**Original Article**

**Oxidation mechanism and kinetics of SiBCN/HfC ceramic composites at high temperatures**

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SiBCN/HfC ceramic composites were obtained via mechanical alloying and hot-press sintering. We evaluated the high-temperature oxidation resistance of the SiBCN/HfC ceramic composites after heat treatments at 1500 and 1750 °C in static air. The SiBCN/HfC composites have an oxidation rate constant \(K_{5.20}\) of 1.1 \(\mu\text{m}^2/\text{h}\) at 1500 °C, which is less than that for other SiBCN-based ceramics (5.4 \(\mu\text{m}^2/\text{h}\)). After oxidation at 1750 °C, HfO\(_3\) and HfSiO\(_4\) spherical nanocrystals resulting from the oxidation of Hf were dispersed in silica layers that acted as a dense continuous protective coating on the surface of the SiBCN/HfC samples and provided a higher resistance to high-temperature exposure.

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**1. Introduction**

SiBCN ceramics are expected to be used as a thermal barrier in spacecrafts due to their good mechanical properties, their thermal stability, their outstanding resistance to oxidation as well as their ablation and creep at high temperatures [1–5]. However, SiO\(_2\) is generated during the oxidation process of SiBCN and cracks are formed because of the phase transformation from amorphous silica to cristobalite [5]. The cracks formed provide direct channel for oxygen diffusion, which accelerates the oxidation of the matrix [6]. Besides, the surface cracks limit any practical application. Therefore, it is critical to improve the oxidation resistance of SiBCN ceramics used as anti-oxidation components [7].

HfC has good physical and chemical properties in ultra-high-temperature oxidative environments, including a high melting point, a high hardness, and a good ablation resistance [8]. The introduction of HfC into Si-based ceramics can improve the high-temperature properties of the composite due to the generation of a silica protective layer dispersed with HfO\(_2\) particles [9–11]. In addition, the formation of a compact glassy HfO\(_2\) layer on the coating surface efficiently prevents the inner composites from being further oxidized [12]. Moreover, the high-temperature stability of the HfSiO\(_4\) phase derived from the solid reaction between HfO\(_2\) and SiO\(_2\) hinders the phase transformation and protects the sample from further oxidation [13,14]. Besides, the HfSiO\(_4\) particles dispersed in the silica matrix can deflect and arrest cracks, which will also improve the oxidation resistance of the ceramics.

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Therefore, we expect that the anti-oxidation properties of SiBCN ceramics at high temperatures can be enhanced by the introduction of HfC component.

The introduction of an Hf-based ceramic into the SiBCN ceramic has been achieved by reactive melt infiltration (RMI) [15] and by polymer infiltration pyrolysis (PIP) [16–18]. However, it is very difficult to obtain fully dense composites because of the closed pores generated during the pyrolysis process [17], which creates a diffusion channel for oxygen and reduces the oxidation resistance of the ceramics. Clearly, the preparation of dense Hf-based SiBCN ceramics is challenging. We have previously reported the direct addition of an HfC powder to a SiBCN matrix [19] and how the ablation properties of the SiBCN under a plasma flame were improved by adding HfC. However, it is necessary to study the oxidation properties and mechanism of the SiBCN/HfC ceramic composites because it can help understand the effect of Ultra-High-Temperature-Ceramics (UHTCs) components on SiBCN ceramics.

In this work, the SiBCN amorphous powder and the HfC nanoparticles were obtained by mechanical alloying, and the SiBCN/HfC ceramic composites were subsequently fabricated by hot-press sintering. The phase composition and the microstructure of the ceramics, as well as their oxidation mechanism and kinetics at 1500 and 1750 °C were investigated.

