In Situ Catalytic Synthesis of Si$_3$N$_4$ Nanowhiskers Reinforced SiC Refractories and Their High-Temperature Properties

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Abstract: Silicon nitride (Si$_3$N$_4$)-bonded silicon carbide (SiC) refractory (Si$_3$N$_4$-SiC) is one of the most important nonoxide refractories, but its mechanical properties still suffer from the residual Si. Herein, we report that the nitridation of Si and properties of Si$_3$N$_4$-SiC refractories can be improved by in-situ formed CoO$_x$ catalysts. The room-temperature modulus of rupture (MOR), high-temperature MOR, thermal shock resistance, and oxidation resistance of as-prepared Si$_3$N$_4$(w)-SiC refractories with catalysts were investigated. The results showed that CoO$_x$ catalysts enhanced the nitridation of Si powders and promoted the formation of Si$_3$N$_4$ whiskers. The high-temperature MOR at 1573 K of as-prepared refractories was improved by 30%, compared with samples without catalysts. Moreover, the thermal shock resistance and oxidation resistance of the former was remarkably higher than that of the latter. The improvement was attributed to in-situ formation of Si$_3$N$_4$ whiskers network structure in the samples due to the catalytic effects of CoO$_x$ catalysts.

1. Introduction

Si$_3$N$_4$-bonded SiC(Si$_3$N$_4$-SiC) refractories have been extensively investigated owing to their excellent mechanical properties, such as high strength, relatively high fracture toughness, high oxidation resistance and corrosion resistance[1-5]. Such comprehensive superior behaviors make them as an ideal structural ceramic for a wide variety of structural application, including heat insulators for nuclear reactors, catalyst carriers, hot gas filter, bioreactors, etc[6].Si$_3$N$_4$-SiC refractories are traditionally synthesized via direct nitridation of Si powders with SiC particles in N$_2$ atmosphere. This process namely reaction-bonded method is widely used to prepare Si$_3$N$_4$-SiC refractories, because of its simple, cost-effective, and suitable for industrial production[7-9]. However, the long nitriding time is an important limitation for the practical application due to the very low diffusion efficiency of N$_2$ in molten Si. The strongly exothermic reaction between Si and N$_2$ causes the local overheating and Si melt, resulting in incomplete nitridation of Si and significant deterioration of performance[10, 11].

In order to overcome this problem, many efforts have been devoted to increase the nitriding rate of silicon, such as increasing the nitrogen pressure, prolonging the soaking time, and using metal or metal oxide as catalysts. The addition of catalysts is considered an efficient strategy to enhance the nitridation of Si. For instance, transition metal catalysts not only effectively accelerate the Si nitridation at a reduced temperature, but also facilitate the in-situ formation of well-grown whisker-like Si$_3$N$_4$, owing to their special electronic characteristics[12, 13]. Among the metal catalysts for silicon nitridation, iron is a favorable catalyst being employed for a low cost. Nevertheless, this strategy still suffers from some other disadvantages including agglomeration and storage costs of the
catalysts, and severe agglomeration due to their small sizes and intrinsic magnetism. Considering these problems, metal-oxide catalysts were further studied. Several metal oxides can accelerate the nitridation process of Si powders, such as Y₂O₃, MgO, Al₂O₃/Y₂O₃, and Al₂O₃/ZrO₂[14, 15]. However, the reports associated with the CoOₓ addition as the nitridation catalyst of silicon limited. The effects of powder size, sintering additive, nitriding temperature and other factor effects on the mechanical properties of Si₃N₄/SiC ceramics are still unclear.

In this paper, Si₃N₄nanowhiskers reinforced SiC(Si₃N₄(w)-SiC) refractories were prepared by catalytic nitridation of Si using CoOₓ nano-particles as catalysts. The influence of procedure parameters on the microstructure and high-temperature properties of the refractories was studied.

2. Experiments

2.1. Raw materials

Silicon powder (Si, purity>99.5%, particle sizes<47 μm, Wuhan Wugang Vesuvius Adv. Ceram. Co. Ltd., Wuhan, China) was used as the starting raw material for the Si₃N₄ formation. Cobalt nitrate hexahydrate(Co(NO₃)₂·6H₂O, purity>99.9%, Sinopharm Chem. Co. Ltd., Shanghai, China), sodium dodecyl benzene sulfonate (C₁₈H₂₉NaO₃S, purity>99.9%, Sinopharm Chem. Co. Ltd., Shanghai, China) and hydrazine hydrate (N₂H₄·H₂O, purity>99.9%, Sinopharm Chem. Co. Ltd., Shanghai, China) were respectively used as the precursor, surfactant and precipitant for the preparation of CoOₓ catalyst. Commercial SiC (purities>99.0%) fines <0.1 mm and aggregates with two size classes of 0.1-1.0 mm and 1.0-3.0 mm were utilized for the preparation of Si₃N₄(w)-SiC refractories. All the raw materials were used directly without further purification.

