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The effects of SiC_p addition on the *z*-value and mechanical properties of β-Sialon–SiC_p refractories

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The effects of SiC_p addition on the *z*-value, microstructure and mechanical properties of β-$Si_{6-z}Al_zO_zN_{8-z}$–SiC_p were investigated. The results showed that *z*-value of β-Sialon decreased from 2.66 to 1.20 with the increase of SiC_p addition, while the apparent porosity of β-Sialon–SiC_p composites increased. The bending strength and compressive strength decreased due to the increase of the apparent porosity and the weak cohesion resulted from the thermal expansion coefficient mismatch between SiC_p and β-Sialon matrix. Moreover, a linear regression model used to identify the relationship between the content of SiC and *z* value of β-Sialon is fitted.

Key-words : β-Sialon–SiC_p, z-Value, Microstructure, Mechanical properties, Refractories

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1. Introduction

β-Sialon–SiC refractories have been widely used especially as blast furnace refractories, which is a critical and dominative factor for the quality of iron smelting and the lifespan of blast furnace,[1)–3)] due to their better alkali resistance, abrasion resistance and thermal shock resistance than high-alumina and corundum bricks, and better oxidation resistance and higher strength properties than carbon products.

Up to now, owning excellent properties, Sialon ceramics,[4),5)] Sialon crystals[6),7)] and Sialon-based composites[8)–10)] have attracted considerable attention as a kind of promising material for various applications. As to Sialon-based refractories, lots of studies have been performed and mainly concentrated on the effects of SiC contents and sintering additives (such as Y_2O_3 and rare-earth oxides RE_2O_3) on preparation, microstructure and mechanical properties of β-Sialon–SiC refractories.[11)–16)] In addition, the effects of *z* value of β-Sialon (general formula of $Si_{6-z}Al_zO_zN_{8-z}$,[17)] where *z*-value reflects the substitution extent of Si, N atoms by Al, O atoms) on properties of β-Sialon–SiC refractories have been investigated as well.[18)] It has been revealed that the strength of materials at ambient temperature as well as high temperature were both found to be the best when *z* value is 2, and with the increase of *z* value, the thermal shock resistance of materials was improved, but alkali and slag resistance was decreased. Almost previous studies show that the formation of β-Sialon using Si_3N_4, AlN, Al_2O_3 and RE_2O_3 as starting materials is via a dissolution–precipitation mechanism.[19)–21)] The mechanism can be described as follows: initially, the SiO_2 presenting on the surface of Si_3N_4 particles reacts with Al_2O_3 and RE_2O_3 forming a eutectic liquid of Al_2O_3–SiO_2–RE_2O_3 system, and then AlN dissolves gradually into the liquid with the increase of temperature; finally, the eutectic liquid can be absorbed partly into Si_3N_4 thereby precipitating β-Sialon. It's well-known that there is a thin SiO_2 film on the surface of SiC particle, which also can be involved in the liquid reaction of β-Sialon during the sintering process of β-Sialon–SiC.[14),15),22)] From those researches, we can conclude that the adding SiC_p should affect the *z* value of β-Sialon. However, there is little literature reporting the effect of SiC_p addition on *z* value of β-Sialon.

In this paper, β-Sialon–SiC refractories were prepared with the powders of Si, Si_3N_4, AlN, Al_2O_3 and SiC particles as starting materials and Y_2O_3 as sintering additive which had been successfully used in the preparation of Si_3N_4, SiC and Sialon materials.[13)–15)] The effects of SiC addition on *z*-value of β-Sialon as well as microstructure and mechanical properties of β-Sialon–SiC refractories prepared by in-situ nitridation reaction were discussed. The present work has a certain signification for designing β-Sialon–SiC refractories.

2. Experimental procedures

Si powder (99 wt%, Beijing Dadi Zelin Silicon Co., Ltd., China), Si_3N_4 powder (99.7 wt%, $D_{50} = 0.7\,\mu m$; α-phase >93.8 wt%, Shanghai Anseml Fine Ceramic Co., Ltd., China), AlN powder (98 wt%, $D_{50} = 0.5\,\mu m$, Advanced Technology & Materials Co., Ltd., China), Al_2O_3 powder (99.5 wt%, grain size <0.5 μm, Beijing F&F Chemical Industrial Co., Ltd., China), SiC particles (98 wt%, 1.5 wt% O, Land Silicon Carbide Co., Ltd., China) as raw materials and Y_2O_3 powder (99.99 wt%, General Research Institute Nonferrous Metals, China) as sintering additive were used to prepare the β-Sialon/SiC refractories. The gradation of SiC particles was: 15 wt% 44 μm, 25 wt% 63 μm, 45 wt% 160 μm and 15 wt% 325 μm.

