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Effects of synthesis temperature and raw materials composition on preparation of β-Sialon based composites from fly ash

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Abstract: β-Sialon based composites were successfully prepared from fly ash and carbon black under nitrogen atmosphere by carbothermal reduction-nitridation process. Effects of heating temperature and raw materials composition on synthesis process were investigated, and the formation process of the composites was also discussed. The phase composition and microstructure of the composites were characterized by X-ray diffraction and scanning electronic microscopy. The results show that increasing heating temperature or mass ratio of carbon black to fly ash can promote the formation of β-Sialon. The β-Sialon based composites can be synthesized at 1723 K for 6 h while heating the sample with mass ratio of carbon black to fly ash of 0.56. The as-received β-Sialon in the composites exists as granular with an average particle size of 2−3 μm. The preparation process of β-Sialon based composites includes the formation of O'-Sialon, X-Sialon and β-Sialon as well as the conversion processes of O'-Sialon and X-Sialon to β-Sialon.
Key words: Sialon; composites; carbothermal reduction-nitridation process; fly ash; synthesis temperature; raw materials composition

1 Introduction

Sialon includes β-Sialon ($Si_{6-z}Al_zO_zN_{8-z}$, $0<z<4.2$), O'-Sialon ($Si_{2-x}Al_xO_{1+x}N_{2-x}$, $0<x<0.3$) and α-Sialon ($M_xSi_{12-(m+n)}Al_{m+n}O_nN_{16-n}$, $0<x\leq2$). β-Sialon has been gained much attention because it displays many outstanding properties, such as high strength, fracture toughness and hardness as well as excellent wear, corrosion and oxidation resistance, and has been found many applications involving engineering ceramics, cutting tools and refractories [1, 2]. β-Sialon can be synthesized successfully by many technical processes, such as solid state reaction process, microwave synthesis [3], sol-gel synthesis [4], combustion synthesis [5], and carbothermal reduction-nitridation process [6]. Carbothermal reduction-nitridation process has been regarded as a potential beneficial method to synthesize β-Sialon with low cost, using cheap raw materials containing aluminum and silicon like clay [7], pyrophyllite [8], bauxite [9], zeolite [10], coal gangue [11, 12] and rice husks [13].

Fly ash emerges as a by-product from the combustion of raw coal in thermal power plants. Until 2020, the present accumulating amount of fly ash in China is approximately three billion tons. The mass waste causes serious environmental problems. Thus, the effective and comprehensive utilization of waste fly ash can provide an important route to solve these problems. Meanwhile, the high value-added products with low cost such as mullite and mullite-zirconia-corundum composites can be produced using fly ash [14, 15].

In the present work, the β-Sialon based composites were synthesized by carbothermal reduction-nitridation process, with fly ash and carbon black as raw materials. The effects of heating temperature and raw materials composition on synthesis process were investigated, and the formation process of the composites was also discussed.

2 Experimental

2.1 Raw materials

Fly ash (mesh size≤74 μm) and carbon black (mesh size≤30 μm) were used as raw materials, and the chemical composition of fly ash (mass fraction) was Al_2O_3 41.20%, SiO_2 48.49%, Fe_2O_3 3.37%, CaO 3.31%, TiO_2 1.30% and MgO 0.20%. In Fig. 1 the crystalline

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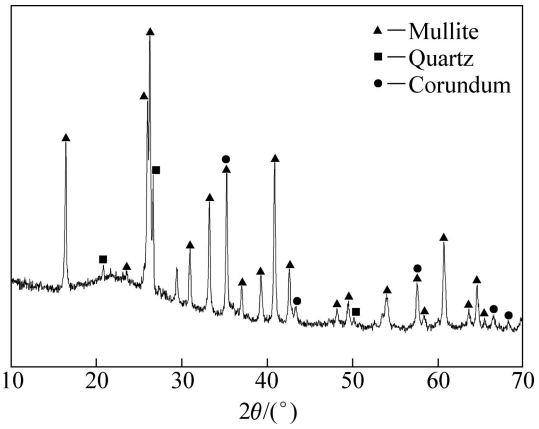

Fig. 1 XRD pattern of fly ash

phases of fly ash mainly include mullite as well as small amounts of corundum (Al_2O_3) and quartz (SiO_2). In addition, the mass fraction of C in carbon black and the volume fraction of nitrogen gas (N_2) were 98.0% and 99.99%, respectively.

