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Synthesis of ZrO_2-SiC composite powder and effect of its addition on properties of Al_2O_3-C refractories

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Abstract: ZrO_2-SiC composite powder was synthesized by carbothermal reduction of zircon in argon atmosphere, and it was used as the additive to prepare Al_2O_3-C refractories. The effects of heating temperature on the synthesis process and the addition of the synthesized composite powder on the properties of the Al_2O_3-C refractories were investigated. The results show that the synthesized composite powder can be easily obtained by heating the mixture of zircon and carbon black at 1 873 K for 4 h in argon atmosphere, and the relative contents of ZrO_2 and SiC in sample reach about 83.7% and 16.3%, respectively. The bulk density, crushing strength and thermal shock resistance of the Al_2O_3-C refractories can be improved obviously by the addition of the synthesized ZrO_2-SiC composite powder.

Key words: ZrO_2-SiC composite powder; carbothermal reduction; crushing strength; thermal shock resistance; Al_2O_3-C refractories

1 Introduction

Al_2O_3-C refractories have been widely used in high temperature metallurgical processes including iron making, steel making and continuous casting owing to the refractories' excellent properties[1]. In order to satisfy the development of continuous casting and hot iron pretreatment technologies, the properties of the refractories need to improve. The oxidation and corrosion resistance of the Al_2O_3-C refractories can be improved obviously by the addition of CaB_6[2], B_4C[3] and the synthesized Al_2O_3-SiC composite from clay[4]. In addition, ZrO_2 and SiC powders can also improve the properties of the Al_2O_3-C refractories due to their high toughness, wear and corrosion resistance[5−6]. However, high price of ZrO_2 and SiC especially ZrO_2 micro powders increases the cost of products and influences the application of them in the refractories.

In terms of economy and efficiency, the carbothermal reduction method is the best choice to synthesize composite powder[7−8]. In recent years, some works have been focused on the use of the carbothermal reduction method to synthesize composites such as Al_2O_3-SiC[9], mullite-SiC[10], mullite-ZrO_2-SiC[10], Al_2O_3-mullite-SiC[11], Al_2O_3-ZrO_2-SiC[7] and Al_2O_3-Sialon-SiC[12]. The starting materials of synthesizing the composites are mostly natural minerals such as pyrophyllite[13], clay[9, 11] and andalusite[14], which can prepare the excellent composites and make the natural resources be utilized fully. So far, there is no report on the synthesis of the ZrO_2-SiC composite powder from zircon.

In this study, ZrO_2-SiC composite powder is synthesized by carbothermal reduction of zircon in argon atmosphere. The effects of the heating temperature on the phase composition, relative content and microstructure of the synthesized ZrO_2-SiC composite powder as well as its addition on the bulk density, apparent porosity, crushing strength and thermal shock resistance of the Al_2O_3-C refractories are investigated.

2 Experimental

Zircon (＜44 μm) and carbon black (＜30 μm) were used as the starting materials, and the chemical composition of zircon is listed in Table 1. In addition, the mass fraction of C in carbon black and the volume frac-

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tion of argon gas are 98.0% and 99.99%, respectively.

According to the reaction (1), the mass ratio of zircon to carbon black is 100/20:

$$ZrSiO_4(s)+3C(s)=ZrO_2(s)+SiC(s)+2CO(g) \quad (1)$$

Zircon and carbon black were weighed in terms of this mass ratio, mixed in a ball mill for 24 h, pressed at 100 MPa into the samples with size of *d* 20 mm×5 mm, dried at 393 K for 24 h and then heated at 1 723, 1 773, 1 823 and 1 873 K for 4 h at a heating rate of 283 K/min, respectively. The flux of the argon gas remained at 1.5 L/min during the heat-up and reaction periods. After the desired reaction temperature reached, the system was cooled to1 273 K at a rate of 279 K/min and then cooled to room temperature in air. The samples heated at 1 723 −1 873 K were calcined at 973 K for 2 h to remove residual carbon. The phase composition and relative content of samples were determined by XRD(X-ray diffraction), and the microstructure was observed by SEM(scanning electronic microscope). The relative contents of phases in sample were estimated by

$$\varphi_i = \frac{I_i' + I_i''}{\sum_i (I_i' + I_i'')} \times 100\% \quad (2)$$

where I_i' and I_i'' are the absolute intensity of diffraction peak of *i* phase from two reflecting surface, φ_i is the relative content of *i* phase in sample.

