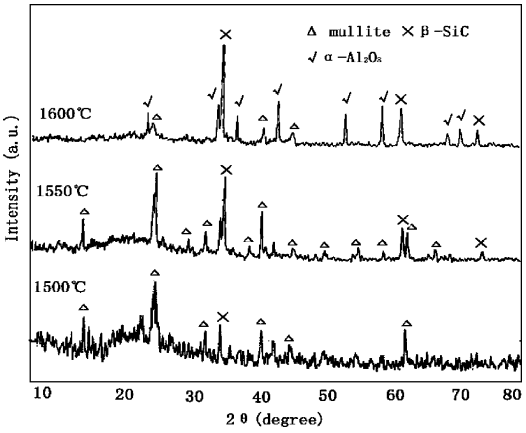

Fig. 2. XRD patterns of the products at various temperatures.

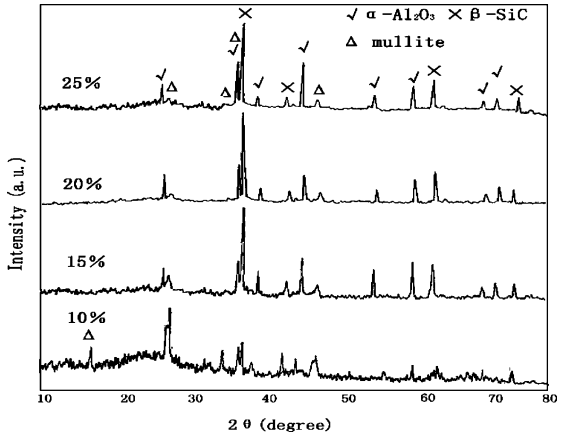

Fig. 3. XRD patterns of the products with excess anthracite content.

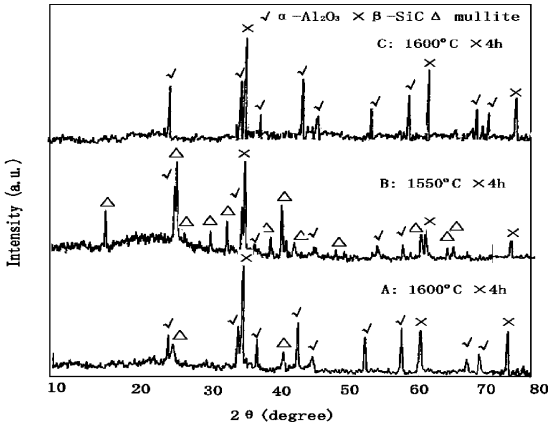

Fig. 5. XRD patterns with the particle size of the raw materials (A: 88 μm; B: 10 μm; C: 10 μm).

increased in the range of anthracite content from 10 to 15 wt.%, while mullite was decreased gradually. However, small amount of mullite was still detected in the product containing 25 wt.% excess anthracite. At the same time, from the XRD patterns, the residual mullite varied slightly when the excess amount is above 15 wt.%, which means it isn't necessary to add more anthracite and the suitable excess anthracite ranges between 15 and 20 wt.%.

3.3. Effect of initial particle size of the raw material

Fig. 5 shows that the particle size of raw materials powder gives great influence on phase composition of products. In the samples made of powder with size less than 88 μm and heated at 1500 °C, there is considerable mullite content. However, in the samples made of powder with size below 10 μm and heated at 1550 °C, there is a little mullite content. In the samples made of powder with size below 10 μm and heated at 1600 °C, mullite cannot be detected. Only SiC, α-Al_2O_3 could be detected at 1600 °C.

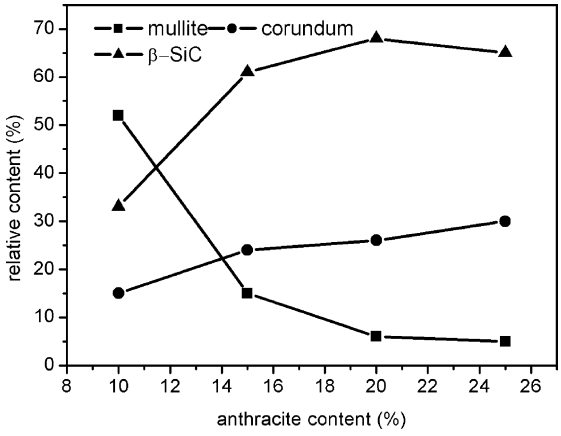

Fig. 4. Relative content of substances in the product with excess anthracite content.

