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In-Situ Synthesis of (0'+β)-Sialon/Mullite Composite Materials from Coal Gangue

ABSTRACT

(0'+β)-sialon/mullite composite materials were synthesized by an in-situ carbothermal reduction nitridation method, with coal gangue and carbon black as raw materials. The influences of temperature and carbon content on the phase composition and microstructure of the pre-synthesized materials were investigated by XRD and SEM. The effects of variation in the phase composition, the microstructure on the bulk density, the bending strength of the pre-synthesized materials were investigated in detail. The results indicated that increasing temperature and carbon content benefit the generation of 0'-sialon and β-sialon. The (0'+β)-sialon/mullite composite material can be synthesized at 1400 °C (6 h) ~ 1500 °C (6 h). The generative process including the formation of β-sialon, 0'-sialon and the conversion process from β-sialon to 0'-sialon. The 0'-sialon and β-sialon in the synthesized materials have needle-like and pillar structures, respectively. Given all that, the (0'+β)-sialon/mullite composite material prepared by coal gangue and carbon black contributes to solving the problem of the recycling of coal gangue, and high-performance composite materials can be obtained.

1. Introduction

With the worldwide comprehensive construction and the increased energy demands of prosperous countries, the need for coal has increased rapidly. Coal gangue is generated by the process of coal mining and coal washing, and cannot be fully used. Coal gangue is stored in most areas due to the vast mining of coal, which will damage and threaten air, water and the environment [1]. Therefore, it is important to solve the recycling problem of coal gangue. The main chemical compositions of coal gangue are SiO_2 and Al_2O_3, which are similar to clay. Meanwhile, it also is the main raw material for generation of sialon, and therefore, coal gangue was chosen as the main raw material to generate sialon.

Both 0'-sialon ($Si_{2-x}Al_xO_{1+x}N_{2-x}$, $0 < x < 0.3$) and β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$, $0 < z < 4.2$) possess excellent characteristics to endure corrosion, oxidation and are stable with respect to thermal shock [2–3]. They have good prospects to be widely used in construction, aviation and metallurgy. Mullite ($Al_6Si_2O_{13}$) possesses high strength, a high melting-point, a low heat expansion coefficient and good chemical stability [4]. It is hoped that other, better composites can be obtained by using different superiority between materials. This study describes research on the preparation of (0'+β)-sialon/mullite composite materials, which are not only easy to synthesize, but can also lower the cost of synthesizing good performance composite materials. Meanwhile, they can also reduce environmental pollution [5–7].

2. 2 Experimental

2.1 Raw materials and method

Coal gangue and carbon black were the raw materials in this experiment and they were fully mixed by wet ball milling. Coal gangue and carbon black were taken with the mass ratios 100:20, 100:30, 100:40, and 100:50. They were placed into a ball milling jar, and in the meantime some agate sphere of different diameters were put into the jar; the ball to raw materials ratio was 1.5:1(mass ratio). Appropriate ethanol with no water was added into the jar at the same time. Finally, the raw materials were ball milled in the ball milling jar at a rate of 200 r/min (6 h) and the mixture was dried at room temperature for 12 h. Then, the powder mixtures were first ground uniformly in the mortar and were weighed 12 g in the analytical balance. The powder mixtures were then put in a steel mould and were moulded under pressure of 30 MPa. The green bodies were dried naturally in at room temperature for 2 days. After drying, the samples were put in a corundum crucible and prepared by an in-situ carbothermal reduction nitridation method at different temperatures (1300, 1400 and 1500 °C) in a furnace for 6 h. Moreover, high-purity nitrogen entered to the furnace during the sintering process.

2.2 Characterization

The bulk density of samples was determined by Archimedes' method. The compressive strength was analyzed by a microcomputercontrolled hydraulic universal testing machine. The microstructures of the samples were analyzed by scanning electron microscopy (SEM) and energy dispersive spectrum (EDS). The phases compositions of the synthesized samples were examined by X-ray diffraction (XRD), using CuK-α radiation ($\lambda = 1.5406$ Å) with a step of 0.02 ° (2θ) and a scanning rate of 4 °/min [8–9].