2.2 Preparation of samples

The overall chemical reaction equation for synthesizing β-Sialon from fly ash by carbothermal reduction-nitridation process can be expressed as

$$Al_6Si_2O_{13}(s)+4SiO_2(s)+15C(s)+5N_2(g)=\!=2Si_3Al_3O_3N_5(s)+15CO(g) \quad (1)$$

According to reaction (1), the mass ratio of carbon black to fly ash (m_c/m_f) was 0.25. Fly ash was mixed with carbon black in m_c/m_f of 0.28, 0.30, 0.42 and 0.56. This over-stoichiometry of carbon black was necessary to promote the carbothermal reduction-nitridation reaction. Mixing was performed in a ball mill with anhydrous ethanol for 12 h, and then the mixed powders were pressed to form the samples with 20 mm in diameter and 10 mm in thickness under a pressure of 20 MPa. Then the formed samples were dried fully at 393 K and put into a graphite crucible. The crucible was placed in an atmosphere-controlled tubular furnace and then heated up to 1673 K and 1723 K for 6 h, respectively. During the synthesis process, the N_2 flow remained at 1.0 L/min. After the predetermined temperature and time reached, the system was cooled to room temperature.

2.3 Characterization of samples

The samples with different m_c/m_f values synthesized at 1673 and 1723 K were oxidized in air at 973 K for 2 h to remove residual carbon. The phase composition and microstructure of the products were characterized by X-ray diffractometer (XRD, Cu K_α radiation, 30 kV and 30 mA), scanning electronic microscopy (SEM) and energy dispersive spectrum (EDS).

3 Results and discussion

3.1 Phase composition and microstructure

Figure 2 shows the XRD patterns of the samples with different m_c/m_f values synthesized at 1673 K for 6 h. With increasing m_c/m_f from 0.28 to 0.30 (Figs. 2(a) and (b)), the diffraction intensities of mullite and *O′*-Sialon phases weaken gradually, and the diffraction intensities of β-Sialon and corundum phase strengthen. This indicates that increasing carbon content in a sample can promote the carbothermal reduction-nitridation reaction. The samples with m_c/m_f of 0.28 and 0.30 all consist of mullite and *O′*-Sialon. In Fig. 2(c), β-Sialon can be detected in the sample with m_c/m_f of 0.42, and the sample is composed of mullite, *O′*-Sialon and β-Sialon. In Fig. 2(d), corundum can be detected in the higher carbon content sample (m_c/m_f=0.56), and the sample mainly includes mullite, corundum, *O′*-Sialon and β-Sialon.

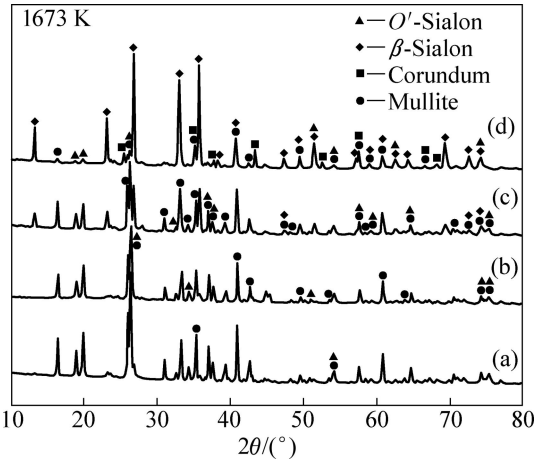

Fig. 2 XRD patterns of samples with different m_c/m_f values synthesized at 1673 K for 6 h: (a) 0.28; (b) 0.30; (c) 0.42; (d) 0.56

Figure 3 shows the XRD patterns of the samples with different m_c/m_f values synthesized at 1723 K for 6 h. With increasing m_c/m_f from 0.28 to 0.56, the diffraction intensities of mullite and *X*-Sialon phases weaken gradually, and the diffraction intensities of β-Sialon and corundum phase strengthen. In Figs. 3(a) and (b) the samples with m_c/m_f of 0.28 and 0.30 all consist of mullite, corundum and *X*-Sialon. β-Sialon can be detected in the sample with m_c/m_f of 0.42 (Fig. 3(c)), and the mullite phase vanishes completely, showing that the sample is composed of *X*-Sialon, β-Sialon and corundum. In Fig. 3(d) the diffraction intensity of *X*-Sialon in the sample with m_c/m_f of 0.56 weakens remarkably, and the main crystalline phase is β-Sialon. Thus, increasing carbon content in a sample can promote the decomposition of mullite and the formation of β-Sialon.