3.4. Effect of carbon source

The carbothermal reduction of clay minerals such as andalusite, kaolinite, kyanite and pyrophyllite using carbon black, lamp black or graphite as carbon source has been reported [7–10]. Reports on carbothermal reduction of SiO_2 or siliceous gangue using carbon black or anthracite as carbon source also could be found [2,3,11]. The XRD patterns of samples made of mix powder with various carbon black were shown in Fig. 6. Mullite and β-SiC were the main phases when the coal gangue was directly calcined at 1600 °C for 4 h without any reducers. β-SiC and α-Al_2O_3 were the dominant phases but small amount of mullite still could be detected when the carbon black was exceed the stoichiometric content by 15 wt %. Comparing Fig. 3 with Fig. 6, it can be concluded that the carbon black can be replaced by cheap anthracite as the reductant to prepare SiC/Al_2O_3 composite at low cost.

3.5. Effect of soaking time

Fig. 7 shows the XRD patterns of the products with soaking time of 3, 4 and 5 h. With increasing soaking time

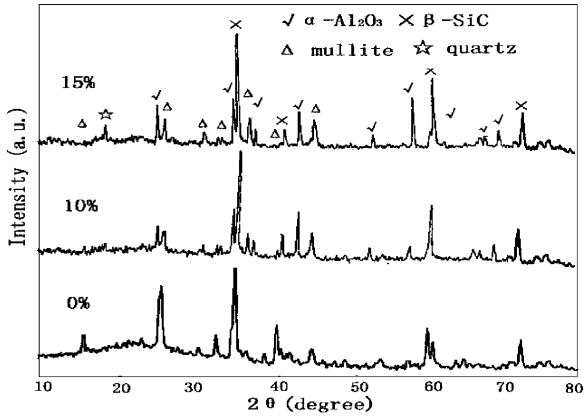

Fig. 6. XRD patterns of the products with various carbon black content.

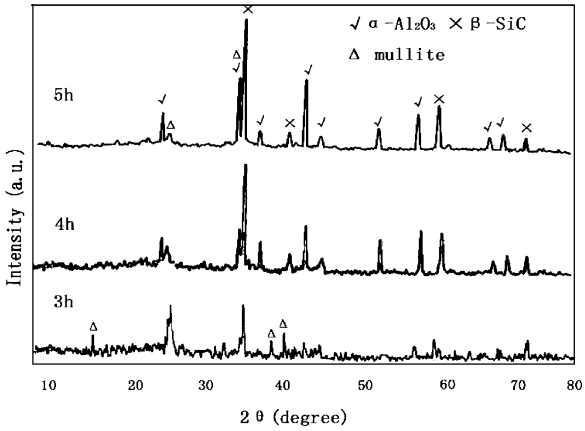

Fig. 7. XRD patterns of the products soaked at 1600 °C with soaking time.

mullite content decreases, which means the prolongation of the soaking time prompts the completion of the carbothermal reduction. When the soaking time is about 5 h there is little mullite in the product, β-SiC and α-Al_2O_3 are the main phases.

3.6. SEM analysis

Fig. 8 shows the scanning electron micrographs of products heated at 1600 °C for 4 h. β-SiC and α-Al_2O_3 particles are distributed homogeneously in the system. Amroune et al. [8], Kimura et al. [9] and Chaklader et al. [10] reported that the morphology of β-SiC whisker was depended on the carbon source. They found β-SiC whisker formed in the carbothermal reduction processing of the andalusite r kaolinite with carbon black as the carbon source. In our study, though XRD analysis proves the product mainly compose of β-SiC and α-Al_2O_3 but it was impossible to identify the SiC whisker with XRD and SEM. From the SEM observation we can conclude that the morphology of the β-SiC particles maybe related with the carbon source. The β-SiC particles coexists with α-Al_2O_3 particles and it is very difficult to distinguish them.