3. Results and discussion

3.1 Analysis of the thermodynamics and reaction process

The main compositions of coal gangue were detected by accurate chemical analysis, constituted by SiO_2 and Al_2O_3. Chemical devise was made based on the main compositions and the z value was set as 3. The chemical composition of coal gangue is shown in Table 1. Carbon black was used as reduction agent, moreover, excess 20, 30, 40 and 50 mass-% in the coal gangue. The reactions in the experiment were as follows [1]:

The kaolinite in coal gangue firstly generated to metakaolin. With a temperature increase, metakaolin changed to mullite:

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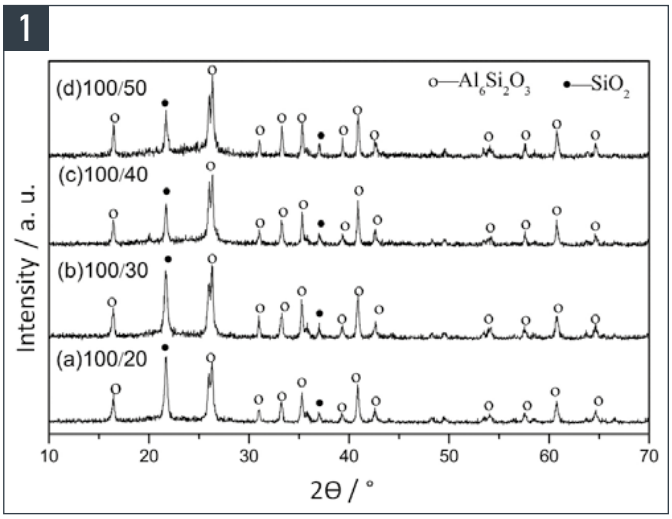

***Fig. 1** • Influence of carbon content on the phase composition of the samples synthesized at 1300 °C for 6 h*

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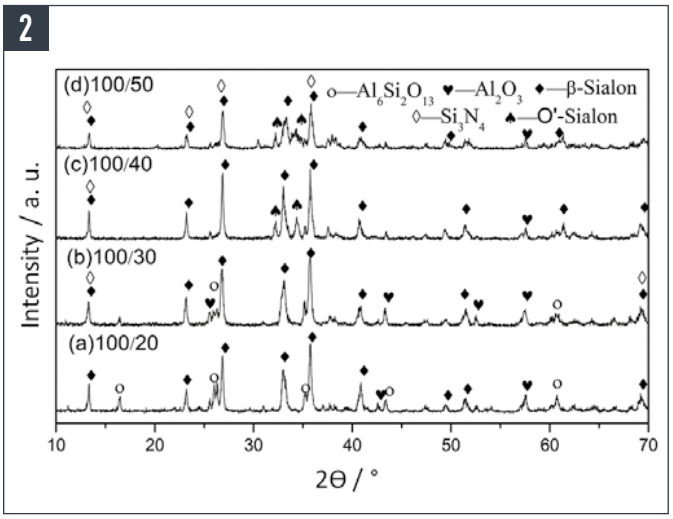

***Fig. 2** • Influence of carbon content on the phase composition of the samples synthesized at 1400 °C for 6 h*

(1) $500–600\ °C: Al_2O_3·2SiO_2·2H_2O \rightarrow (Al_2O_3·2SiO_2+2H_2O$

(2) $980\ °C: 2\ (Al_2O_3·2SiO_2) \rightarrow 2Al_2O_3·3SiO_2+SiO_2$

(3) $1100–1400\ °C: 3\ (2Al_2O_3·3SiO_2) \rightarrow 2\ 3Al_2O_3·2SiO_2+5SiO_2$

When the temperature exceeded 1400 °C, the content of mullite decreased and the reaction was almost complete:

