

## Research Article

# Si<sub>3</sub>N<sub>4</sub>-SiC<sub>p</sub> Composites Reinforced by *In Situ* Co-Catalyzed Generated Si<sub>3</sub>N<sub>4</sub> Nanofibers

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Si<sub>3</sub>N<sub>4</sub>-SiC<sub>p</sub> composites reinforced by *in situ* catalytic formed nanofibers were prepared at a relatively low sintering temperature. The effects of catalyst Co on the phase compositions, microstructures, and physicochemical-mechanical properties of samples sintered at 1350°C–1450°C were investigated. The results showed that the catalyst Co enhanced the nitridation of Si. With the increase of Co addition (from 0 wt% to 2.0 wt.%), the apparent porosity of as-prepared refractories was initially decreased and subsequently increased, while the bulk density and the bending strength exhibited an opposite trend. The Si<sub>3</sub>N<sub>4</sub>-SiC<sub>p</sub> composites sintered at 1400°C had the highest strength of 60.2 MPa when the Co content was 0.5 wt.%. The catalyst Co facilitated the sintering of Si<sub>3</sub>N<sub>4</sub>-SiC<sub>p</sub> composites as well as the formation of Si<sub>3</sub>N<sub>4</sub> nanofibers which exhibited network connection and could improve their strength.

## 1. Introduction

Because of its high strength, good excellent thermal shock resistance and remarkable erosion, and corrosion resistance, Si<sub>3</sub>N<sub>4</sub>-SiC<sub>p</sub> composite refractories have been widely used in metallurgical and chemical industry as advanced refractories and high-temperature structural materials. In particular, as a large and medium-sized blast furnace refractory, it played a pivotal role in prolonging the lifespan of blast furnace in the past few decades [1–4].

Traditional technique to manufacture Si<sub>3</sub>N<sub>4</sub>-SiC<sub>p</sub> composite refractories is usually through *in situ* nitridation reaction of Si powders and SiC particles/powders at high-temperature in tunnel kiln. It usually suffers some quality problems of “black” and “sandwich” due to an incomplete nitridation in the preparation process, thus affecting their applications. Furthermore, because the formation of Si<sub>3</sub>N<sub>4</sub>-SiC<sub>p</sub> composite refractories was achieved by vapor reaction, there still exist some technical problems such as high porosity and high nitridation temperature. In addition, the bond between matrix and aggregate needs to be further

strengthened, and the strength as well as thermal shock resistance of the products needs to be further improved.

In past few years, controlling microstructural development to optimize materials' mechanical properties has been the focus of intensive research [5–9]. The previous studies show that single or mixed additives such as Y<sub>2</sub>O<sub>3</sub>, MgO, Al<sub>2</sub>O<sub>3</sub> + Y<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub> + ZrO<sub>2</sub> are useful for enhancing the mechanical properties of Si<sub>3</sub>N<sub>4</sub>-SiC<sub>p</sub> composite refractories [10–13]. However, the nitrided temperature was higher than 1450°C, and the increase rate of strength was lower. With the development of nanotechnology [14–16], nanofibers/wires, having larger interfacial areas, the excellent mechanical and thermal properties make them ideal reinforcements for improving the strength and toughness of materials. Previous efforts have been mainly devoted to introduce the second nanofiber/wire-phase to matrix [17–21], although the increasing interest has emerged recently in *in situ* formation of nanofibers/wires in matrix [22–24].

Because of their characteristics to easily lend and take electrons from other molecules, transition metals are good metal catalysts. Recently, we have investigated the effect