The match ratio of Si, Si_3N_4, AlN and Al_2O_3 powders in the starting materials was designed to obtain β-$Si_{6-z}Al_zO_zN_{8-z}$ with $z = 2$ according to the Ref. 18). Si powder is not only translated into nitride reinforcement, but also plays the plastic role in shaping and sintering.[23)] The mol ratio of Si/Si_3N_4 was 3, and 2 wt% Y_2O_3 powder was extra-added. The composition of the samples investigated in this work is listed in **Table 1**. The extra oxygen contents presented in the nitrides were taken into account.

The mixtures of Si, Si_3N_4, AlN and Al_2O_3 powders were milled with agate media in water-free ethanol for 6 h and

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Table 1. Composition of the samples

Samples	Full Composition (wt%)					
	Composition of $Si_4Al_2O_2N_6$				SiC	Y_2O_3 (additional)
	Si	Si_3N_4	AlN	Al_2O_3		
S1	22.89	38.15	11.17	27.79	0.00	2.00
S2	19.46	32.43	9.49	23.62	15.00	2.00
S3	16.02	26.71	7.82	19.45	30.00	2.00
S4	12.59	20.98	6.14	15.28	45.00	2.00
S5	9.15	15.26	4.47	11.12	60.00	2.00

subsequently dried at 70°C for 24 h, then the mixtures were mixed with different amount of SiC particles (0, 15, 30, 45 and 60 wt%) and additional Y_2O_3 powder in a fast ball mill with alumina grinding balls for 10 min. The final mixtures (designated as S1, S2, S3, S4 and S5, respectively) were uniaxial pressed into a shape of 6 mm × 6 mm × 40 mm, and cold isostatic pressed at 200 MPa. The samples (S1–S5) were placed in the graphite crucible and buried in pure BN powder, then sintered by in-situ nitridation reaction in flowing N_2 atmosphere (99.999 wt% purity) in a multi-functional furnace at 1600°C for 3 h. To ensure that silicon could be well nitrided thereby developing suitable microstructure, the heating process included four temperature holding stages: the samples were heated up from ambient temperature to 1150°C with a rate of 15°C/min holding for 1 h under 0.12 MPa of nitrogen pressure, and raised to 1280 and 1430°C with a rate of 10°C/min holding for 1 h under 0.9 MPa of nitrogen pressure, respectively, then heated to 1600°C from 1430°C with a rate of 10°C/min and finally sintered at this temperature for 3 h with a nitrogen pressure of 0.9 MPa.

The density and apparent porosity of the sintered samples were investigated by the Archimedes' method. The bending strength of the samples was measured by a three-point bending test with a 30 mm span at a crosshead speed of 0.5 mm/min at room temperature. The compressive strength of the samples was tested by exerting an axial compression. Phase identification was carried out by X-ray diffraction (XRD) using a XD-3 XRD equipment (Purkinje General, Cu Kα_1 radiation, $\lambda = 1.5406$ Å). The lattice parameters of β-Sialon were calculated by the following equation:

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + hk + k^2) + \left(\frac{a}{c}\right)^2 \cdot l^2}} \quad (1)$$

where a and c is the unit lattice parameters of the final β-Sialon, d_{hkl} is the space distance between reflection planes (hkl). Parameters a and c were calculated using the (200), (101) and (210) reflections of β-Sialon. The z value of β-Sialon phase in materials was obtained from the average values of z_a and z_c calculated from the following equations:[24]

$$a = 7.603 + 0.0296z \text{ Å} \quad (2a)$$

$$c = 2.907 + 0.0255z \text{ Å} \quad (2b)$$

The microstructure of the samples was observed by scanning electron microscopy (SEM; JSM-6460, Japan) with an energy dispersive spectroscopy detector (EDS; INCAX-Sigh, Oxford, UK).