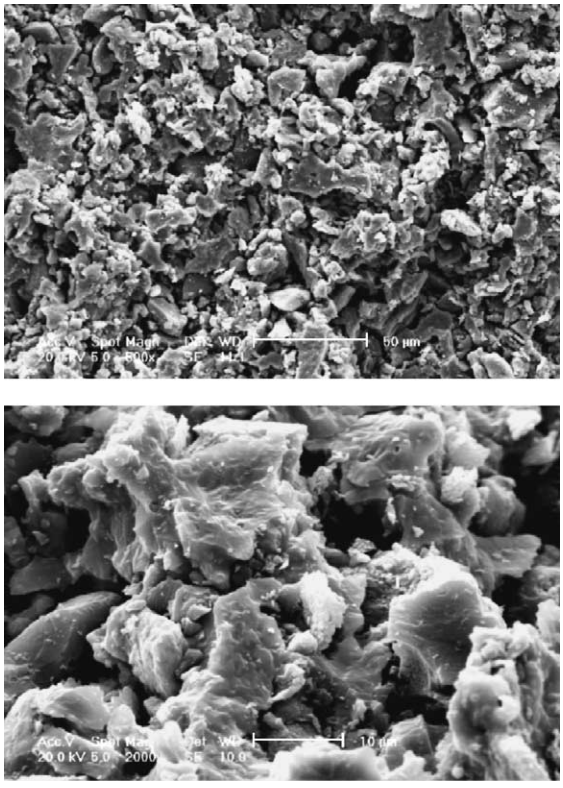

Fig. 8. SEM photographs of product at 1600° for 4 h with anthracite as carbon source.

3.7. Discussion

There are many reports on the phase transformation and microstructure of fired kaolinite [12–14]. when a typical kaolinite is heated at 500–600 °C, dehydration of the kaolinite takes place and metakaolin was formed. As the heating proceeds, the metakaolin is partially replaced by a spinel phase, and mullite also begins to form at this stage. These transformations take place at about 900–1000 °C. Cristobalite begins to crystallize at about 1000–1200 °C, until eventually mullite and cristobalite are the only crystalline phases. Chaklader et al. [10] indicated that the following reactions take place in the carbothermal reduction of gangue.

$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O(s) \xrightarrow{500-1200\,^\circ C} Al_6Si_2O_{13}(s) + 4SiO_2 + 6H_2O(g) \quad (1)$$

$$Al_6Si_2O_{13}(s) + 4SiO_2(s) + 12C(s) \xrightarrow{>1350\,^\circ C} 3Al_6Si_2O_{13}(s) + 4SiC(s) + 8CO(g) \quad (2)$$

$$Al_6Si_2O_{13}(s) + 4SiO_2(s) + 18C(s) \xrightarrow{>1500\,^\circ C} 3Al_2O_3(s) + 6SiC(s) + 12CO(g) \quad (3)$$

It is important to note that the carbothermal reduction of gangue must pass through an intermediate step forming mullite and cristobalite. Firstly, SiO_2 will react with C to form SiC. The final reaction that leading to the formation of β-SiC and α-Al_2O_3 is equation (3), which determine the composition of the final product. At the same time, from Eqs. (2) and (3), the partial pressure of CO controlled the mullitization of gangue and the yield of β-SiC. The less of the partial pressure of the CO, the higher of the yield of the SiC. The release of CO is help to the completion of the reduction. In our study, the samples were heated in coke bed. According to Dalton's law of partial pressure, when the system came to balance, the CO and N_2 were the dominant gas phases and the value of partial pressure can be regarded unchanged in the heating process. So the release of CO at high temperature becomes difficult and inhibit the

carbothermal reduction of gangue. Furthermore, organic substance (carbon is the main phase) in the coal gangue will influences the carbothermal reduction of the gangue. Firstly, the combustion of organic substance prompts the decomposition of kaolinite. Secondly, the combustion of organic substance prompts the mullitization and makes the carbothermal reduction more difficult. In Kimura et al. [9] and Chaklader et al. [10] reports, the carbothermal reduction was completed about at 1500 °C. However, in our study, the carbothermal reduction was finished until 1600 °C. The above factors maybe the reason that kaolinite gangue is difficult to reducing.

4. Conclusions

Anthracite can replace carbon black as the reductant to prepare β-SiC/Al_2O_3 composite from kaolinite gangue at low cost.

Temperature is a major factor that influences the carbothermal reduction of the gangue. The yield of β-SiC and Al_2O_3 increase with the raising of the temperature. The initial particle size of the raw material and the added content of the anthracite also have important influence on the processing. When the particle size is about 10 μm, the gangue can covert to β-SiC and Al_2O_3 completely at 1600 °C for 4 h. When the excess amount of anthracite is about 15–20%, most of gangue has been converted to β-SiC and Al_2O_3, only small amount mullite was detected in the product.

Kaolinite gangue is difficult to reducing than ordinary kaolinite. The organic substances in the gangue have a considerable influence on the carbothermal reduction of gangue. The combustion of organic substances prompts the dehydration and mullitization of the kaolinite, which makes the reducing more difficult.

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