Figures 4(a) and (b) show the SEM images of the

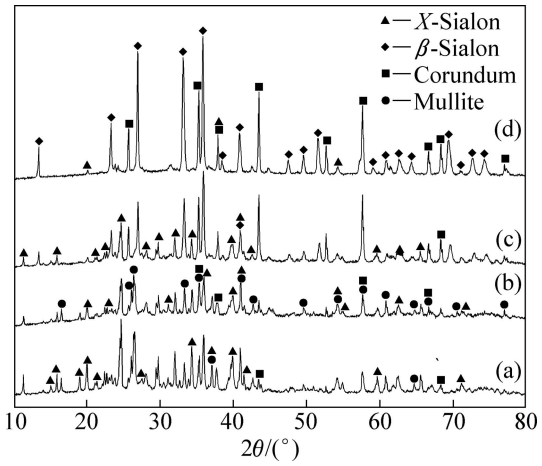

Fig. 3 XRD patterns of samples with different m_c/m_f values synthesized at 1723 K for 6 h: (a) 0.28; (b) 0.30; (c) 0.42; (d) 0.56

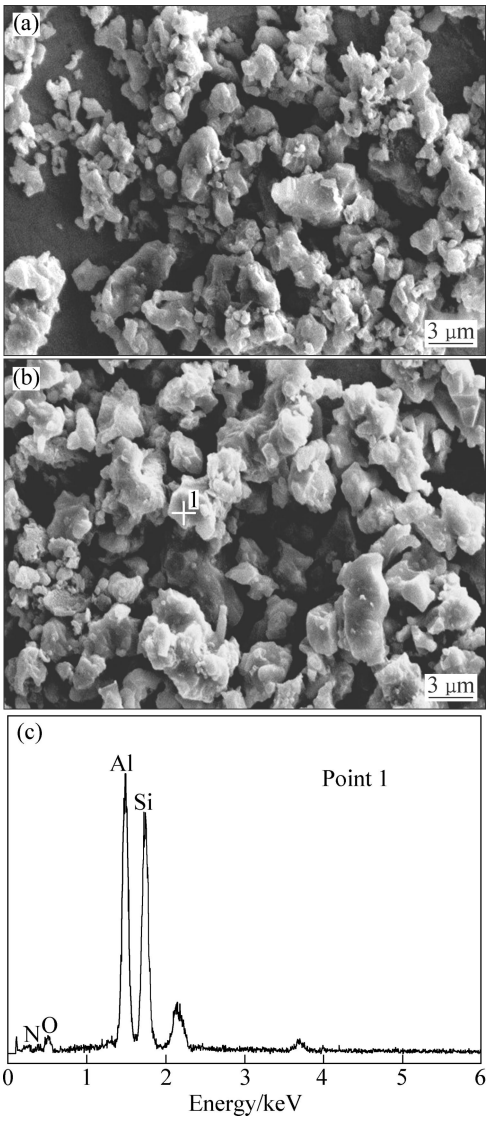

Fig. 4 SEM images of samples with m_c/m_f of 0.56 synthesized at 1673 K (a) and 1723 K (b), and EDS pattern of point 1 in Fig. 4(b)

samples with m_c/m_f of 0.56 synthesized at 1673 K and 1723 K for 6 h, respectively. The particles in the composites exist as granular. The average particle size synthesized at 1673 K and 1723 K reaches 1−2 μm (Fig. 4(a)) and 2−3 μm (Fig. 4(b)), respectively. EDS analysis (Fig. 4(c)) indicates that the particle (point 1) as shown in Fig. 4(b) is composed of Si, Al, O and N elements. By combing with XRD pattern (Fig. 3(d)), point 1 is *β*-Sialon.

3.2 Analysis of formation process

The carbothermal reduction-nitridation reaction process for synthesizing *β*-Sialon based composites from fly ash is very complex and involves many chemical reactions. During the synthesis process, CO, SiO, Si_2N_2O, Si_3N_4 and AlN are regarded as important intermediate products. With changing heating temperature and raw materials composition, *O′*-Sialon, *X*-Sialon and *β*-Sialon may be formed.

