

Fabrication of β -Sialon/ZrN/ZrON composites using fly ash and zircon

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Abstract: β -Sialon/ZrN/ZrON composites were successfully fabricated by an in-situ carbothermal reduction–nitridation process with fly ash, zircon and active carbon as raw materials. The effects of raw materials composition and holding time 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 means of XRD and SEM. It was found that increasing carbon content in a sample and holding time could promote the formation of β -Sialon, ZrN and ZrON. The proper processing parameters to synthesize β -Sialon/ZrN/ZrON composites were mass ratio of zircon to fly ash to active carbon of 49:100:100, synthesis temperature of 1550 °C and holding time of 15 h. The average grain size of β -Sialon and ZrN(ZrON) synthesized at 1550 °C for 15 h reached about 2 and 1 μm , respectively. The fabrication process of β -Sialon/ZrN/ZrON composites included the formation of β -Sialon and ZrO_2 as well as the conversion of ZrO_2 to ZrN and ZrON.

Key words: Sialon; ZrN; ZrON; in-situ synthesis; carbothermal reduction-nitridation process; fly ash; zircon

1 Introduction

β -Sialon ($\text{Si}_{6-z}\text{Al}_z\text{O}_2\text{N}_{8-z}$, where $0 < z < 4.2$) has been widely used in many applications such as engineering ceramics, cutting tools and refractory materials due to its excellent resistance to thermal shock, corrosion and oxidation and wear [1]. Zirconium nitride (ZrN) and zirconium oxide nitride (ZrON) also display excellent properties such as high hardness and strength, good corrosion and oxidation resistance [2,3]. The β -Sialon/ZrN/ZrON composites prepared from ZrN, ZrON and β -Sialon might yield remarkable high temperature properties.

β -Sialon has been fabricated successfully via a reaction–bonding method [4], carbothermal reduction–nitridation (CTRN) process [5], combustion synthesis [6], microwave synthesis [7] and sol–gel synthesis [8]. CTRN method has the potential of being an economical synthesis process, utilizing inexpensive and abundant natural minerals and solid wastes containing alumina (Al_2O_3) and silica (SiO_2) such as kaolin [9], pyrophyllite [10], bauxite [11], coal gangue [12] and fly ash [13].

Fly ash emerges as a by-product from the

combustion of raw coal in thermal power plants. In recent years, mass waste fly ash has been causing serious environmental problems. So it is necessary to find an effective and comprehensive utilization of fly ash. Zircon (ZrSiO_4) consists of zirconia (ZrO_2) and SiO_2 . So far, fly ash and ZrSiO_4 have been chosen as the raw materials to synthesize ceramic materials such as β -Sialon [5,13], SiC–AlN [14], SiC–mullite [15], mullite [16], ZrO_2 –mullite– Al_2O_3 [17] and ZrO_2 –SiC [18], etc.

In this work, the β -Sialon/ZrN/ZrON composites were fabricated from fly ash and zircon by a CTRN process. The effects of raw materials composition and holding time on the phase composition and microstructure of the products were investigated, and the formation process of the composites was also discussed.

2 Experimental

2.1 Raw materials

Fly ash (mesh size $\leq 74 \mu\text{m}$), zircon (mesh size $\leq 44 \mu\text{m}$) and active carbon (analytical reagent) were used as the raw materials. The main crystalline phase of fly ash was mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$). The composition of the raw materials was listed in Table 1.

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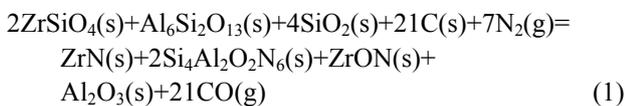
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Table 1 Composition of raw materials (mass fraction, %)

Composition	Fly ash	Zircon
Al ₂ O ₃	41.20	0.42
SiO ₂	48.49	32.34
Fe ₂ O ₃	3.37	0.07
CaO	3.31	0.02
TiO ₂	1.30	0.11
MgO	0.20	0.02
ZrO ₂	–	66.75