2.2. Preparation of Si₃N₄(w)-SiC refractories

First, the preparation of Co(OH)₂/Si composite powders were prepared on the basis of our previous reports[16,17]. SiC aggregates of different particle sizes were mixed in a mechanical mixture for about 5 minutes, then the liquid polyvinyl alcohol (PVA)solution was added and mixed for another 10 minutes. After that, the SiC powders and Co(OH)₂/Si composite powders were added to the mixture and further mixed for about 20 minutes before being aged at room temperature for 24 hours. After 24 h aging, the resultant powder mixtures were pressed under 150 MPa forming green compacts with dimensions of 25 mm×25 mm×140 mm, and then cured at 393 K for 24 hours. The green compacts were placed in a controlled nitrogen atmosphere furnace and sintered at 1673 K for 2 hours.

2.3. Sample characterization

Phase compositions of samples were identified by powder X-ray diffraction (XRD) using a Philips X’Pert PRO diffractometer (40 mA, 40 kV, Cu Kα radiation, λ = 0.1542 nm, step size of 0.05°, PANalytical, Netherlands). Microstructures and phase morphologies of samples were examined by using a field-emission scanning electronic microscope (FE-SEM, Nova 400 Nano FESEM, PHILIPS, Netherlands, 15 kV) equipped with energy dispersive spectroscopy (EDS). Modulus of rupture (MOR) of a sample (25 mm×25 mm×140 mm) was examined (according to the China standard GB/T3001-2007 and GB/T3002-2004 for room-temperature) under a three-point bending mode using an electronically controlled device (DKZ-600, Wuxi Jianyi Instrument and Machinery Co. Ltd., China) with a span of 100 mm and a loading rate of 0.5 mm/min. Room-temperature MOR and high-temperature MOR of Si₃N₄/SiC refractories were carried out in air and reducing atmosphere, respectively. Cold compressive strength (CCS) of a sample (20 mm×20 mm×20 mm) was tested using an electronically controlled device (LM-02, Longsheng Test Facility Co. Ltd., China) with across head rate of 0.5 mm/min at room temperature. Thermal shock resistance of sample was evaluated by the water quenching method. The samples fired at 1673 K were heated up to 1073 ~ 1573 K and soaked for 30 minutes. Then, the samples were taken out and quickly quenched into a large container of water at room temperature. The quenched samples were dried at 383 K for 24 h before being subjected to residual MOR testing. Five samples were normally tested to obtain a mean value for above testing
experiment. Oxidation resistance of samples (25 mm×5 mm×5 mm) was monitored by a thermal balance (RT-817, accuracy of 0.1 g, Wuhan, China) at 1673 K with a heating rate of 5 K/min in flowing air.

![Figure 1](image1)

**Figure 1.** XRD patterns of Si$_3$N$_4$/SiC refractories nitrided at 1673 K with a flowing N$_2$ atmosphere.

![Figure 2](image2)

**Figure 2.** SEM images and EDS results of the Si$_3$N$_4$/SiC refractories nitrided at 1673 K with 1 wt% CoO$_x$ as catalysts: SiC grains (a) and Si$_3$N$_4$ whiskers (b).

3. Results and discussion

Figure 1 shows the XRD patterns of Si$_3$N$_4$/SiC refractories prepared after 1673 K/2 h nitrided. It can be seen that there were still diffraction peaks of Si in the XRD pattern of the sample without catalyst. However, in the sample prepared by adding 1 wt% of CoO$_x$ nanoparticles as a catalyst, the peaks of Si in the XRD pattern of the sample disappeared, indicating that the Si powder has been completely converted into Si$_3$N$_4$. Comparing with the sample without catalyst, it can be seen that the addition of the catalyst CoO$_x$ effectively increases the nitriding efficiency of the Si powders.

Figure 2 shows SEM images of Si$_3$N$_4$/SiC refractories prepared after 1673 K/2 h nitridation with 1 wt% CoO$_x$ as catalysts. A number of whiskers with 90-270 nm in diameter and tens of micrometers in length were fabricated in the final products. EDS showed that the whiskers(Fig. 2b) contained mainly Si and N, confirming that the whisker was Si$_3$N$_4$. The whiskers were interspersed among the SiC aggregates and twined around each other to form a network structure.
Figure 3. The influences of temperature and catalyst on the room temperature MORs and CCS of Si₃N₄/SiC refractories.