(4) $3Al_2O_3·2SiO_2+4SiO_2+15C+5N_2 \rightarrow 2Si_3Al_3O_3N_5+15CO$

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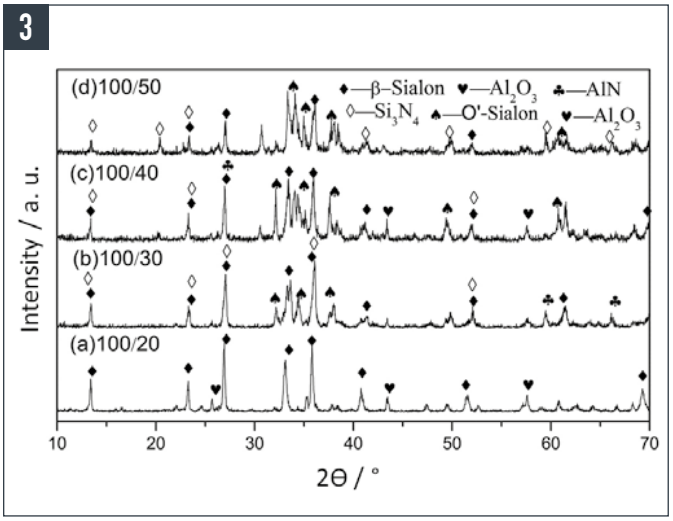

***Fig. 3** • Influence of carbon content on the phase composition of the samples synthesized at 1500 °C for 6 h*

3.2 XRD patterns analysis

Figure 1 shows the XRD pattern of samples with different carbon content after heat treatment at 1300 °C for 6 h. As the figure shows, mullite and quartz were the main phases. The intensity of mullite increased gradually and the intensity of the quartz phase decreased gradually with an increase of carbon content. This demonstrated that the sialon phase was not available at 1300 °C. Mullite and quartz phases were the main phases existing in the samples.

Figure 2 shows the XRD pattern of samples with different carbon content after heat treatment at 1400 °C for 6 h. As the figure shows, mullite, quartz and β-sialon phase were generated in the synthesized samples when the mass ratio of coal gangue and carbon black was 100:20. Mullite and β-sialon were the main phase and quartz phase disappeared. New phase Si_3N_4 generated with an increase of the carbon content of samples (Fig. 2b), but the intensity was weak. Other phase compositions did not change obviously while the intensity of mullite fell and the intensity of β-sialon grew. Continued to increase carbon content, the 0′-sialon appeared while mullite and quartz phase disappeared in the XRD patterns when the mass ratio of coal gangue and carbon black was 100:40. Besides, the intensity of β-sialon fell while the intensity of 0′-sialon and Si_3N_4 grew with an increase of the carbon content (Fig. 2d). It indicated that β-sialon and 0′-sialon were available in the samples at 1400 °C. Meanwhile, β-sialon converted to 0′-sialon with an increase of the carbon content of the samples. It was available for composites where β-sialon and 0′-sialon co-existed.

Figure 3 shows the XRD pattern of samples with different carbon content after heat treatment at 1500 °C for 6 h. As the figure shows, β-sialon and corundum phase were the main phases in the synthesized samples when the mass ratio of coal gangue and carbon black was 100:20. 0′-sialon, Si_3N_4 and AlN appeared with an increase of the carbon content

Table 1 · Chemical composition of coal gangue

Chemical composition / mass-%						
SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	C	z
41.3	39.2	0.142	0.0350	0.326	4.38	3