2.2 Preparation of samples

The overall chemical reaction equation for synthesizing β -Sialon/ZrN/ZrON from fly ash and zircon by a CTRN process can be expressed as follows:



According to Eq. (1), the mass ratio of zircon to fly ash to active carbon ($m_z:m_f:m_c$) was 49:100:34. Over-stoichiometry of active carbon was added to promote the CTRN reaction. Zircon, fly ash and active carbon were weighed and mixed in different mass ratios $m_z:m_f:m_c$ of 49:100:40, 49:100:60, 49:100:80 and 49:100:100, respectively. Mixing was conducted in a ball mill with anhydrous ethanol for 6 h, fully dried at 60 °C, and the samples with 20 mm in diameter and 10 mm in thickness were formed under a pressure of 20 MPa. Then the formed samples were fully dried at 120 °C and put into a graphite crucible. The crucible was placed in an atmosphere-controlled tubular furnace and then heated up to 1550 °C for 6, 9, 12 and 15 h, respectively. During the synthesis process, the N₂ flow remained to be 1.0 L/min. After the predetermined temperatures and holding time reached, the system was cooled to room temperature.

2.3 Characterization of samples

The samples synthesized at different reaction conditions were oxidized in air at 700 °C for 2 h to remove residual carbon. The phase composition and microstructure of the products were characterized by X-ray diffraction (XRD, Cu K α radiation, 30 kV and 30 mA) and scanning electronic microscopy (SEM).

3 Results and discussion

3.1 Phase composition

Figure 1 shows the XRD patterns of the samples with different raw materials composition synthesized at 1550 °C for 12 h. It can be observed that raw material composition has a great influence on the phase

composition of the synthesized samples. The synthesized products with $m_z:m_f:m_c$ values of 49:100:40 and 49:100:60 are mainly composed of mullite, m -ZrO₂, Al₂O₃ and Fe₃Si. Sialon and zircon phase are not detected, which indicates that zircon is decomposed completely and forms m -ZrO₂ and SiO₂. The formed SiO₂ can react with C and Fe₂O₃ to form Fe₃Si, where Fe₂O₃ is an impurity in fly ash and zircon. Increasing carbon content in a sample ($m_z:m_f:m_c=49:100:80$) causes the phase composition of the products to have a great change. Mullite vanishes completely. β -Sialon and ZrN can be detected. The sample consists of β -Sialon, ZrN, m -ZrO₂, Al₂O₃ and FeSi. By varying the value of $m_z:m_f:m_c$ from 49:100:80 to 49:100:100, the peak intensities of β -Sialon and ZrN strengthen remarkably, however, the peak intensity of m -ZrO₂ decreases. Meanwhile, Al₂O₃ phase vanishes, new phase ZrON forms, and its diffraction intensity is lower. The main crystalline phases of the sample with $m_z:m_f:m_c$ value of 49:100:100 includes β -Sialon and ZrN. Thus, increasing carbon content in a sample is favorable for the CTRN reaction, and the proper raw materials composition ($m_z:m_f:m_c$) to synthesize β -Sialon/ZrN/ZrON is 49:100:100.

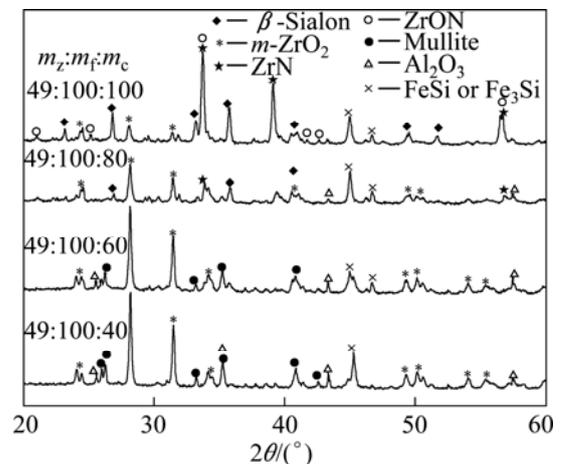


Fig. 1 XRD patterns of samples with different $m_z:m_f:m_c$ values synthesized at 1550 °C for 12 h