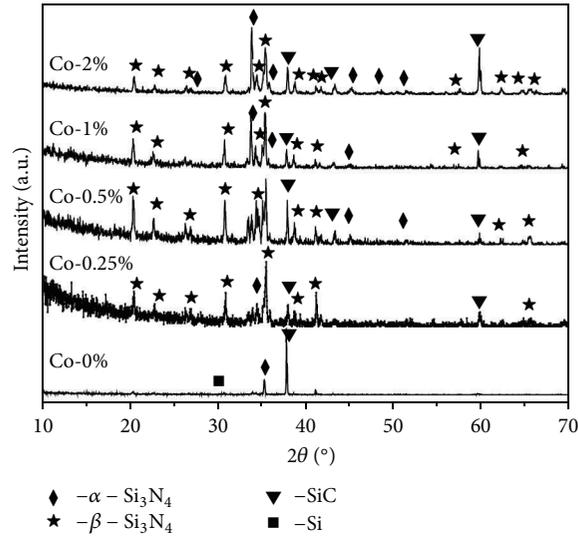


FIGURE 1: XRD patterns of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories with various contents of Co nitrided at  $1400^\circ\text{C}$ .

of transition metal Co on the direct nitridation of silicon (Si) powders and morphologies of the nitridation products [25], showing primarily that Co played an important role in accelerating the Si nitridation as well as the *in situ* growth of  $\alpha\text{-Si}_3\text{N}_4$  nanorods/fibers. These results provided a guide for fabricating SiC-based composite refractories reinforced by *in situ* generating  $\text{Si}_3\text{N}_4$  nanorods/fibers. A large number of pores in the refractories are benefit for the growth of one dimension nanostructures. Therefore, in this work, the transition metal Co was introduced as a catalyst into the raw materials of Si powders and SiC particles to prepare *in situ* formed  $\text{Si}_3\text{N}_4$  with nanostructures bonded SiC refractories by nitridation reaction. The effects of Co contents on the phase compositions, microstructures, and properties of products sintered at  $1350^\circ\text{C}$ – $1450^\circ\text{C}$  were investigated. The catalyst Co facilitated the formation of  $\text{Si}_3\text{N}_4$  nanofibers and improved the strength of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composites. This work provided a new insight into the nitride bonded composites reinforced by such *in situ* catalytic formed nanofibers.

## 2. Experimental Procedure

Si powders (>99 wt.%, 325 mesh, Aldrich Chemical Company, Inc., UK), Co powders (99.8 wt.%,  $<2\ \mu\text{m}$ ; Sigma-Aldrich, Co., UK), SiC particles (98 wt.%, Aldrich Chemical Company, Inc., UK) with three gradation of  $38\ \mu\text{m}$ ,  $125\ \mu\text{m}$ , and  $380\ \mu\text{m}$  were used as raw materials to prepare the  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories.  $\text{N}_2$  (99.99%) and polyvinyl alcohol (PVA) (concentration = 8 wt.%) were used as reactive gas and binder, respectively. The components of the samples investigated in this work are listed in Table 1.

The mixtures of Si and Co powders, in a batch of 100 g, were dry-milled by corundum balls in a corundum jar for 0.5 h with 300 r/min and then mixed with different gradation of SiC particles for 1 h with 100 r/min. The final mixtures (designated as S1, S2, S3, S4, and S5, resp.) with 5 wt.% PVA were molded into a shape of  $6\ \text{mm} \times 6\ \text{mm} \times 45\ \text{mm}$  by

TABLE 1: The components of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  specimens (wt.%).

Samples	Si	SiC (wt.%)			Co extra-added (wt.%)
		380 $\mu\text{m}$	125 $\mu\text{m}$	38 $\mu\text{m}$	
S1	20	44	16	20	0
S2	20	44	16	20	0.25
S3	20	44	16	20	0.50
S4	20	44	16	20	1.00
S5	20	44	16	20	2.00

uniaxial pressing at 50 MPa in a steel die and then compacted at 200 MPa by cold isostatic pressing. After drying at  $80^\circ\text{C}$  for 6 h, the specimens were put in a corundum porcelain boat and then into an alumina-tube furnace. Finally, they were, respectively, heated at  $1350^\circ\text{C}$ ,  $1400^\circ\text{C}$ , and  $1450^\circ\text{C}$  for 5 h in flowing nitrogen.