$$SiO_2(s)+C(s)=SiO(g)+CO(g) \quad (2)$$

$$2SiO(g)+C(s)+N_2(g)=Si_2N_2O(s)+CO(g) \quad (3)$$

$$2SiO_2(s)+3C(s)+N_2(g)=Si_2N_2O(s)+3CO(g) \quad (4)$$

$$3SiO(g)+3C(s)+2N_2(g)=Si_3N_4(s)+3CO(g) \quad (5)$$

$$3SiO_2(s)+6C(s)+2N_2(g)=Si_3N_4(s)+6CO(g) \quad (6)$$

$$3Si_2N_2O(s)+3C(s)+N_2(g)=2Si_3N_4(s)+3CO(g) \quad (7)$$

$$Al_2O_3(s)+3C(s)+N_2(g)=2AlN(s)+3CO(g) \quad (8)$$

$$1.83Si_2N_2O(s)+0.17Al_2O_3(s)=2Si_{1.83}Al_{0.17}O_{1.17}N_{1.83}(s) \quad (9)$$

$$Al_2O_3(s)+Si_3N_4(s)+AlN(s)=Si_3Al_3O_3N_5(s) \quad (10)$$

$$1/2Al_6Si_2O_{13}(s)+2SiO_2(s)+15/2C(s)+5/2N_2(g)=Si_3Al_3O_3N_5(s)+15/2CO(g) \quad (11)$$

$$0.17/6Al_6Si_2O_{13}(s)+5.32/3SiO_2(s)+5.49/2C(s)+1.83/2N_2(g)=Si_{1.83}Al_{0.17}O_{1.17}N_{1.83}(s)+5.49/2CO(g) \quad (12)$$

$$Al_6Si_2O_{13}(s)+SiO_2(s)+3C(s)+N_2(g)=Si_3Al_6O_{12}N_2(s)+3CO(g) \quad (13)$$

The Gibbs free energies of formation of $Al_6Si_2O_{13}$, SiO_2, Al_2O_3, CO, *O′*-Sialon and *β*-Sialon are listed in Table 1 [16, 17]. When the partial pressure of N_2 is equal to p^{Θ}(0.1 MPa), the Gibbs free energies for reactions (11) and (12) as well as the relationship between partial pressure of CO gas (p_{CO})and temperature can be further obtained. It is noted that the Gibbs formation free energy of *O′*-Sialon (*x*=0.17) is lack, so it is approximately equal to that of *O′*-Sialon (*x*=0.2) during the process of calculating relational thermodynamics data.

$$\Delta G_{11}^{\Theta}/(J\cdot mol^{-1})=1527605-844.13T,\ \lg(p_{CO}/p^{\Theta})=5.88-10637.65/T \quad (14)$$

$$\Delta G_{12}^{\Theta}/(J\cdot mol^{-1})=338819-293.97T,\ \lg(p_{CO}/p^{\Theta})=5.59-6446.46/T \quad (15)$$

Table 1 Gibbs free energies of formation of some compounds in Al_2O_3−SiO_2−C−N_2 system

Chemical reaction	ΔG^{Θ}/(J·mol^{-1})
$Al_2O_3(s)+SiO_2(s)=Al_6Si_2O_{13}(s)$	20150−28.55T
$Si(L)+O_2(g)=SiO_2(s)$	−946350+197.64T
$2Al(L)+3/2O_2(g)=Al_2O_3(s)$	−1682900+323.24T
$C(s)+1/2O_2(g)=CO(g)$	−114400−85.77T
$0.1Al_2O_3(s)+1.8SiO_2(s)+2.7C(s)+0.9N_2(g)=Si_{1.8}Al_{0.2}O_{1.2}N_{1.8}+2.7CO(g)$	−1024776+291.14T
$3/2Al_2O_3(s)+3SiO_2(s)+15/2C(s)+5/2N_2(g)=Si_3Al_3O_3N_5(s)+15/2CO(g)$	−1537680−858.41T

Figure 5 shows the predomination region diagram for Al_2O_3−SiO_2−C−N_2 system plotted by the thermodynamic data as shown in Eqs. (14) and (15). It indicates that when the partial pressure of CO gas (p_{CO}) in the reacting furnace remains constant, with increasing heating temperature, C in a sample can react with SiO_2, Al_2O_3 and N_2 to form O'-Sialon (reactions (2)−(4), (9), (12)) and further produce β-Sialon (reactions (2), (5)−(8), (10), (11)). The predomination regions change from $Al_2O_3(s)$ + $SiO_2(s)$ + C(s) to $Al_2O_3(s)$ + O'-Sialon(s) + C(s) and $Al_2O_3(s)$ + β-Sialon(s) + C(s), respectively. When the temperature remains constant, with decreasing p_{CO}, the predomination regions change from $Al_2O_3(s)$ + $SiO_2(s)$ + C(s) to $Al_2O_3(s)$ + O'-Sialon(s) + C(s) and $Al_2O_3(s)$ + β-Sialon(s) + C(s), respectively. Thus, proper partial pressure of CO gas and temperature are key factors for the synthesis of β-Sialon based composites.