Figure 2 shows the XRD patterns of the samples with $m_z:m_f:m_c$ value of 49:100:100 synthesized at 1550 °C for 6, 9, 12 and 15 h, respectively. It can be seen that holding time also has a great influence on the phase composition of the products. The samples heated at 1550 °C for 6 and 9 h all involve β -Sialon, ZrN, ZrON, m -ZrO₂, Al₂O₃ and FeSi, and their main crystalline phases are β -Sialon and m -ZrO₂. When the holding time reaches 12 h, Al₂O₃ phase vanishes. The peak intensities of β -Sialon, ZrN and ZrON strengthen obviously, however, the diffraction intensity of m -ZrO₂ weakens. In

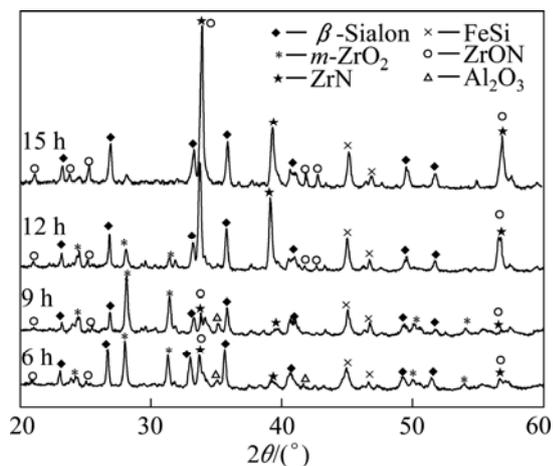


Fig. 2 XRD patterns of samples with $m_z:m_f:m_c$ of 49:100:100 synthesized at 1550 °C for 6, 9, 12 and 15 h

the sample fabricated at 1550 °C for 15 h, m -ZrO₂ phase vanishes, the peak intensities of β -Sialon, ZrN and ZrON further strengthen, and the main crystalline phases include β -Sialon, ZrN and ZrON. It indicates that increasing holding time is good for the formation of β -Sialon, ZrN and ZrON.

It can be observed from Figs. 1 and 2 that the proper processing parameters to synthesize β -Sialon/ZrN/ZrON

are $m_z:m_f:m_c$ value of 49:100:100, synthesis temperature of 1550 °C and holding time of 15 h.

3.2 Microstructure

Figure 3 shows the SEM images of the samples with different raw materials composition ($m_z:m_f:m_c$) synthesized at 1550 °C for 12 h. There exist many fine particles in the sample with $m_z:m_f:m_c$ values of 49:100:40 and 49:100:60 (Figs. 3(a) and (b)), and their average grain size is about 1 μ m. EDS analysis and XRD pattern (Fig. 1) indicate that they are ZrO₂. Some big particles with an average grain size of 2–3 μ m can also be observed. They consist of Si, Al and O elements. Combining with the XRD pattern as shown in Fig. 1, they are mullite. Increasing carbon content in a sample (Figs. 3(c) and (d)) can promote the CTRN reaction and make the fine particles grow up.

Figure 4 shows the SEM images of the samples with $m_z:m_f:m_c$ value of 49:100:100 synthesized at 1550 °C for 6–15 h. Big flaky and fine particles can be observed in the products synthesized at 1550 °C for 6 h, and their average grain size are 3 and 1 μ m, respectively. EDS analysis indicates that the big flaky particles are β -Sialon, and the fine particles are composed of Zr, O and N elements, they are composite body of ZrO₂, ZrN and ZrON, which can be confirmed by the XRD pattern