After *in situ* nitriding reaction sintering, the phase compositions of products were determined by X-ray diffraction (XRD; XD-3, Purkinje General,  $\text{CuK}\alpha_1$  radiation,  $\lambda = 1.5406\ \text{\AA}$ ). 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 (i.e.,  $22^\circ$ ). The microstructure of the samples was observed by scanning electron microscopy (SEM; JSM-6460, Japan) with an energy dispersive spectroscopy detector (EDS; INCA X-Sight, Oxford, UK).

## 3. Results and Discussion

**3.1. Phase Composition and Microstructure of Products.** A slight difference existed in the products of samples nitrided at different temperatures. Basically, at  $1350^\circ\text{C}$  and  $1400^\circ\text{C}$ , some residual Si remained in the sample without Co, while

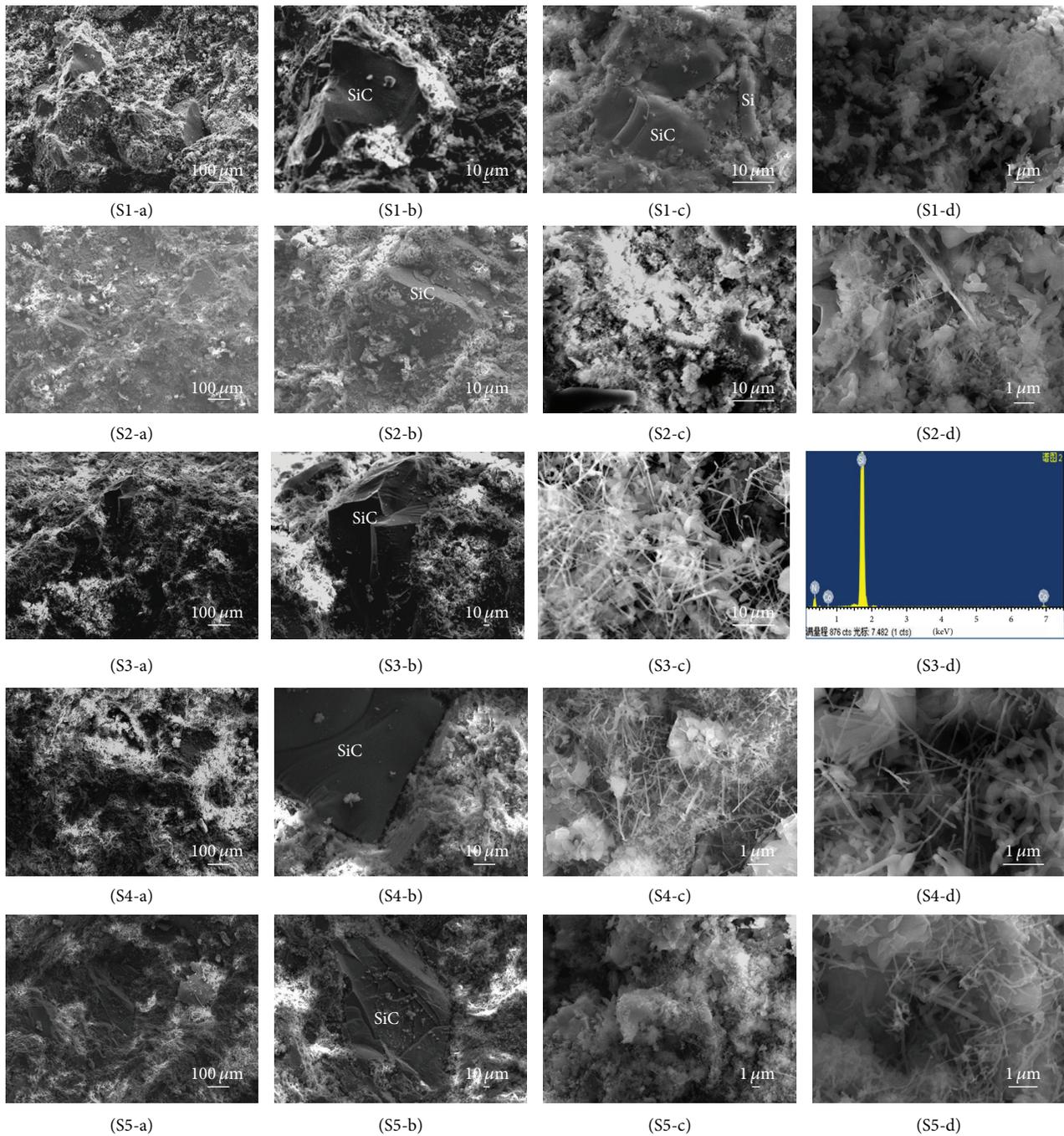


FIGURE 2: SEM images and EDS pattern of the fracture of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories with various contents of Co nitrided at  $1400^\circ\text{C}$ .