3. Results

3.1 XRD analysis

Figure 1 shows the XRD patterns of the samples sintered in nitrogen atmosphere at the temperature of 1600°C holding for 3 h. It is obvious that α-SiC and β-Sialon synthesized by in-situ nitridation reaction were presented in the samples after the high-temperature reaction. From the partial amplified XRD patterns shown in the inset of Fig. 1, it can be seen that the positions of diffraction peaks of β-Sialon phase were shifted to the high-angle direction with the increase of SiC_p content. According to the Eqs. (1) and (2), the z values of β-Sialon calculated from the XRD pattern are shown in **Fig. 2**. It is revealed that the z value of β-Sialon decreased from 2.66 to 1.20 with the increase of weight percentage (x) of SiC_p in the sample.

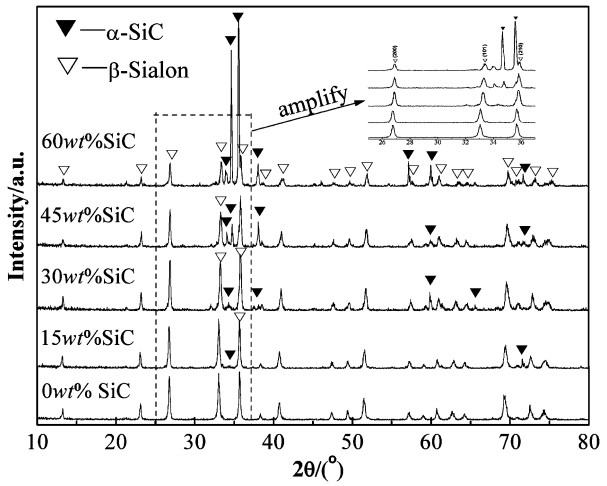

Fig. 1. XRD patterns of samples sintered at 1600°C for 3 h by in situ nitridation reaction.

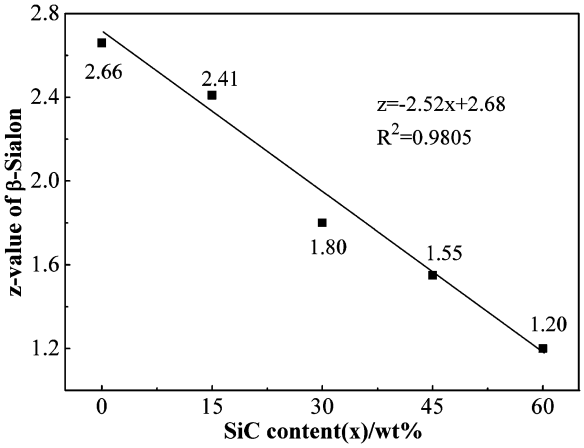

Fig. 2. Effect of the SiC addition on the z value of β-Sialon.

3.2 SEM analysis

SEM micrographs of fracture samples with different addition of SiC sintered at 1600°C for 3 h by in-situ nitridation reaction are shown in **Fig. 3**. It clearly indicates that sample S1 with a few pores was well sintered [Fig. 3(a)]. The SiC particle was closely wrapped by β-Sialon matrix in sample S2 with 15 wt% SiC_p [Fig. 3(b)], in which there were numbers of elongated β-Sialon with high aspect ratios. With the increase of SiC addition, more voids between SiC particles and β-Sialon matrix were present in the samples as shown in Figs. 3(c)–3(e). Moreover, we also observed the surfaces of the SiC particles in the β-Sialon–SiC_p composites refractories, shown in the **Fig. 4**. The dense SiC particle has the surfaces with smooth areas and rough areas, where