The synthesized ZrO_2-SiC composite powder was used as the additive to prepare the Al_2O_3-C refractories. The starting materials were weighed in terms of the compositions as listed in Table 2, mixed fully, pressed at 200 MPa into the samples with size of *d* 50 mm×20 mm, dried at 523 K for 24 h and then sintered at 1 673 K for 2 h covered up with carbon. The sintered samples at 1673 K were put into the high temperature furnace (1 473 K) to investigate the thermal shock resistance. In this study, the thermal shock resistance of the refractories was judged by comparing the conservation rate of strength. Moreover, the conservation rate of strength is equal to the crushing strength before thermal shock, and dividing the residual strength after thermal shock. In addition, the apparent porosity and bulk density of samples were measured.

3 Results and discussion

3.1. Effect of heating temperature on synthesis of ZrO_2-SiC composite powder

As shown in Fig.1 the synthesized ZrO_2-SiC composite powder includes ZrO_2, SiC and $ZrSiO_4$ phases when the samples are heated at 1 723−1 823 K, and the diffraction peak intensity of SiC phase increases gradually with increasing the heating temperature. However, that of the $ZrSiO_4$ phase weakens, and vanishes when the heating temperature rises to 1 873 K. During the heating process, the diffraction peak intensity of ZrO_2 increases. In Fig.2 the relative contents of ZrO_2 and SiC increase with increasing the heating temperature, while the content of $ZrSiO_4$ decreases and becomes zero when the sample is heated at 1 873 K for 4 h, and the relative contents of ZrO_2 and SiC in sample are about

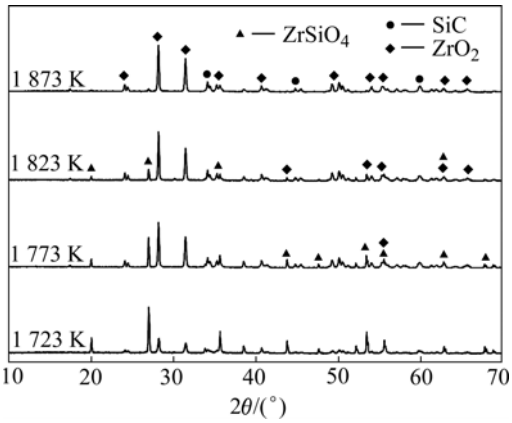

Fig.1 Phase compositions of samples heated at 1 723−1 873 K for 4 h

Table 1 Chemical composition of zircon (mass fraction, %)

ZrO_2	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO
66.75	32.34	0.42	0.11	0.07	0.02	0.02

Table 2 Composition of Al_2O_3-C refractories (mass fraction, %)

Composition	A0	A1	A2	A3	B0	B1	B2	B3
Fused corundum	85	85	85	85	85	85	85	85
Natural graphite	15	15	15	15	15	15	15	15
Phenolic resin	5	5	5	5	5	5	5	5
ZrO_2-SiC composite powder	0	2	4	6	0	2	4	6

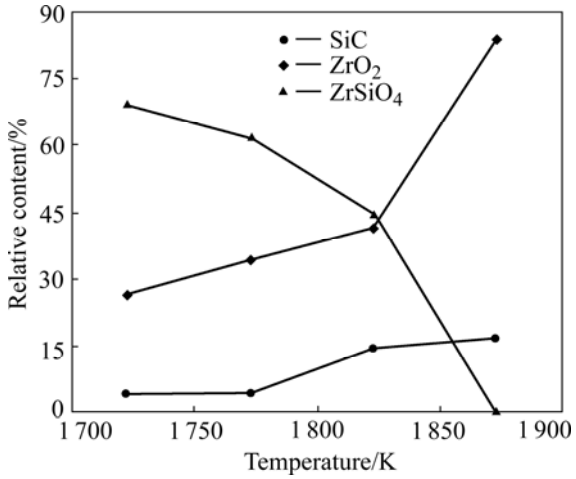

Fig.2 Effect of heating temperature on relative content of phases

83.7% and 16.3%, respectively.

Fig.3 shows the SEM image and EDS spectrum of the sample heated at 1 873 K for 4 h. They show that the formed particles are about 1 μm when zircon and carbon black are heated at 1 873 K for 4 h and the materials are composed of ZrO_2 and SiC, perhaps because the initial formed SiC particles develop and grow up on the surface of ZrO_2 matrix.