it disappeared in the sample with Co added. And when the temperature was increased to  $1450^\circ\text{C}$ , the Si powders were fully nitrided. Figure 1 shows the XRD patterns of the samples nitrided at  $1400^\circ\text{C}$ . The main crystalline phase was SiC, and Si was nitrided and transformed to  $\alpha\text{-Si}_3\text{N}_4$  with  $\beta\text{-Si}_3\text{N}_4$  as a minor phase in the products with Co, whereas some unreacted silicon remained when it was without Co.

SEM images and EDS pattern of fracture samples with various contents of Co nitrided at  $1400^\circ\text{C}$  are shown in

Figure 2, indicating that the  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories were mostly well sintered. SiC particles were closely wrapped by  $\text{Si}_3\text{N}_4$  matrix, and some regions had a few pores. Some small dense particles with relatively smooth fracture surface were seen in the products without Co. They must be silicon particles (Figure 2(S1-c)), identified by the EDS (not shown here) along with the XRD result (Figure 1). It is well known that the nitridation of silicon particles proceeded from the surface to the centre, *via* [N] diffusion. In the case

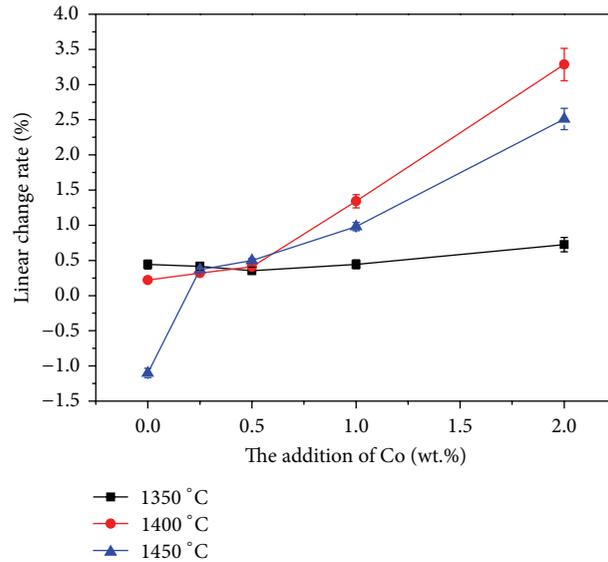


FIGURE 3: Linear change rates of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories with various contents of Co nitrided at different temperatures.