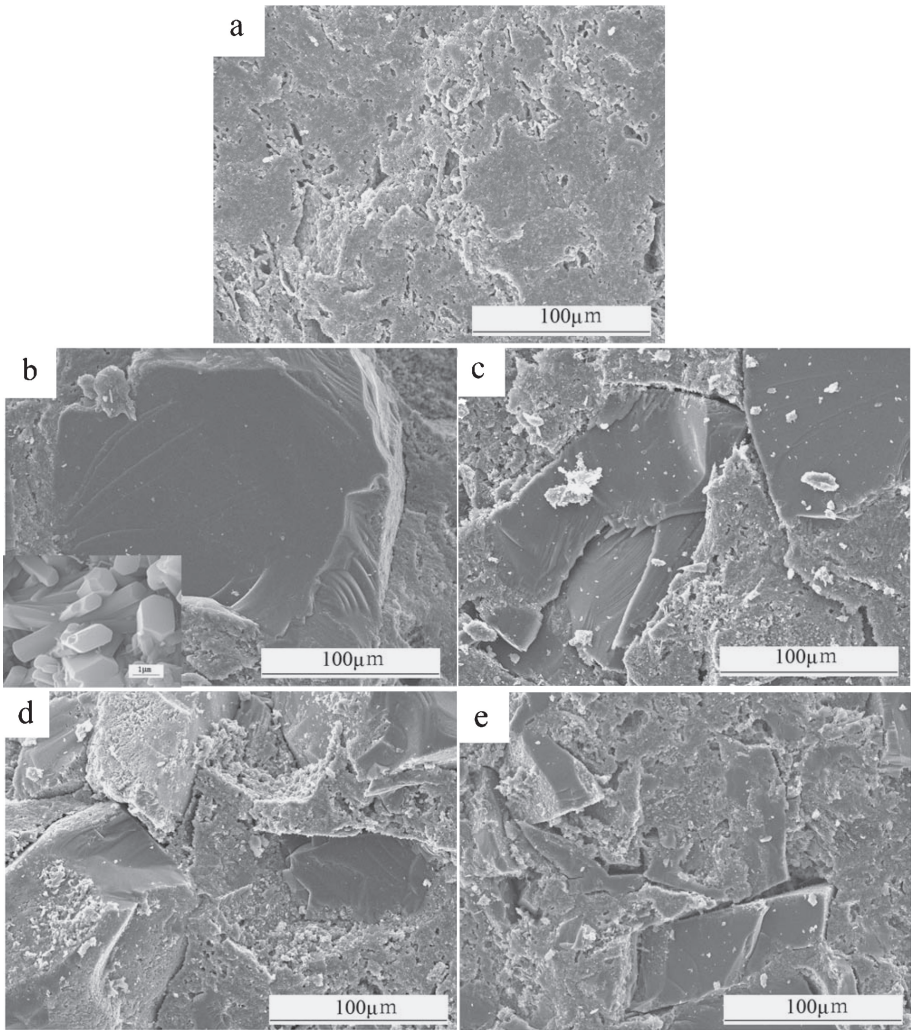

Fig. 3. Fracture surface microstructure of samples with different SiC contents sintered at 1600°C for 3 h (a) 0 wt % SiC, (b) 15 wt % SiC, (c) 30 wt % SiC, (d) 45 wt % SiC, (e) 60 wt % SiC.

besides Si and C elements, signals of Al, O and N elements can also be found in the EDS patterns [Figs. 4(c) and 4(d)].

3.3 Mechanical properties of β-Sialon–SiC_p refractories

Figure 5 shows the apparent porosity and bulk density of β-Sialon–SiC_p refractories as function of the SiC_p addition. It is indicated that the sample S2 with 15 wt % SiC_p had the highest bulk density of 2.86 g·cm^{-3} and the lowest apparent porosity of 1.59% among the six samples. With the increase of SiC_p addition, the apparent porosity of β-Sialon–SiC_p refractory gradually increased, while the bulk density decreased.

The results of bending strength and compressive strength of the sintering samples as function of SiC_p additions are shown in **Fig. 6**. It is obvious that, with the increase of SiC_p content, the bending strength and compressive strength of the sintered samples decreased from 228 to 189 MPa and from 1080 to 428 MPa, respectively.

4. Discussion

4.1 Effect of SiC_p addition on z value of β-Sialon

The positions of diffraction peaks of β-Sialon phase were shifted to the high-angle direction with the increase of SiC_p content (inset in Fig. 1), which should be attributed to the changed interplanar spacing d. It is well known that z-value of β-Sialon reflects the substitution extent of Si, N atoms by Al, O atoms, and the average Al–N bond (1.87 Å), Al–O bond (1.75 Å) is longer than the Si–N bond (1.74 Å), which is related to the unit lattice parameters.[25] According to the Eq. (1), the unit lattice parameters have relationship with the interplanar spacing. Thus, the substitution extent, in other word, z value effects the interplanar spacing d of β-Sialon. As is shown in Fig. 2, the z value of β-Sialon decreased from 2.66 to 1.20 with the increase of weight percentage (x) of SiC_p in the sample. Thereby, the interplanar spacing d decreased, consequently, resulting in the shift to the high-angle θ, according to Braggs equation $2d\sin\theta = n\lambda$.