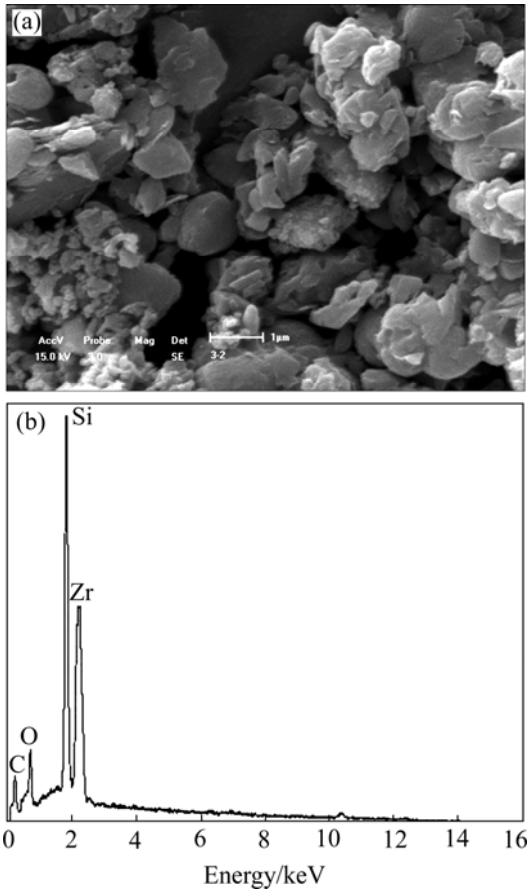

Fig.3 SEM image (a) and EDS spectrum (b) of sample heated at 1 873 K for 4 h

3.2 Thermodynamic analysis of carbothermal reduction reaction process

$ZrSiO_4$ can be decomposed and form ZrO_2 and SiO_2 during the process of heating the mixture of zircon and carbon black, and the chemical reaction equation can be written as

$$ZrSiO_4(s)=ZrO_2(s)+SiO_2(s) \quad (3)$$

The formed ZrO_2, SiO_2 and C cannot coexist at high temperature and can form SiC and ZrC during the heating process[15−16]:

$$SiO_2(s)+C(s)=SiO(g)+CO(g) \quad (4)$$

$$SiO(g)+2C(s)=SiC(s)+CO(g) \quad (5)$$

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

$$\Delta G_6^{\Theta}/(\mathrm{J\cdot mol^{-1}})=603\ 150-331.98T$$

$$\lg[p(\mathrm{CO})/p^{\Theta}]=8.67-15\ 750.39/T$$

$$ZrSiO_4(s)+3C(s)=ZrO_2(s)+SiC(s)+2CO(g) \quad (7)$$

$$ZrO_2(s)+C(s)=ZrO(g)+CO(g) \quad (8)$$

$$ZrO(g)+2C(s)=ZrC(s)+CO(g) \quad (9)$$

$$ZrO_2(s)+3C(s)=ZrC(s)+2CO(g) \quad (10)$$

$$\Delta G_{10}^{\Theta}/(\mathrm{J\cdot mol^{-1}})=666\ 550-346.04T$$

$$\lg[p(\mathrm{CO})/p^{\Theta}]=9.04-17\ 406.00/T$$

$$ZrSiO_4(s)+6C(s)=ZrC(s)+SiC(s)+4CO(g) \quad (11)$$

Fig.4 shows the domain areas of the condensed phases in Zr-Si-C-O system plotted by the thermodynamic data for reactions (6) and (10). During the whole heating process, C in sample will react with SiO_2 to form SiC (reactions (3)−(7)). When the partial

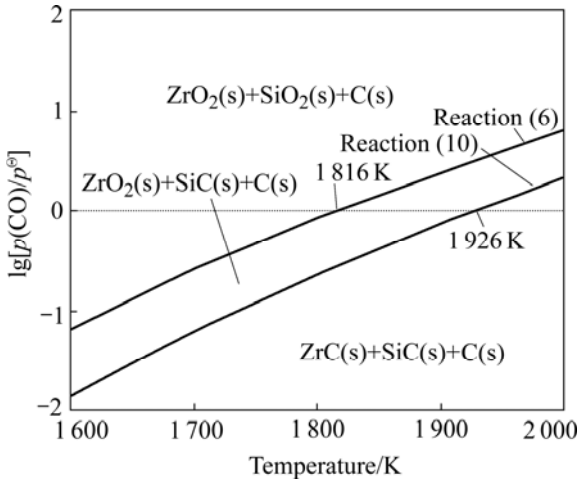

Fig.4 Domain areas of condensed phases in Zr-Si-C-O system

pressure of CO(p(CO)) in the reacting furnace remains constant, the stability domain of the condensed phases changes from ZrO_2(s)+SiC(s)+C(s) to ZrC(s)+SiC(s)+C(s) with increasing the heating temperature. For example, when p(CO) is 1.0×10^5 Pa, the temperatures to form SiC and ZrC are about 1 816 K and 1 926 K, respectively. When the heating temperature remains constant, the domain area will change from ZrO_2(s)+SiO_2(s)+C(s) to ZrO_2(s)+SiC(s)+C(s) and ZrC(s)+SiC(s)+C(s) with decreasing the p(CO).