Figure 3 shows a graph of the MOR and CCS of Si₃N₄/SiC refractories prepared at various nitriding temperatures. The results showed that the MOR and CCS of the specimens increased with the nitriding temperature from 1573 K to 1673 K were on the rise. This is because as the nitriding temperature increased, the nitriding rate of the Si powders increased, and the content of the Si₃N₄ binding phase in the samples increased, thereby enhancing the bonding strength between the matrix and the aggregate of the samples. The MOR and CCS of the samples with CoOₓ catalysts were 23.9% and 15.6% higher than the samples without catalyst. Comparing with the samples without catalyst, the addition of CoOₓ catalyst significantly improved the MORs and CCS at room temperature of Si₃N₄/SiC refractories. The reason for this can be attributed to the fact that the introduction of the catalyst effectively promotes the formation Si₃N₄ whiskers.

Figure 4. HMOR of Si₃N₄/SiC refractories prepared at 1673 K with and without CoOₓ catalysts tested at various temperatures.

The HMORs of Si₃N₄/SiC refractories sintered at 1673 K is illustrated in Figure 4. HMOR of samples with CoOₓ catalysts was higher than that of the sample without catalysts at all tested temperatures. For instance, compared with the sample without any catalysts, the value of the HMOR of the sample containing 1 wt% CoOₓ was improved almost 30% at 1573 K. The enhanced HMOR of the samples containing catalysts could be attributed to the complete conversion of Si and the formation of Si₃N₄ whiskers network structure. Moreover, It is apparent that that the HMOR of Si₃N₄/SiC
refractories increases first and then decreases with the increase of testing temperature. Crack healing of surface flaws and the relief of residual thermal stresses formed during the sintering might contribute to the increase in the strength. When the testing temperature is up to 1573 K, new thermal stress generated from the mismatch of thermal expansion coefficients between SiC and Si₃N₄, resulting in the degradation of the strength.

Figure 5 displays the residual MORs and residual MOR ratios of the samples quenched at different temperatures. It can be seen that residual MORs and residual MOR ratios of all the samples exhibited a downtrend in general. Residual MORs of the samples containing 1 wt% CoOₓ catalysts were higher than the samples without catalysts. The residual MOR ratio of the sample with catalyst was higher than the sample without catalyst at 1573 K. It exhibited that the use of catalysts had no negative impact on the thermal shock resistance of the prepared Si₃N₄/SiC refractories. The enhanced thermal shock resistance of the samples containing catalysts could be attributed to the following: 1) The introduction of the CoOₓ catalysts promoted formation of Si₃N₄ whiskers, their strengthening and toughening mechanisms, including crack deflection, bridging, fracture, and pull-out, delayed the crack propagation. 2) The homogeneously dispersed Si₃N₄ whiskers not only absorbed and relieved thermal stresses but also reduced stress concentration of thermal stresses in the interiors of the refractories, thus improving the thermal shock resistance.

![Figure 5](image1.png)

**Figure 5.** Thermal shock resistance of Si₃N₄/SiC refractories prepared at 1673 K with and without CoOₓ catalysts tested at various temperatures.

![Figure 6](image2.png)

**Figure 6.** Mass gain plot of Si₃N₄/SiC refractories prepared with and without CoOₓ catalysts.
Figure 6 shows the oxidation behavior of Si$_3$N$_4$-SiC refractories with and without catalysts. When the experimental temperature is up to 1273 K, a dramatic increasing of the mass gain present in the plot, indicating the oxidation occurred at the temperature. However, the mass gain value of the samples with CoO$_x$ catalysts is clearly lower than that of the sample without catalysts. The reason may be that the residual Si remained in the catalyst-free sample have poor oxidation resistance, comparing with Si$_3$N$_4$. On another hand, the in-situ formed Si$_3$N$_4$ nanowhiskers might block the pores in the structure of Si$_3$N$_4$-SiC refractories, preventing the diffusion of oxygen molecules. These results indicate that the introduction of the CoO$_x$ catalysts improves the oxidation resistance of the as-prepared refractories.

4. Conclusions

In this work, Si$_3$N$_4$(w)-SiC refractories were prepared by the catalytic nitridation method using CoO$_x$ as catalysts and Si powders, SiC fines, and aggregates as raw materials. The influence of CoO$_x$ addition on microstructure and high-temperature properties of the Si$_3$N$_4$-SiC refractories has been investigated.

(1) The introduction of the CoO$_x$ catalysts not only facilitated the nitridation of Si powders but also promoted the formation of Si$_3$N$_4$ whiskers.

(2) The room-temperature MOR, high-temperature mechanical properties, thermal shock resistance, and oxidation resistance of as-prepared Si$_3$N$_4$(w)-SiC refractories with CoO$_x$ catalysts were greatly improved comparing with those of samples without catalysts. The reason is attributed to the formation of a network structure built by in-situ formed Si$_3$N$_4$ whiskers.

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