2. Materials and methods

The amorphous SiBCN powder was obtained by mechanical alloying using silicon powders (δ_{Si} = 5 μm, 99.9% in purity), hexagonal boron nitride (h-BN) (δ_{h-BN} = 1 μm, 99.9% in purity), graphite powders (δ_{graphite} = 5 μm, 99.9% in purity), and a hafnium carbide powders (δ_{HfC} = 1 μm, 99.9% in purity) as raw materials (Haotian Nano Technology Co., Ltd, Shanghai, China). The molar ratio of Si: BN: C: HfC was 2:1:3: x for x = 0 and 0.5, which was named SiBCN and SiBCN/HfC0.5 (SiBCN/HfC), respectively. Then, we loaded the SiBCN and HfC mixed powders into silicon nitride jars with tungsten carbide balls in an Ar atmosphere. The balls to powder mass ratio was 30:1. The mixed powder was milled for 30 h by a planetary ball mill (FRISTCH P 4, FRISTCH Scientific Instruments Company, Germany) at a rotational speed of the main disk and the planet disk was of 300 and 700 rpm, respectively. Finally, the milled powder was passed through a 100-mesh sieve and placed in a graphite mold coated with BN, heated to 1500 °C for 1 h at a rate of 20 °C/min, and hot-pressed at a pressure of 60 MPa in a nitrogen atmosphere.

The oxidation experiments were conducted in a horizontal tube furnace (GSL-1800X, Hefei “Ke Jing” Materials Technology Co., Ltd., China) equipped with a MoSi2 heating element. The sample was cut into 3 mm × 4 mm × 10 mm bars and four different bars were considered for each oxidation time. Then, the samples were loaded in an Al2O3 crucible and placed in the Al2O3 tube with open ends. The target oxidation temperatures were 1500 and 1750 °C with a heating rate of 10 °C/min and for holding times of 1, 3, 5, 10, 15, and 20 h in static air. After a set soaking time, the samples were cooled down to room temperature in the furnace. The scale thickness was measured using at least ten points on the oxidized samples from scanning electron microscopy (SEM) images. The scale thickness was plotted as a function of oxidation time and the parabolic oxidation rates of the SiBCN and SiBCN/HfC ceramics at 1500 °C were determined using Eq. (1)

\[ y^2 = Kp \times t \]  

(1)

Where \( y \) is the thickness of oxide layer (in μm) and \( Kp \) is the parabolic oxidation rate.

The structural analysis of the samples before and after the oxidation test was performed using X-ray diffraction (XRD, D8 ADVANCE, Germany), field-emission scanning electron microscope (SEM, Magellan 400, FEI, USA) equipped with an energy dispersive spectrometer, and a 200-kV field emission transmission electron microscope (TEM, JEM-2100F, JEOL, Japan). The focused ion beam (FIB) slices were prepared using an FEI Versa 3D Dual Beam system. The High-Angle Annular Dark Field (HADDF), Scanning transmission electron microscope (STEM) and selected-area electron diffraction (SAED) characterizations were performed on the TEM.

3. Results and discussion

3.1. Phases and microstructure of the sintered SiBCN and SiBCN/HfC composites

Fig. 1 shows the XRD spectra of the SiBCN and the SiBCN/HfC. The main phases of the SiBCN ceramics are β-SiC, α-SiC and BN(C). The XRD pattern of the SiBCN/HfC composites indicates that the main phases of the samples are β-SiC, HfC and BN(C). The peak at 2θ = 12° is observed in both samples; and it is attributed to the BN(C) (002) planes. The reflection peaks at 2θ = 35, 61, and 72° are attributed to the (111), (220), and (311) planes of β-SiC or the (102), (110), and (116) planes of α-SiC [3], respectively. The reflection peaks at 2θ = 33, 39, 56, 67, and 70° are attributed to...
the (111), (200), (220), (311), and (222) planes of HfC [16]. The peak at 14° in SiBCN/HfC composites is attributed to the (100) plane of WO₃ that is induced by the WC mill balls. The microstructure of the SiBCN samples was also characterized by TEM and high-resolution TEM, as shown in Fig. 2. Some nanoparticles with a size of about 100 nm (Fig. 2a) form “capsule-like” structures. The inner part of the “capsule-like” nanoparticle has a size of 40 nm (Fig. 2b) and lattice fringes with a spacing of 0.26 nm (Fig. 2c) were ascribed to the (111) crystal face of β-SiC, as identified by SAED (Fig. 2d). The outer shell of the “capsule-like” nanoparticle has a size of 10 nm, and the lattice fringes with a spacing of 0.36 nm (Fig. 2c) were ascribed to the (002) crystal face of BN(C) (turbostatic BN(C) t-BN(C)). It prevents the inner SiC nanocrystal from growing further. Fig. 2(b, c) also show the stacking faults and twins in the SiC grains, which corresponds to the SAED pattern in Fig. 2(d).