The decreased z value of the synthesized β-Sialon with the increase of SiC_p addition can be explained by the following analysis. It is normally recognized that there is a thin SiO_2 film on the surface of SiC particle.[15),22)] Such a SiO_2 film could be involved in the liquid reaction generating β-Sialon phase, which was indicated by the EDS results of SiC_p layers (Fig. 4). From the EDS patterns, it can be seen that besides Si and C elements existed in the SiC particle itself, signals of Al, O and N elements can also be found in the patterns. The z value was associated with

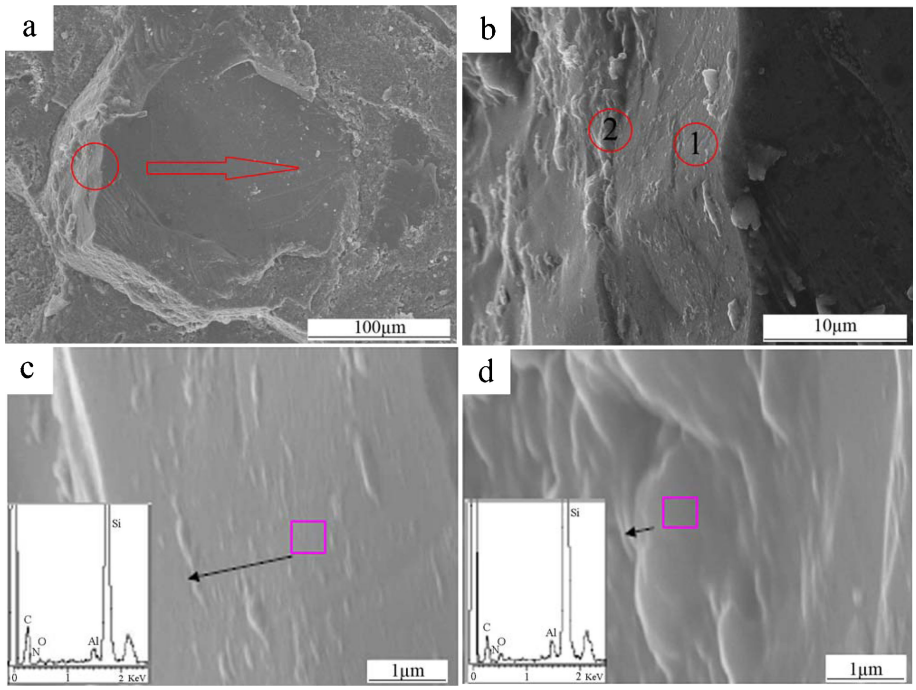

Fig. 4. (Color online) Morphologies of SiC surfaces in the sample with 15 wt % SiC sintered at 1600°C for 3 h (a) SiC particle, (b) Enlarged SEM image of surface of SiC particle in (a) as marked by the circle, (c) and (d) is zone 1 and zone 2 of (b) with the insert EDS pattern, respectively.

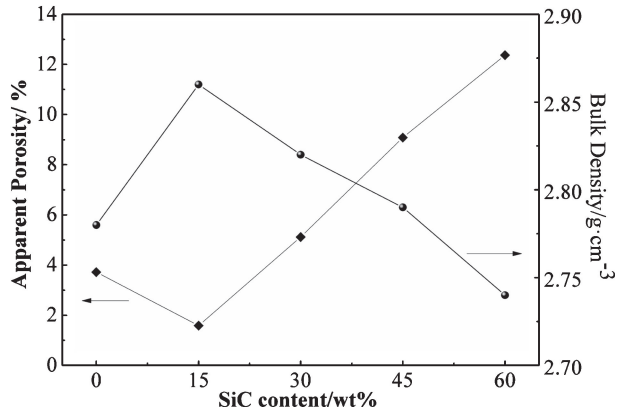

Fig. 5. Effect of the SiC addition on the apparent porosity and bulk density of β-Sialon–SiC composites.