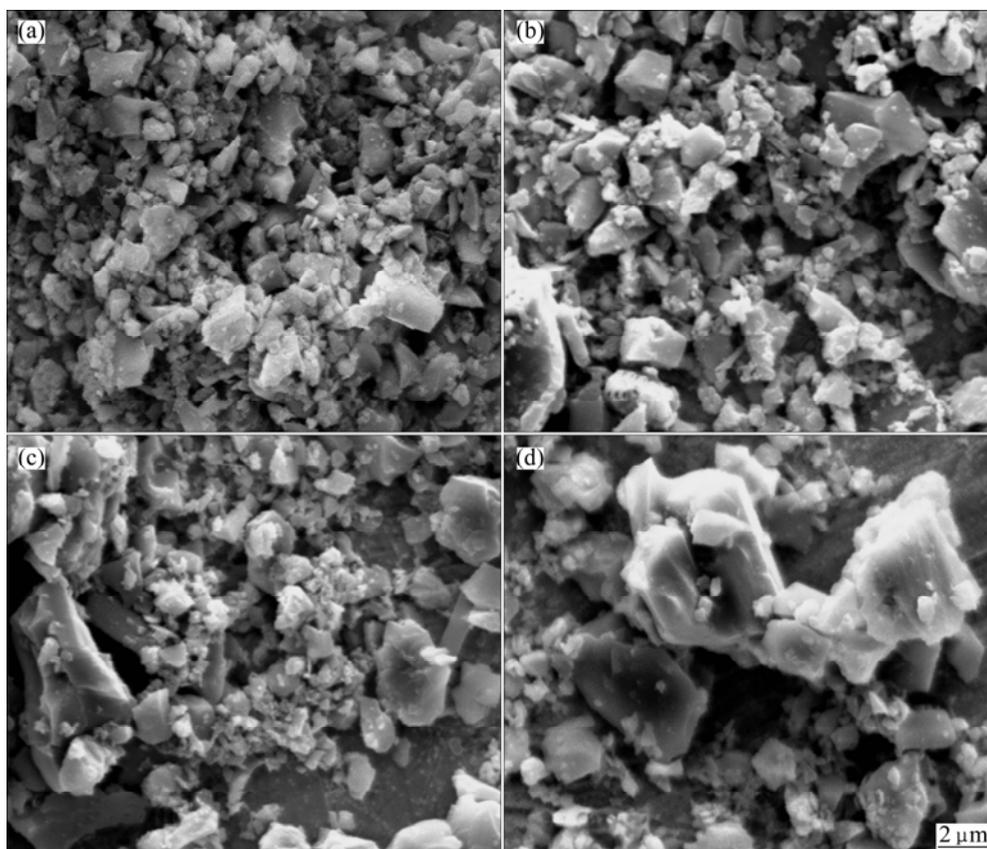


Fig. 3 SEM images of samples with different $m_z:m_f:m_c$ values synthesized at 1550 °C for 12 h: (a) 49:100:40; (b) 49:100:60; (c) 49:100:80; (d) 49:100:100