Fig. 3(a) shows that the HfC grains with sizes within 100–500 nm are dispersed randomly in the SiBCN matrix. The grain size was comparable to that of SiC. The grains in the SiBCN/HfC ceramic composites were coarser than in SiBCN, which may be attributed to HfC promoting grain growth in the matrix. The t-BN(C) phase was mainly distributed between the grain boundaries of the SiC and HfC crystals based on the observations from Fig. 3(a, b). The three phases are agglomerated, which damages the SiC-BN(C) “capsule-like” structure. Fig. 3(c) shows that the HfC grain is wrapped by t-BN(C), which corresponds to an SAED pattern where the diffraction spots for t-BN(C) and HfC appear simultaneously.

3.2. Oxidation of SiBCN and the SiBCN/HfC composites

Fig. 4 shows the XRD spectra of SiBCN and the SiBCN/HfC composites after oxidation. Cristobalite is observed because of the oxidation of SiC. The intensity of the cristobalite diffraction peaks increases with the temperature. m-HfO₂ is present (Fig. 4b) since it originates from the oxidation of HfC. The high-temperature stability of HfSiO₄ is due to the reaction between HfO₂ and SiO₂ when the temperature is above 1300 °C, according to the binary phase diagram of HfO₂ and SiO₂ [20].

Fig. 5(a, c) shows the cross-section and the surface morphology of SiBCN after oxidation at 1500 °C for 5 h. The cross section of the SiBCN sample is composed of three structures: (a) a surface oxide layer of cristobalite distributed in silica glass with some unpenetrated cracks, (b) a transition silica layer distributed with SiC and BN(C), and (c) the unreacted ceramic matrix. When combining the EDS analysis in Fig. 6(a, b) with the EDS elemental maps of the oxide layer of SiBCN (Fig. 5e), we demonstrate the existence of a partially dissipative SiC layer and a layer rich in N (B). The map for B is not shown because the SEM energy spectra had a poor accuracy for such light elements. However, the distribution of B can be seen in the N map because B is always present as BN(C). Fig. 5(c) indicates that the flaky cristobalite peeled off from the oxide layer and a continuous silica layer remained below. The cristobalite preferentially nucleated at the interface between the glass and the atmosphere, then grew in the depth direction and in the horizontal direction [21]. The cracks formed are caused by the thermal expansion coefficient mismatch between cristobalite (8 x 10⁻⁶/K) and the amorphous silica (0.4 x 10⁻⁶/K) [22] during the phase transformation. Moreover, the cracks provide a direct diffusion channel for O₂, which reduces the oxidation resistance of the SiBCN ceramics.