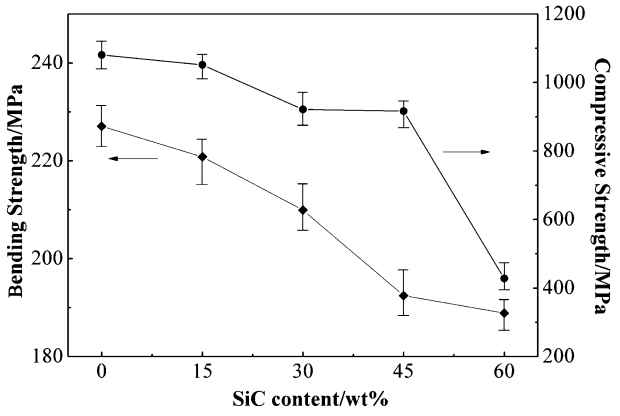

Fig. 6. Effect of the SiC addition on the bending strength and compressive strength of β-Sialon–SiC composites.

total content of SiO_2 existed in the samples, while the content of SiO_2 was affiliated with the addition of SiC particles. The SiO_2 contents increased as the SiC_p content increased, resulted in large amount of SiO_2 being involved in the liquid reaction of β-Sialon. It can be analyzed by the following reaction equations:

$$\left(9-\frac{3z}{2}\right)\mathrm{Si}+(6-z)\mathrm{N_2}+\left(3-\frac{z}{2}\right)\mathrm{Si_3N_4}+z\mathrm{Al_2O_3}+z\mathrm{AlN}\rightarrow 3\mathrm{Si_{6-z}Al_zO_zN_{8-z}} \quad (3)$$

$$\left(9-\frac{3z}{2}\right)\mathrm{Si}+\left(6-z+\frac{a}{2}\right)\mathrm{N_2}+\left(3-\frac{z}{2}\right)\mathrm{Si_3N_4}+z\mathrm{Al_2O_3}+z\mathrm{AlN}+a\mathrm{SiO_{2(SiC)}}\rightarrow 3\mathrm{Si_{6-z'}Al_{z'}O_{z'}N_{8-z'}}+3a[\mathrm{O}] \quad (4)$$

Equation (3) is the reaction equation of β-Sialon without $SiO_{2(SiC)}$, i.e. the SiO_2 on the surface of SiC particles, where z is the value of β-Sialon in the sample without SiC particles. Equation (4) is the reaction equation of β-Sialon with $SiO_{2(SiC)}$, where z' is the real z value of β-Sialon after absorbed the SiO_2 composition, and a is a coefficient in direct ratio to the content of $SiO_{2(SiC)}$. The Eq. (4) can be abstractly understood to be that SiO_2 on the surface of SiC particles participated in the reaction of Eq. (3), which can be concisely expressed to be Eq. (5). Thus, the Eq. (6) can be easily derived according to the mass conservation of silicon element according to the Eq. (5), which reflects that z' value of β-Sialon decreased with the increase of coefficient a.

$$3\mathrm{Si_{6-z}Al_zO_zN_{8-z}}+\frac{a}{2}\mathrm{N_2}+a\mathrm{SiO_{2(SiC)}}\rightarrow 3\mathrm{Si_{6-z'}Al_{z'}O_{z'}N_{8-z'}}+3a[\mathrm{O}] \quad (5)$$

$$z'=z-\frac{a}{3} \quad (6)$$

The tendency of z value of β-Sialon in β-Sialon/SiC_p composites against the SiC_p addition shown in Fig. 2 was consistent with the anti-linear relationship between z' value of β-Sialon

and coefficient a. A fitted linear regression model can be used to identify the relationship between the independent variable x (the content of SiC) and the dependent variable z (z value of β-Sialon) by the following equation with a reliability value of $R^2 = 0.9805$:

$$z = -2.52x + 2.68 \quad (7)$$

The results strongly prove that the effect of SiC_p additions on the z value of β-Sialon must be taken into account during the design process of β-Sialon/SiC_p refractories, if an accurate z value is required.