3.3. Effect of ZrO_2-SiC composite powder addition on properties of Al_2O_3-C refractories

In Fig.5 the bulk density of samples tends to increase with increasing the synthesized composite powder. The bulk density of the sample by the addition of 4% ZrO_2-SiC composite powder reaches the maximum, however, the apparent porosity decreases to the minimum, and their values are 2.79 g/cm^3 and 18.8%, respectively.

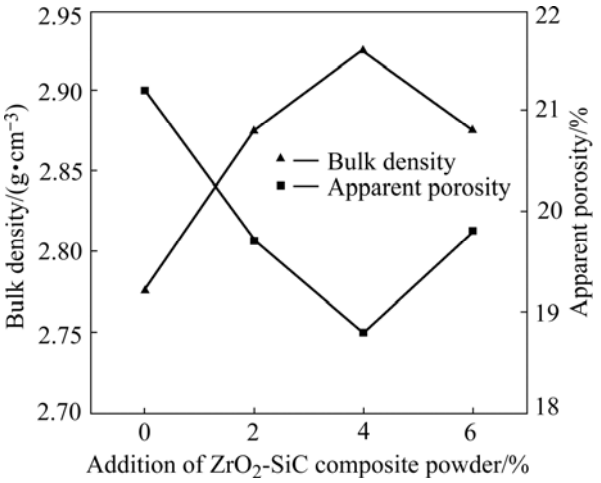

Fig.5 Effect of addition of ZrO_2-SiC composite powder on bulk density and apparent porosity of samples sintered at 1 673 K for 2 h

In Table 3 the cycle times of thermal shock, residual strength and conservation rate of strength of the samples increase with increasing the content of the ZrO_2-SiC composite powder, while the crushing strength increases and then decreases, which indicates the strength of the Al_2O_3-C refractories can be improved by the addition of the ZrO_2-SiC composite powder due to the high toughness of ZrO_2 and SiC as well as their active effect on the sintering of refractories. However, the micro-flaws will become bigger due to the increasing of additive and the difference of thermal expansion coefficient between additive and refractories, which makes the crushing strength decrease. The conservation rate of strength of the sample with 6% ZrO_2-SiC composite powder addition reaches the maximum, which shows the synthesized composite powder can also improve the thermal shock resistance of the Al_2O_3-C refractories.

Table 3 Effect of addition of ZrO_2-SiC composite powder on properties of Al_2O_3-C refractories

Content of ZrO_2-SiC composite powder/%	Cycle times (1 473 K)	Residual strength/ MPa	Crushing strength/ MPa	Conservation rate of strength/%
0	6	1.68	33.02	5.1
2	10	10.24	39.59	25.9
4	＞10	14.27	41.73	34.1
6	＞10	16.71	40.82	40.9

The volume change of 3.5% (volume fraction) is accompanied by the reversible phase transformation of ZrO_2 (Eqn.(12)) during the cooling process, and the amounts of micro-flaws come up around grain boundary. The shorter flaws extend mainly by dynamic expansion and the longer ones extend by quasi-static expansion. The edges and tips of the micro-flaws can be inactivated owing to the amounts of micro-flaws and their expansion forms, which can prevent the flaws from extending quickly and breaking of the materials, and further improve the thermal shock resistance of the Al_2O_3-C refractories.

$$t\text{-}ZrO_2 \underset{1\,443\ K}{\overset{1\,073\sim1\,273\ K}{\rightleftharpoons}} m\text{-}ZrO_2 \quad (12)$$

4 Conclusions

1) The ZrO_2-SiC composite powder with the particle size of about 1 μm is synthesized by carbothermal reduction method in argon atmosphere. When heating the mixture of zircon and carbon black at 1 873 K for 4 h, the relative contents of ZrO_2 and SiC in the synthesized composite powder are about 83.7% and 16.3%, respectively.

2) The bulk density, crushing strength and thermal shock resistance of the Al_2O_3-C refractories can be improved obviously by the addition of the synthesized ZrO_2-SiC composite powder.

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