Fig. 5(b, d) show the cross-section and surface morphology of SiBCN/HfC after oxidation at 1500 °C for 5 h. The HfO₂ and HfSiO₄ grains precipitate at the outer surface of the oxide layer and no apparent cracks are observed. The coefficient of thermal expansion (CTE) of HfSiO₄ (3.8 x 10⁻⁶/K) [23] and HfO₂ (5.6 x 10⁻⁶/K) [24] compensate for the difference in the CTE between the cristobalite and the silica, which explains the absence of crack formation. The HfSiO₄ phase stable at high temperatures is formed by the reaction between HfO₂ and SiO₂. It improves the stability of the silica glass and the oxidation resistance of the SiBCN/HfC composites. Furthermore, the HfSiO₄ formed has a significantly lower oxygen diffusivity than borosilicate or silica, which further enhances the oxidation resistance of the ceramic composites [14]. The diffusion coefficient of oxygen in HfO₂O₂, HfO₂ is lower than in HfC [25]. The EDS elemental analysis in Fig. 5(a, b) reveals that N (B) is enriched at the interface between the matrix and the silica layer. After the formation of a continuous protective layer on the surface of the samples, the partial pressure of oxygen at the interface between the oxide layer and the matrix is lower than that at the surface. Under these conditions, the active oxidation of SiC occurs before the oxidation of BN(C) [26]. Therefore part of BN(C) survives after a continuous oxide layer is formed. This demonstrates that the intermediate layer is a partially dissipative SiC layer. Moreover, boron remains in the oxide layer of SiBCN/HfC, according to the EDS analysis of spot1 (insert in Fig. 5b). This benefits the healing of cracks at high temperatures. The EDS map of boron is shown in Fig. S1 (Supporting information). Although the scale thickness of both samples is equivalent, many cracks were observed in SiBCN, whereas the oxide layer of SiBCN/HfC remains intact, thereby indicating a better oxidation resistance.

Fig. 6(a, b) show the surface and the fracture morphology of the SiBCN/HfC ceramic oxidized at 1750 °C for 3 h. Compared with the SiBCN/HfC oxidized at 1500 °C, spherical nano-grains with a diameter within 20–50 nm are unevenly distributed in the silica layer in addition to the large particles of HfO₂ and HfSiO₄. First, the segregation of the components occurred in the amorphous silica, then HfSiO₄ nucleus with size of several nanometers appeared and grew. This is consistent with the reaction between SiO₂ and HfO₂ that is accompanied by the formation of an HfSiO₄ stable at high temperatures. The oxide layer of the SiBCN/HfC sample has a good adhesion to the matrix without the partially depleted SiC layer (Fig. 5f). Fig. 7c, d) show the HADDAF image and the EDS line analysis. The core is composed of HfSiO₄ whereas the shell is composed of BN(C). Fig. 6e, f) show the surface and the fracture morphology of the SiBCN ceramic oxidized at 1750 °C for 3 h. Numerous pores and bubbles are observed on the surface of the SiBCN ceramic. They probably originate from the escape of gaseous by-products. The destruction of the oxide layer reduces the integrity of the diffusion barrier, which reduces the oxidation resistance of the internal matrix. The generation of bubbles on the surface of the sample is critical for practical applications. However, a dense continuous protective silica layer still
remains on the surface of the SiBCN/HfC composite at 1750 °C, which reveals that the introduction of HfC overall improves the high-temperature oxidation resistance of the SiBCN ceramics.

3.3. Oxidation kinetics and mechanism of the SiBCN and SiBCN/HfC ceramic composites

Figs. S4 and S5 show the oxide scale thickness measured from the fracture morphology of the SiBCN and SiBCN/HfC ceramic composites. Fig. 7b shows the evolution of the scale thickness with the oxidation time. The scale thickness change in the SiBCN and SiBCN/HfC ceramic composites at 1500 °C follows a parabolic evolution, suggesting that the oxidation process is diffusion limited. The Pearson coefficient $r$ is close to 1 (Table 1) (Supporting Information), which indicates a high degree of conformity with a parabolic law. In the short-term range (1–5 h), SiBCN and SiBCN/HfC oxidized rapidly at parabolic oxidation rates of 10.8 and 8.1 $\mu$m$^2$/h, respectively. This correlates with the rapid oxidation of the HfC and BN(C) phases and the generation of gas products. However, the parabolic oxidation rate slowed down when the oxidation time further increase (>5 h), which indicated the formation of a continuous protective oxide layer. The parabolic oxidation rate of the SiBCN/HfC ceramic composites was 1.1 $\mu$m$^2$/h, which is less than that of the SiBCN ceramics (5.4 $\mu$m$^2$/h).