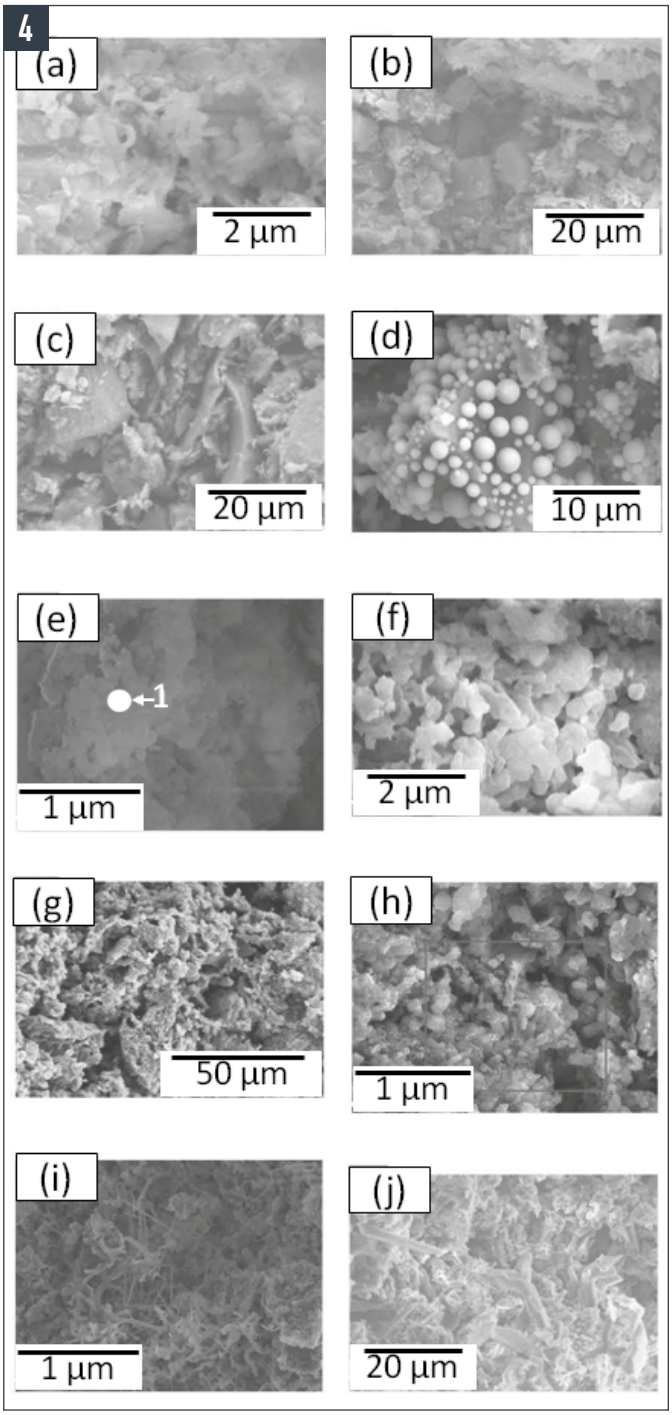

***Fig. 4** • Influence of carbon content on the microstructure of the samples synthesized at 1300 °C (a, b, c, d), 1400 °C (e, f, g, h), and 1500 °C (i, j) for 6 h; ratios were (a, b, e, f, i) 100:20 and (c, d, g, h, j) 100:50*