4.2 Effect of SiC_p addition on the microstructure, bulk density and apparent porosity of β-Sialon–SiC_p refractories

When the sintering temperature is 1600°C, pure SiC is hardly sintered, but, Sialon bonding phase can change the sintering property of SiC. The bulk density of Sialon–SiC composites is detected by the sintering of green body. The increasing of bulk density means more compact sintered materials, better bond between different components. Holes in the materials are continuously closed during the sintering process so that the apparent porosity decreased, however, the variation of bulk density showed the opposite trend, and vice versa. Figure 5 shows the relationship between the bulk density and apparent porosity just agreed with that variation law.

It is quite easily seen from SEM microstructure of the samples (Fig. 3) that more voids between SiC particles and β-Sialon matrix with the increase of SiC addition. SiC_p could be closely wrapped by enough Sialon matrix when the SiC_p content was low. In contrast, the SiC particles could not be fully packed by Sialon fine grains thereby generating pores among adjacent SiC particles with the increase of SiC_p addition. Such bonding station between SiC_p and Sialon resulted in the increase of the apparent porosity and the decrease of the bulk density with the increase of SiC_p addition, which had similar phenomenon with other works established in different systems.[12),26)]

4.3 Effect of SiC_p addition on the mechanical properties of β-Sialon–SiC_p refractories

With the increase of SiC_p addition, the bending strength and compressive strength of the sintered samples decreased (Fig. 6). Though the z-value of β-Sialon partly affect the mechanical properties of β-Sialon–SiC refractories according to the Ref. 18), where the content of SiC is constant. In this work, we investigated emphatically the effect of SiC addition on z-value of β-Sialon in order to illustrate that the effect of SiC addition on z-value of β-Sialon should be taken into account when designing β-Sialon–SiC refractories. Herein, the effect of SiCp addition which is variable on the mechanical properties of β-Sialon–SiCp refractories was also discussed. In this paper, relative to the effect of z-value, the porosity and the interface cohesion between SiCp and β-Sialon should be the main responsible for the mechanical properties.

As is well-known, the strength-porosity dependence can be approximated by the following exponential equation:[27)]

$$\sigma = \sigma_0 \cdot \exp(-np) \quad (8)$$

Where σ_0 is the strength of a nonporous structure, σ is the strength of the porous structure at a porosity p, and n is a constant.

Generally, the mechanical strength of inorganic non-metallic materials decreases with the increase of the porosity. In this work, the strength-porosity relationship of the sintering samples added with SiC_p (S2–S5) could comply with it. In comparison, the bending strength of the sample with 15 wt % SiC_p (S2) was no higher than pure β-Sialon ceramic (S1), even though sample S2 had a lower apparent porosity. Thus, in this case, the decrease of mechanical properties is attributed to the weak cohesion resulting from thermal expansion coefficient mismatch between SiC ($\alpha = 4.3 \times 10^{-6}\,K^{-1}$)[14)] and β-Sialon matrix ($\alpha = 3.2 \times 10^{-6}\,K^{-1}$).[28)] The increase of the SiC_p content in samples S2–S5 resulted in lower densification of materials. The reduction of the area on which the stress loaded caused the decrease of compressive strength. Though the mechanical properties of the β-Sialon–SiC_p composites decreased, they could still satisfy the requirements of refractories in the blast furnace.

5. Conclusions

β-Sialon–SiC_p refractories were prepared by in-situ nitridation reaction at 1600°C for 3 h using a mixture of Si, Si_3N_4, AlN, Al_2O_3 and Y_2O_3 powders with different amount of SiC particles. The results showed that, with the increase of SiC_p addition (from 0 to 60 wt %), the z-value of the β-Sialon in the β-Sialon–SiC_p composites decreased from 2.66 to 1.20. Meanwhile, the bending strength and compressive strength of the composites exhibited a certain decrease from 228 to 189 MPa and from 1080 to 428 MPa, respectively. Moreover, β-Sialon–SiC_p refractories had the bulk density of 2.86 $g \cdot cm^{-3}$ and the apparent porosity of 1.59% with the optimized SiC_p addition of 15 wt %. The relevant mechanical properties of the β-Sialon–SiC_p composites with SiC_p addition of 0–60 wt % could match the corresponding requires of blast-furnace refractories.

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