A dense and continuous SiO$_2$ layer dispersed with HfSiO$_4$ and HfO$_2$ particles covered the surface of the SiBCN/HfC ceramic composites and reduced the diffusion of oxygen diffusion into the ceramic matrix. When the cristobalite on the surface of the SiBCN is peeled off, the oxidation resistance of the ceramics is reduced. By combining the oxidation curves and the surface morphology (Fig. 7), we demonstrate that the oxidation of SiBCN and SiBCN/HfC ceramics are controlled by oxygen diffusion. The enriched HfO$_2$ and HfSiO$_4$ on the surface of the oxide layer effectively reduce the inward diffusion rate of oxygen [13], which reduces the growth rate of the oxide layer and increases the oxidation resistance of the SiBCN ceramics.

Fig. 8a,b,c,d and Fig. 6 illustrate that many nano-spheres with a “capsule-like” structure and diameters of several nanometers to tens of nanometers are dispersed homogeneously in the cross-section and the outer surface of the oxide scale. The uniformly dispersed HfSiO$_4$ nanoparticles effectively inhibit the crystallization of the silica. Meanwhile, it also matches the difference in the CTE and reduces the occurrence of cracks. The core of the spherical nano-grains in the HfSiO$_4$ crystals is identified by SAED, a shown in the insert in Fig. 8c.
The shell has a BN(C) phase, as confirmed by the EDS line analysis (Fig. 6(d)). However, the mechanism of the formation of the “capsule-like” structure cannot be clearly explained. The ceramic composites are gradually oxidized from the surface to the inside as the oxygen diffuses into the pores, cracks, and grain boundaries. The EDS line analysis of L₁ indicates that white particles at the surface are HfSiO₄. The “capsule-like” structure is destroyed by the oxidation of BN(C) near the surface, leaving an HfSiO₄ core. However, the oxidation of the BN(C) shell leads to the formation of borosilicate that fills the
Fig. 5 – Cross-section and surface microstructure of samples after oxidation at 1500 °C for 5 h: (a) and (c) SiBCN; (b) and (d) SFC05; (e) EDS elemental maps of (e) SiBCN and (f) SiBCN/HfC05.

Two classic models have been proposed for grain growth in the presence of a liquid phase: (a) coalescence process [27] and (b) solution-reprecipitation process. The theoretical grain-growth through solution-reprecipitation was first predicted by the Lifshitz-Slyozov-Wagner (LSW) theory [28,29]. In this experiment, the grains will grow by solution-reprecipitation and by coalescence of the solid phase. The transport paths in adjacent grains are composed of (a) the grain boundary migration via solid-state diffusion, (b) the grain-boundary migration via diffusion across an intermediate thin liquid layer, and (c) the solution-reprecipitation from a small grain to a large one [28,29]. The driving force for the grain growth is the reduction of the total system energy by reducing the grain boundary area. Fig. 8(b,d) and Fig. 9(a) show that HfSiO۴ with a diameter of several nanometers first precipitates in the middle of the amorphous silica layer. Then, spherical HfSiO۴ crystals diffuse from the matrix to the scale surface and the grain size gradually increases near the scale surface (Fig. 8(b)). Fig. 9(a), (c) show that, a HfSiO۴-depleted region (diffusion zone) appears near the large particles. Fig. 8(d) and Fig. 9 shows a typical feature of the Ostwald ripening mechanism, namely the growth of spherical nano-grains by absorbing small grains. The red arrows labeled in Fig. 9(a), (b), (d) show the grain growth via precipitation from the small grain [30] to larger one.
Fig. 6  –  (a) Cross-section and (b) surface microstructure of the SiBCN/HfC samples after oxidation at 1750 °C for 3 h. (c) HADDF image of the core-shell structure. (e) EDS elemental line analysis of (c), (e), and (f) SiBCN.