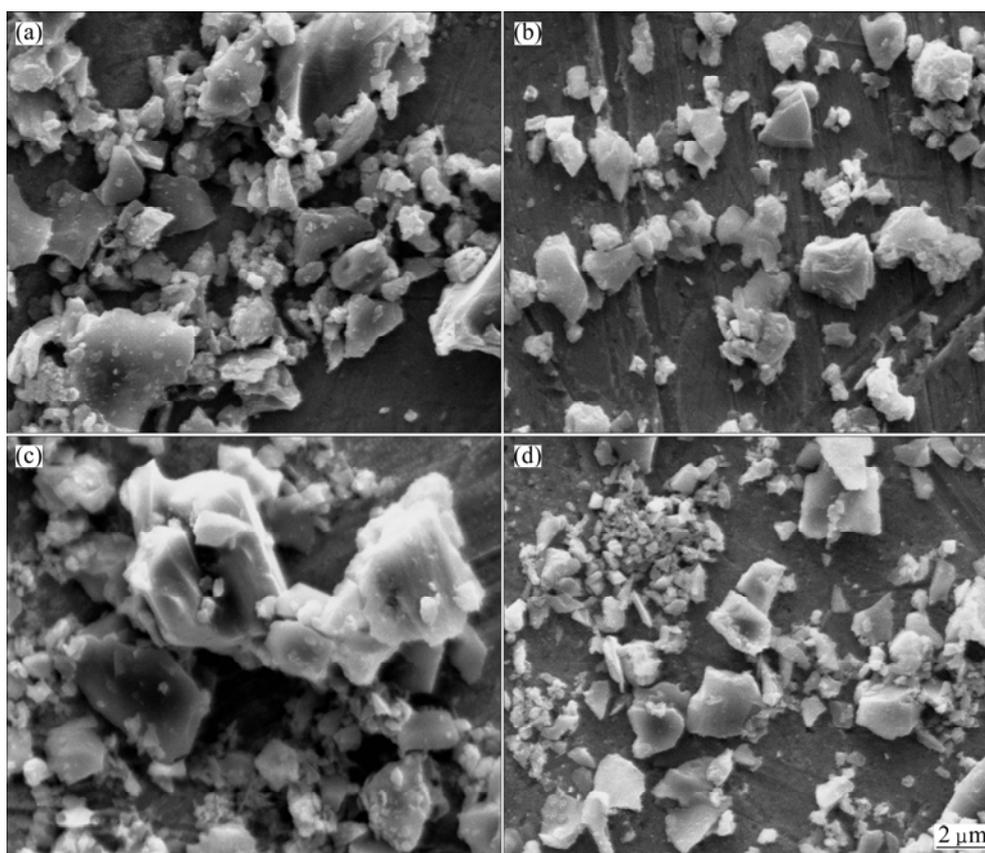


Fig. 4 SEM images of samples with $m_z:m_f:m_c$ value of 49:100:100 synthesized at 1550 °C for 6 h (a) , 9 h (b), 12 h (c) and 15 h (d)

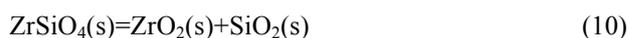
(Fig. 2). As increasing the holding time from 6 to 9, 12 and 15 h, respectively (Figs. 4(b), (c) and (d)), fine particles increase gradually, and their average grain size decreases. The reason is that during the CTRN process, ZrO_2 in a sample can react with C and N_2 to form new fine ZrN and ZrON particles. The average grain size of β -Sialon and ZrN(ZrON) synthesized at 1550 °C for 15 h reaches 2 and 1 μm , respectively.

3.3 Analysis of formation process

In this work, the fabrication process of β -Sialon/ZrN/ZrON composites is very complex and involves many chemical reactions. During the CTRN process, an important intermediate gas phase is carbon monoxide (CO). As changing the raw materials composition ($m_z:m_f:m_c=49:100:40, 49:100:60, 49:100:80$ and $49:100:100$) and holding time (6, 9, 12 and 15 h), $ZrO_2, SiO_2, Al_2O_3, \beta$ -Sialon ($z=2, Si_4Al_2O_2N_6$), ZrN and ZrON may be formed. Table 2 lists the Gibbs free energy changes of some compounds in $ZrO_2-Al_2O_3-SiO_2-C-N_2$ system [19,20]. The relationship between standard Gibbs energy change (ΔG^\ominus) and temperature (T) can be calculated according to these thermodynamic data. The chemical reactions are likely to occur during the CTRN process and the relational expression of ΔG^\ominus and T ($\Delta G^\ominus-T$) are as follows:

Table 2 Gibbs free energy changes of formation of some compounds in $ZrO_2-Al_2O_3-SiO_2-C-N_2$ system

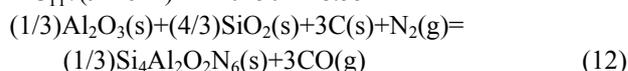
No.	Chemical reactions	$\Delta G^\ominus/(J \cdot mol^{-1})$
2	$Zr(s)+O_2(g)=ZrO_2(s)$	$-1092000+183.70T$
3	$Si(L)+O_2(g)=SiO_2(s)$	$-946350+197.64T$
4	$2Al(L)+3/2O_2(g)=Al_2O_3(s)$	$-1682900+323.24T$
5	$C(s)+1/2O_2(g)=CO(g)$	$-114400-85.77T$
6	$2Al(L)+4Si(L)+O_2(g)+3N_2(g)=Si_4Al_2O_2N_6(s)$	$-2598080+868.10T$
7	$Zr(s)+1/2N_2(g)=ZrN(s)$	$-363600+92.00T$
8	$ZrO_2(s)+SiO_2(s)=ZrSiO_4(s)$	$-26800+12.60T$
9	$3Al_2O_3(s)+2SiO_2(s)=Al_6Si_2O_{13}(s)$	$20150-28.55T$