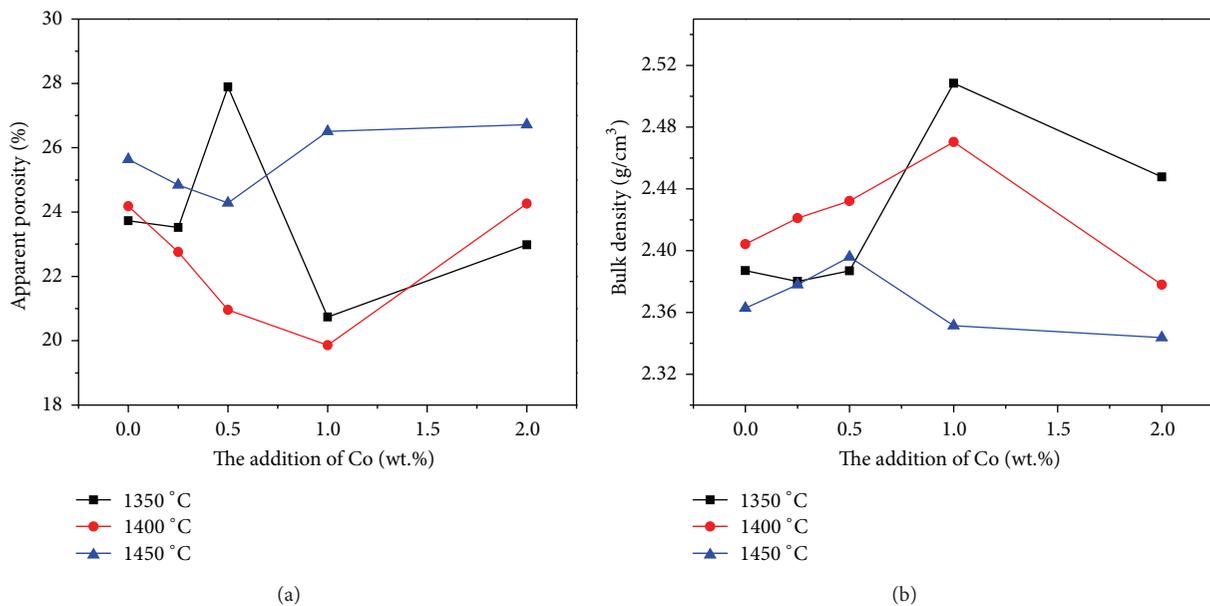


FIGURE 4: (a) Apparent porosity and (b) bulk density of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories with various contents of Co nitrided at different temperatures.

of no Co, the “black” phenomenon could still appear in the product. When adding Co, the Si was fully nitrided in the product, and the quantity of nanofibers was enhanced. Those nanofibers exhibited network connection, which could improve strength of samples. EDS analysis (Figure 2(S3-d)) reveals that those nanofibers were composed of  $\text{Si}_3\text{N}_4$  phase, containing a small amount of Co. The formation of as-formed  $\text{Si}_3\text{N}_4$  nanofibers was through well-established VLS mechanism [26, 27].

### 3.2. Physicochemical Properties of As-Prepared $\text{Si}_3\text{N}_4\text{-SiC}_p$ Composite Refractories.

The linear change rates of  $\text{Si}_3\text{N}_4\text{-SiC}_p$

composite refractories nitrided at different temperatures are shown in Figure 3. After nitridation at 1350°C, linear change rate of the samples was almost 0.5%, revealing that slight expansion occurred during the nitridation process. At 1400°C, the linear change rate was 0.25% in the case of Co absent and slightly increased but also less than 0.5% in the case of adding Co ( $\leq 0.5$  wt.%), whereas it continued to increase when Co was higher than 1.0%. After nitriding at 1450°C, the linear change rate of the sample without Co was  $-1.1\%$ , implying the sample being shrunk. It should be due to the increasing of temperature so that the external force required for the sintering process was improved, which

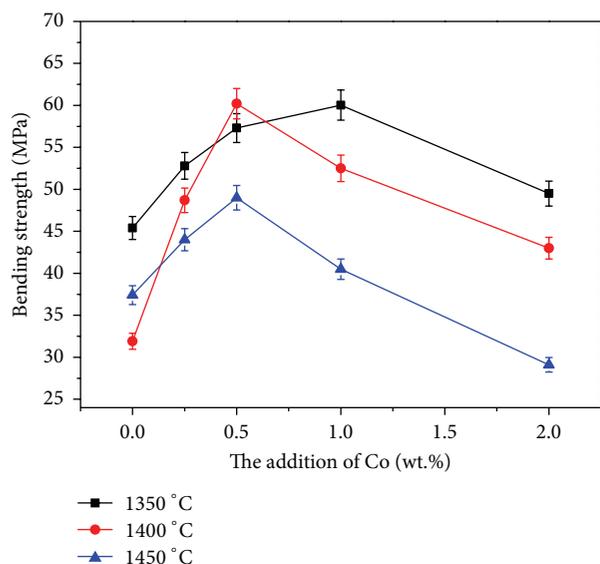


FIGURE 5: The bending strength of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories with various contents of Co nitrided at different temperatures.

promoted the migration of solid-gas interface in the samples during the sintering process and the removal of the more pores. However, the expansion formed after fully nitridation of silicon was not enough to offset the shrinkage from the removal of the pores, resulting in the final shrinkage of samples. The samples with Co at this high temperature had a bit of expansion. When the Co was  $\leq 0.5$  wt.%, the linear change rate of the samples was maintained at 0.5%, whereas it was increased with Co  $> 0.5$  wt.%.