Fig. 7  –  Thickness of the oxide layer as a function of time at 1500 °C.
Fig. 8 – FIB slice of SiBCN/HfC after oxidation at 1750 °C for 3 h. (a) Surface morphology (b) HAADF image (c) Enlarged top area of the FIB slice. (d) Enlarged image of (b). (e) EDS line analysis of L1 in (c). (f) EDS line analysis of L2 in (b).

The oxidation process and the formation of the oxide layer structure can be summed up as follows. In the initial stage, at relatively low temperatures within 400–900 °C, B₂O₃ formed by the oxidation of BN(C) spreads on the sample surface and protects the interior matrix. Meanwhile, the HfC on the outer surface of the SiBCN/HfC ceramics reacts with oxygen and forms HfO₂. When the temperature increases to 900–1300 °C, the oxidation product from the reaction of SiC with B₂O₃ forms borosilicate glass, according to the phase diagram [31]. The latter can withstand up to 1500 °C but will decompose at higher temperatures. At high temperatures within 1300–1750 °C, the highly-stable HfSiO₄ phase formed from the solid reaction between HfO₂ and SiO₂ improves the stability of the silica glass and has a low oxygen diffusivity. Furthermore, HfSiO₄ hindered the phase transformation of amorphous silica into cristobalite, which is evidenced by the difference in the diffraction intensity of the cristobalite peaks in SiBCN and SiBCN/HfC after oxidation (Fig. 4). There are no significant cristobalite peaks in the XRD pattern of Fig. S3, which indicates that HfO₂ can effectively hinder the crystallization of the amorphous silica. Based on this analysis, a dense continuous protective layer dispersed with HfO₂ and HfSiO₄ is tightly bound to the ceramic matrix in the entire oxidation temperature range and reduces the oxidation of the inner matrix.

The cross-section of the SiBCN/HfC ceramic after oxidation can be divided into three regions: (1) a dense continuous SiO₂ layer dispersed with HfO₂ and HfSiO₄, (2) an amorphous silica layer dispersed with spherical HfSiO₄ nanoparticles with a “capsule-like” structure, and (3) the unreacted matrix. A dense continuous oxide layer uniformly distributed with HfSiO₄ and
HfO$_2$ particles is formed in the oxide scale. It offers an effective diffusion barrier against oxygen and improves the oxidation resistance of the SiBCN ceramics.

4. Conclusions

We studied the oxidation mechanism and the oxidation kinetics of SiBCN and SiBCN/HfC ceramic composites at 1500 ºC. Both followed a parabolic kinetic evolution law at 1500 ºC. The oxidation kinetics constant $K_{1500}$ of SiBCN/HfC drops to 1.1 $\mu$m$^2$/h upon introduction of HfC, which is less than that for the SiBCN ceramics (5.4 $\mu$m$^2$/h). A dense continuous silica layer dispersed with HfO$_2$ and HfSiO$_4$ particles effectively reduces the formation of cracks and the inward oxygen diffusion. The HfO$_2$ and HfSiO$_4$ grains enriched on the surface of the oxide layer are formed through an Oswald ripening mechanism. After oxidation at 1750 ºC, an integral protective silica layer remains on the surface of the SiBCN/HfC ceramic composites. However, the silica layer of SiBCN is heavily destroyed by the gas products formed. Above all, the homogenous HfO$_2$ and HfSiO$_4$ resulting from the oxidation of HfC in silica helps improve the oxidation resistance of the SiBCN ceramics.

Conflict of interest statement

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled “Oxidation behavior, mechanism and kinetics of SiBCN/HfC ceramic composites at high temperatures”.

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Appendix A. Supplementary data

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