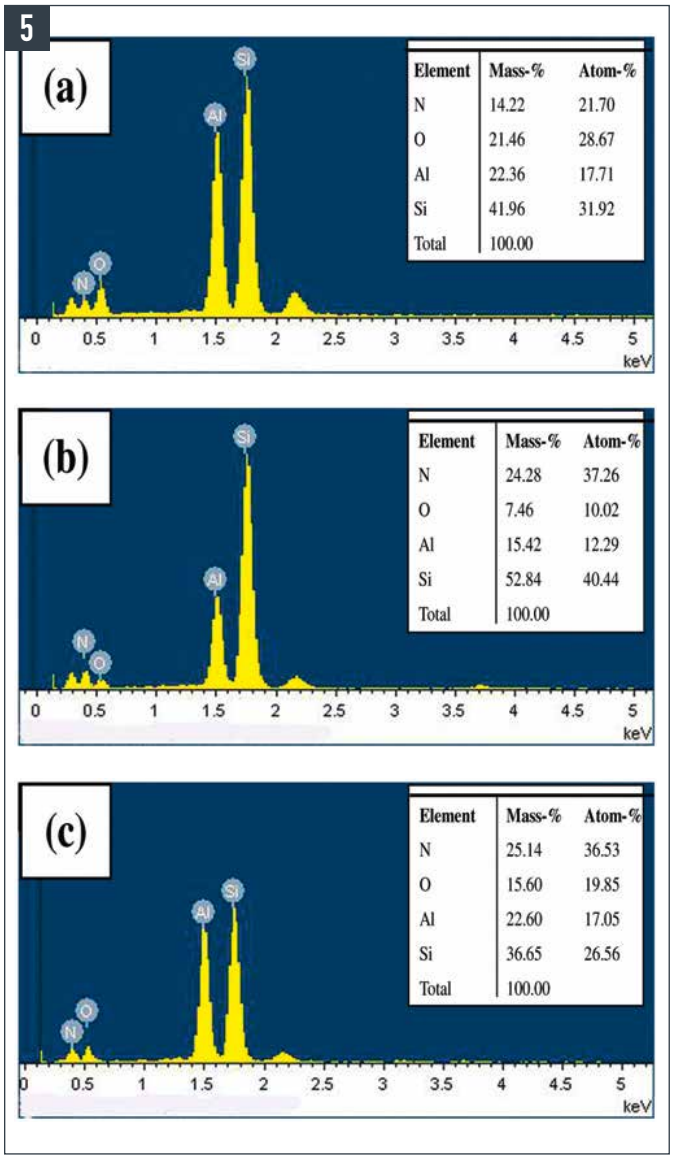

***Fig. 5** • EDS spectrum*

in the samples. The intensity of β-sialon fell and the corundum phase disappeared (Fig. 3b). With a continued increase of the carbon content, there was no significant change of phase compositions in the samples when the mass ratio of coal gangue and carbon black was 100:40. The intensity of 0'-sialon grew and weak corundum phase generated (Fig. 3c). The intensity of β-sialon fell continually with an increase of the carbon content. When the mass ratio of coal gangue and carbon black was 100:50, corundum phase disappeared again and β-sialon, 0'-sialon and Si_3N_4 formed the synthesized samples (Fig. 3d). It demonstrated that β-sialon and 0'-sialon were available in the samples and β-sialon converted to 0'-sialon with an increase of carbon content in the samples.

3.3 SEM images analysis

Figure 4 shows the SEM images of samples with different carbon content after heat treatment at 1300, 1400 and 1500 °C for 6 h, and Fig. 4 (a–d) are the SEM images of samples heated at 1300 °C for 6 h. As the figures show, all the samples were incompact and there were many holes. Mullite had a sheet structure and there was some spherical mullite attached to coal gangue, while coal gangue melted partly. Figure 4 (e–h) shows the SEM images of samples heated at 1400 °C for 6 h. As the figures show, big particles disappeared when the carbon content of the samples was 100:20 (Fig. 4e, f), indicating that mullite was fully reacted. Point 1 in Fig. 4e refers to the new phase β-sialon when comparing the EDS spectrum (Fig. 5a) and XRD analysis (Fig. 2a). There were many molten phases, and hexagonal column phases co-existed in Fig. 4h, which was β-sialon according to the analysis of the energy spectrum. Figure 4 (i, j) shows the SEM images of samples heated at 1500 °C for 6 h. As shown, there were many needle-like phases and hexagonal prism