$$\Delta G_{10}^\ominus/(J \cdot mol^{-1}) = 26800 - 12.60T$$



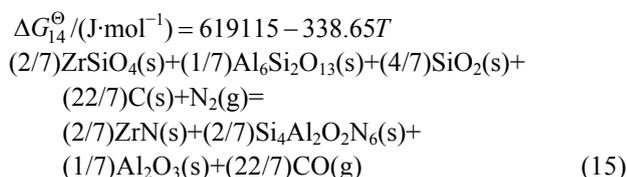
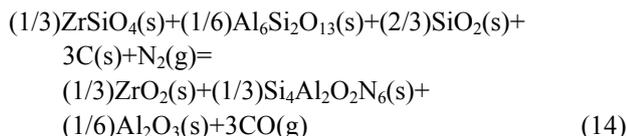
$$\Delta G_{11}^\ominus/(J \cdot mol^{-1}) = -20150 + 28.55T$$



$$\Delta G_{12}^\ominus/(J \cdot mol^{-1}) = 613540 - 339.21T$$



$$\Delta G_{13}^\ominus/(J \cdot mol^{-1}) = 999200 - 526.48T$$



$$\Delta G_{15}^{\ominus}/(\text{J}\cdot\text{mol}^{-1})=673413-365.48T$$

Figure 5 shows the diagram of $\Delta G^{\ominus}-T$ for $\text{ZrO}_2-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{C}-\text{N}_2$ system which were obtained from Eqs. (10)–(15). It can be seen that ΔG_{10}^{\ominus} and ΔG_{11}^{\ominus} for Eqs. (10) and (11), respectively, keep positive when the temperature is less than 1850 °C, which reveals that Eqs. (10) and (11) can not easily generate at the experimental temperature of 1550 °C. ΔG_{12}^{\ominus} , ΔG_{13}^{\ominus} , ΔG_{14}^{\ominus} and ΔG_{15}^{\ominus} for Eqs. (12)–(15), respectively, become negative at about 1630 °C, and they decrease sharply as increasing the temperature. At 1550 °C, the ΔG^{\ominus} values for Eqs. (10)–(15) are as follows: $\Delta G_{12}^{\ominus} < \Delta G_{14}^{\ominus} < \Delta G_{10}^{\ominus} < \Delta G_{11}^{\ominus} < \Delta G_{13}^{\ominus} < \Delta G_{15}^{\ominus}$. It indicates that the β -Sialon can be easily formed from Al_2O_3 and SiO_2 by the CTRN reaction. However, the CTRN reaction of ZrO_2 to form ZrN is very difficult. Increasing holding time to 12–15 h benefits the formation of ZrN (Fig. 2).

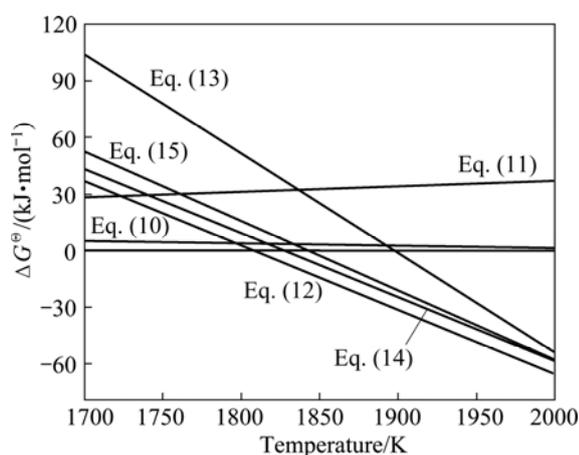
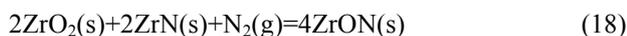