The apparent porosity and bulk density of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories nitrided at different temperatures are shown in Figure 4. After nitriding at 1350°C, the apparent porosity of sample without Co was 23.7%, which was larger than those with Co. At 1400°C, the sample without Co had a large apparent porosity of 25.3%, and it was initially decreased and subsequently increased with the increase of Co. It reached at the smallest value (19.8%) when the content of Co was 1%. When the nitriding temperature was elevated to 1450°C, it was reduced to 24.8% in the sample without Co, and its change trend in the samples with Co was the same as that at 1400°C. The bulk density of the samples under different conditions had an opposite trend, compared to the apparent porosity. As can be seen from the results, the sample with Co content of 0.5 wt.%–1.0 wt.% had the minimum apparent porosity and maximum bulk density.

**3.3. Bending Strength of As-Prepared  $\text{Si}_3\text{N}_4\text{-SiC}_p$  Composite Refractories.** The bending strength of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories with various contents of Co at different temperatures is shown in Figure 5, indicating that it was initially increased and subsequently decreased with the increasing of Co. At 1350°C, it was 45.4 MPa in the case of without Co and reached the highest strength when 1.0 wt.% Co content was added and then decreased with the increasing of Co content. At 1400°C, it had been reduced to 31.9 MPa when

it was without Co, lower than that at 1350°C. It should be relative to the increased apparent porosity rate at 1400°C. As the Co content was 0.5%, the highest strength of 60.2 MPa was achieved. Although the variation tendency at 1450°C was similar to 1400°C, the bending strength of samples became lower. The initially improved strength with the increasing of Co content should be attributed to the increasing content of nanofibers. However, when the Co exceeded a certain amount, the overmuch nanofibers lead to an expansion of the samples, and an evaporation of Si facilitated by the formation of Co-Si liquid phase resulted in an increase in porosity. As is well known, the quantity, shape, size, and distribution of pores generated during the sintering process have a significant impact on the fracture strength of materials. The strength-porosity dependence can be approximated by the following exponential equation [28]:

$$\sigma = \sigma_0 \cdot \exp(-np), \quad (1)$$

where  $\sigma_0$  is the strength of a nonporous structure,  $\sigma$  is the strength of the porous structure at a porosity  $p$ , and  $n$  is a constant. Generally, the bending strength of inorganic nonmetallic materials decreases with the increase of the porosity. In this work, the strength-porosity relationship of the sintering samples could comply with it. Based on the results, we concluded that it was necessary to add catalyst for enhancing nitridation of silicon, facilitating the sintering as well as improving the strength of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories. Herein, the Co content of 0.5% and the temperature of 1400°C were the optimal experimental conditions.

## 4. Conclusions

In this research, we produced *in situ* Cocatalytic nitrided  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories at a relatively low sintering temperature using Si and  $\text{SiC}_p$  as raw materials. The cobalt facilitated the nitridation of Si to form  $\text{Si}_3\text{N}_4$  grain and nanofibers. At 1350°C and 1400°C, the sample without Co still had unreacted Si, whereas the samples with Co were fully nitrided. With the increase of Co addition (from 0 wt% to 2.0 wt%), the liner change rate of as-prepared refractories was increased, and their apparent porosity was initially decreased and subsequently increased, while the bulk density and the bending strength exhibited an opposite trend. The as-prepared  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories had the highest strength of 60.2 MPa when the Co content was 0.5 wt.%. The addition Co accelerated the formation of  $\text{Si}_3\text{N}_4$  nanofibers exhibiting network connection and promoted the sintering of  $\text{Si}_3\text{N}_4\text{-SiC}_p$  composite refractories, thus improving their strength.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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