During the carbothermal reduction-nitridation reaction process, X-Sialon can be formed (reaction (13)). With increasing synthesis temperature and carbon content, X-Sialon and O'-Sialon can be nitridized to produce β-Sialon (reactions (16) and (17)). This can be confirmed by the XRD patterns as shown in Figs. 2 and 3.

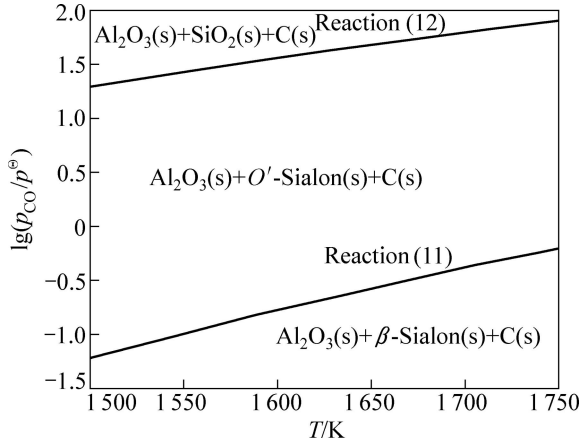

Fig. 5 Predomination region diagram for Al_2O_3−SiO_2−C−N_2 system (p_{N_2} =0.1 MPa)

$$Si_3Al_6O_{12}N_2(s)+3SiO_2(s)+12C(s)+4N_2(g)=2Si_3Al_3O_3N_5(s)+12CO(g) \quad (16)$$

$$Si_{1.83}Al_{0.17}O_{1.17}N_{1.83}(s)+0.83Al_2O_3(s)+1.83C(s)+0.61N_2(g)=0.61Si_3Al_3O_3N_5(s)+1.83CO(g) \quad (17)$$

Additionally, Al_2O_3 and SiO_2 in fly ash can also react with C and N_2 to form O'-Sialon, X-Sialon and β-Sialon (reactions (18)−(20)):

$$0.17Al_2O_3(s)+3.66SiO_2(s)+5.49C(s)+1.83N_2(g)=2Si_{1.83}Al_{0.17}O_{1.17}N_{1.83}(s)+5.49CO(g) \quad (18)$$

$$3Al_2O_3(s)+3SiO_2(s)+3C(s)+N_2(g)=Si_3Al_6O_{12}N_2(s)+3CO(g) \quad (19)$$

$$3Al_2O_3(s)+6SiO_2(s)+15C(s)+5N_2(g)=2Si_3Al_3O_3N_5(s)+15CO(g) \quad (20)$$

The formation process of β-Sialon based composites can be summarized as follows.

1) In a sample with lower carbon content (m_c/m_f= 0.28−0.42), O'-Sialon and X-Sialon can be fabricated at 1673 K and 1723 K, respectively. And they can be further converted into β-Sialon by increasing synthesis temperature and carbon content.

2) In a sample with higher carbon content (m_c/m_f= 0.56), β-Sialon can be directly produced at 1673 K and 1723 K.

4 Conclusions

1) The β-Sialon based composites can be successfully prepared from fly ash by carbothermal reduction-nitridation process, and the proper technological parameters are m_c/m_f of 0.56 and heating temperature of 1723 K.

2) The as-received β-Sialon exists as granular, and the average particle size of β-Sialon is 2−3 μm.

3) The preparation processes of β-Sialon based composites includes the formation of O'-Sialon, X-Sialon and β-Sialon as well as the conversion process of O'-Sialon and X-Sialon to β-Sialon.

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合成温度和配料组成对粉煤灰制备 β-Sialon 基复合材料的影响

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摘 要：以粉煤灰和炭黑为原料，采用碳热还原氮化法成功制备出 β-Sialon 基复合材料。研究了加热温度和配料组成对合成过程的影响，分析了材料的生成过程。采用 XRD 和 SEM 手段表征了合成材料的相组成和显微结构。结果表明：升高加热温度，增大炭黑与粉煤灰的质量比均可以促进 β-Sialon 的生成；将炭黑与粉煤灰质量比为 0.56 的试样加热至 1723 K 并保温 6 h，可以合成 β-Sialon 基复合材料；合成材料中 β-Sialon 多以粒状形式存在，平均粒径为 2~3 μm；β-Sialon 基复合材料的生成过程包括 *O′*-Sialon、*X*-Sialon 和 β-Sialon 的生成及 *O′*-Sialon 和 *X*-Sialon 向 β-Sialon 的转化过程。

关键词：赛隆；复合材料；碳热还原氮化法；粉煤灰；合成温度；配料组成

(Edited by LI Xiang-qun)