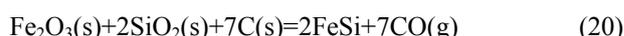
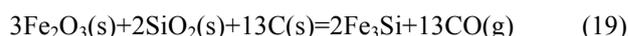
Fig. 5 Diagram of $\Delta G^{\ominus}-T$ for $\text{ZrO}_2-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{C}-\text{N}_2$ system

During the CTRN process, a small amount of ZrON can be formed from ZrO_2 , ZrSiO_4 and ZrN (Eqs. (16)–(18)), which can be confirmed by the XRD pattern as shown in Figs. 1 and 2.



As shown in Figs. 1 and 2, Fe_3Si and FeSi can be

detected in the products synthesized at 1550 °C. The reason is that there exists Fe_2O_3 in fly ash and zircon. During the CTRN process, Fe_2O_3 can react with SiO_2 and C to form Fe_3Si and FeSi (Eqs. (19) and (20)). An important fact is that FeSi forms in a sample with higher carbon content ($m_z:m_f:m_c=49:100:80$, $49:100:100$), and Fe_3Si can be detected in a sample with lower carbon content ($m_z:m_f:m_c=49:100:40$, $49:100:60$). There are many efforts needed to make to investigate the effect of processing parameters on the formation mechanisms of FeSi and Fe_3Si .



In this work, the formation process of β -Sialon/ ZrN/ZrON composites can be summarized as follows:

1) For the samples with lower carbon content ($m_z:m_f:m_c=49:100:40$, $49:100:60$), the CTRN process includes the formation of ZrO_2 due to the decomposition of zircon, the other decomposition product (SiO_2) reacts with Fe_2O_3 and C to synthesize Fe_3Si and FeSi .

2) For the samples with higher carbon content ($m_z:m_f:m_c=49:100:80$, $49:100:100$), the CTRN process includes the formation of β -Sialon and the conversion of ZrO_2 to ZrN and ZrON .

4 Conclusions

1) Increasing carbon content in a sample and holding time can promote the formation of β -Sialon, ZrN and ZrON . The β -Sialon/ ZrN/ZrON composites can be successfully fabricated at 1550 °C for 15 h while heating the samples with $m_z:m_f:m_c$ value of $49:100:100$.

2) The average grain size of β -Sialon and $\text{ZrN}(\text{ZrON})$ synthesized at 1550 °C for 15 h are about 2 and 1 μm , respectively.

3) The fabrication process of β -Sialon/ ZrN/ZrON composites includes the formation of β -Sialon and ZrO_2 as well as the conversion of ZrO_2 to ZrN and ZrON .

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用粉煤灰和锆英石制备 β -Sialon/ZrN/ZrON 复合材料

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摘要: 以粉煤灰、锆英石和活性炭为原料, 采用原位碳热还原氮化法成功制备 β -Sialon/ZrN/ZrON 复合材料。研究配料组成和保温时间对合成过程的影响, 并讨论材料的生成过程。通过 XRD 和 SEM 表征材料的相组成和显微组织。结果表明: 增加试样中的碳含量以及延长保温时间均能促进 β -Sialon、ZrN 和 ZrON 的生成。合成 β -Sialon/ZrN/ZrON 复合材料的适宜工艺参数为锆英石、粉煤灰和活性炭的质量比 49:100:100、合成温度 1550 °C、保温时间 15 h。在 1550 °C 保温 15 h 合成的 β -Sialon 和 ZrN(ZrON) 的平均粒径分别约为 2 和 1 μm 。 β -Sialon/ZrN/ZrON 复合材料的制备过程包括 β -Sialon 和 ZrO₂ 的生成过程以及 ZrO₂ 向 ZrN 和 ZrON 的转化过程。

关键词: Sialon; ZrN; ZrON; 原位合成; 碳热还原氮化法; 粉煤灰; 锆英石

(Edited by Chao WANG)