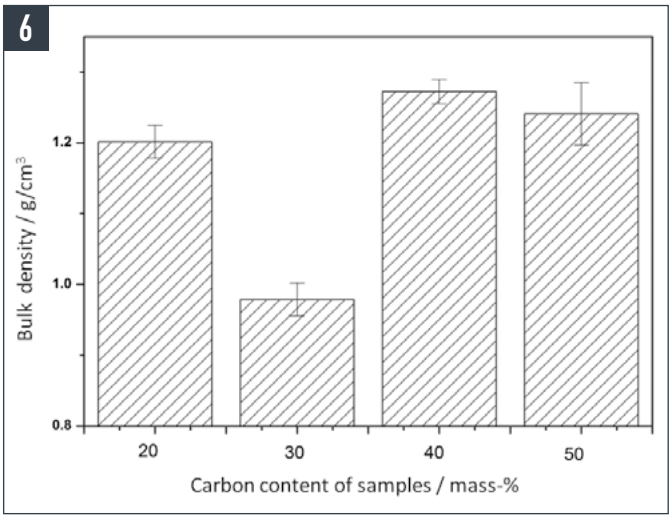

***Fig. 6** • Bulk density of samples with different carbon content at 1400 °C*

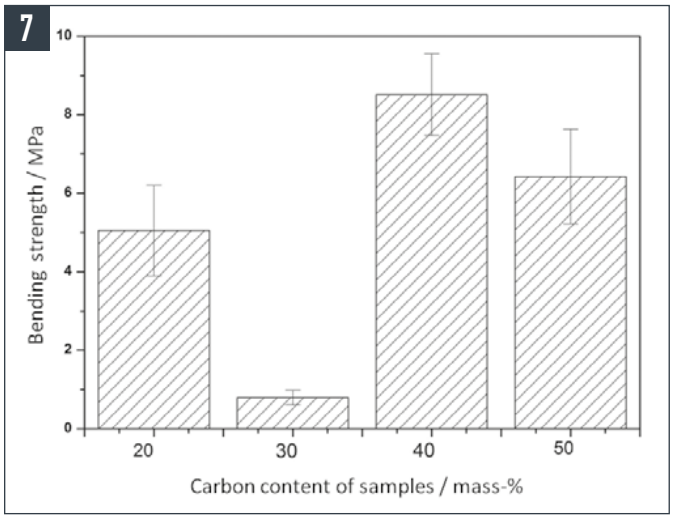

***Fig. 7** • Bending strength of samples with different carbon content at 1400 °C*

particles were reduced, which was 0′-sialon according to the analysis of the energy spectrum (Fig. 5c) to the square area in Fig. 4i. The needlelike phase thickened and increased in number when the mass ratio of coal gangue and carbon black was 100:50 (Fig. 4j). The layered and columnar particles decreased because of the conversion from β-sialon to 0′-sialon.

3.4 Analysis of mechanical properties

3.4.1 Bulk density analysis

Through the phase composition and microstructure analysis of the synthetic samples, it can be known that the sialon phase can be generated in the synthetic samples; one of the most obvious ones being at 1400 °C. The microstructures of phases were clear in the SEM images and the samples synthesized at 1400 °C were chosen for the analysis of the relevance mechanical properties. Figure 6 shows the bulk density of samples after heat treatment at 1400 °C for 6 h. The dry bulk density means the ratio of the quality to the total volume and this was determined by Archimedes' method [8]. As Fig. 6 shows, the bulk density of samples fell obviously when the mass ratio of coal gangue and carbon black changed from 100:20 to 100:30. Comparing the XRD patterns (Fig. 2a, b) and SEM images (Fig. 4e, f), it can be seen that the decrease of the bulk density was due to the generation of corundum. The bulk density increased with a continued increase of the carbon content in the samples, which was due to the decrease of holes in the samples and the full conversion from β-sialon to 0′-sialon.

3.4.2 Bending strength analysis

Figure 7 shows the bending strength of samples after heat treatment at 1400 °C for 6 h. The bending strength of samples was measured by a three-point bending method. As the figure shows, the bending strength of samples obviously fell when the mass ratio of coal gangue and carbon black changed from 100:20 to 100:30. This is due to the disappearance of quartz and the generation of corundum. With a continued increase in the carbon content of samples, the bending strength of synthetic samples increased. This is because the sialon phase was generated completely and the holes decreased.

4. Conclusions

(0′+β)-sialon/mullite composite materials were synthesized by an in-situ carbothermal reduction nitridation method at 1400 and 1500 °C, with coal gangue and carbon black as raw materials. The generative process of (0′+β)-sialon/mullite composite materials including the generation of β-sialon, 0′-sialon and the conversion process from β-sialon to 0′-sialon. In these synthetic materials, β-sialon mostly exists in the form of sheet structure and hexagonal column. 0′-sialon exists in the form of needle-like structures. The increase of carbon content is conducive to synthesizing β-sialon and 0′-sialon and benefits the conversion from β-sialon to 0′-sialon. The bending strength and bulk density of the composite materials fell when corundum was generated.

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