Microstructural evolution and mechanical properties of *in situ* nano Ta₄HfC₅ reinforced SiBCN composite ceramics

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Received: March 11, 2020; Revised: June 25, 2020; Accepted: July 16, 2020

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Abstract: The *in situ* nano Ta₄HfC₅ reinforced SiBCN–Ta₄HfC₅ composite ceramics were prepared by a combination of two-step mechanical alloying and reactive hot-pressing sintering. The microstructural evolution and mechanical properties of the resulting SiBCN–Ta₄HfC₅ were studied. After the first-step milling of 30 h, the raw materials of TaC and HfC underwent crushing, cold sintering, and short-range interdiffusion to finally obtain the high pure nano Ta₄HfC₅. A hybrid structure of amorphous SiBCN and nano Ta₄HfC₅ was obtained by adopting a second-step ball-milling. After reactive hot-pressing sintering, amorphous SiBCN has crystallized to 3C–SiC, 6H–SiC, and turbostratic BN(C) phases and Ta₄HfC₅ retained the form of the nanostructure. With the *in situ* generations of 2.5 wt% Ta₄HfC₅, Ta₄HfC₅ is preferentially distributed within the turbostratic BN(C); however, as Ta₄HfC₅ content further raised to 10 wt%, it mainly distributed in the grain-boundary of BN(C) and SiC. The introduction of Ta₄HfC₅ nanocrystals can effectively improve the flexural strength and fracture toughness of SiBCN ceramics, reaching to 344.1 MPa and 4.52 MPa·m^{1/2}, respectively. This work has solved the problems of uneven distribution of ultra-high temperature phases in the ceramic matrix, which is beneficial to the real applications of SiBCN ceramics.

Keywords: Ta₄HfC₅; SiBCN; microstructure evolution; mechanical properties

1 Introduction

With the development of aerospace technology, more

stringent property requirements are put forward for advanced structural-functional integration of ceramic materials. Among many high-temperature structural materials, SiBCN non-oxide ceramics have attracted considerable attention due to their light-weight, high specific strength, excellent thermal stability, and resistance to thermal shock, oxidation, and ablation [1–3].

Polymer/precursor derived ceramics (PDCs), one of

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the very first routes to prepare SiBCN materials, remain amorphous nature at least up to 1400 °C, and do not undergo microstructural changes at this temperature [3]. The chemistry, microstructure, and properties of the PDCs SiBCN can be tailored effectively by controlling the initial reagent structure, chemical reaction, and processing parameters [4]. However, this method also has some nonnegligible shortcomings that limit its wide applications. The starting materials (such as SiCl_3CH_3 , and BCl_3) are usually expensive and some organic solvents used are harmful to human health and the environment [5]. During pyrolysis, the gas release and mass loss require careful monitoring to avoid porous structure and to carefully control shrinkage (even microcracks) [5–7].

Mechanical alloying and solid-state sintering techniques (also referred to as inorganic method) to obtain dense nano or amorphous SiBCN monoliths and their ceramic composites were proposed [6]. One of the significant advantages of this processing route is to provide centimeter-sized samples convenient for evaluating the basic mechanical and thermophysical properties [7,8]. However, the previous studies showed that the heterogeneous microstructure leading to poor mechanical properties of the SiBCN ceramics are needed to be further optimized for the real applications at high temperatures [9,10].

The addition of ultra-high temperature ceramics (UHTCs) into the SiBCN ceramic matrix is believed to be an effective strategy to improve the mechanical performance and high temperature properties of SiBCN ceramics [11–14]. In previous attempts, the microstructural evolution and thermal stability of the porous PDCs ZrB_2 -SiBCN and HfN -SiBCN composite ceramics have been investigated [15,16]. However, due to the limitation of sample size, the mechanical properties of these composite ceramics have not been evaluated. In another contribution, Liang *et al.* [17–19] have introduced some LaB_6 into the SiBCN matrix by the inorganic method, obtaining desirable mechanical properties compared with pure SiBCN. However, during the sintering process, some LaB_6 has reacted with SiBCN ceramic matrix to generate $\text{La}_2\text{B}_2\text{C}_6$, and consequently, the strengthening and toughening effects of LaB_6 were significantly reduced. Further, Miao *et al.* [20–21] have prepared SiBCN- ZrB_2 composite ceramics by mechanical alloying combined with the sol-gel method. The results suggested that the *in situ* ZrB_2 can improve the mechanical properties of SiBCN ceramic

materials to some extent; however, the particle size of the *in situ* ZrB_2 has grown up to a maximum value of $\sim 1\ \mu\text{m}$.

Generally, the following factors should be considered when the external UHTCs are selected as reinforcements in SiBCN ceramics: (i) They should not react with the SiBCN matrix to form strong bonding interfacial structure during annealing or sintering; (ii) they could be uniformly dispersed in the ceramic matrix in the form of nanocrystals; and (iii) they are supposed to have good physical-chemical compatibility with SiBCN.

The chemically stable Ta_4HfC_5 , the current highest melting point compound, was theoretically forecasted by Agte and Alterthum. [23] and the experiment confirmed by Andrievskii *et al.* [24]. Up to the present, various strategies are used to the synthesis of the high pure Ta_4HfC_5 . For example, Simonenko *et al.* [25] have reported a sol-gel technology for preparing Ta_4HfC_5 using metal oxide and gel of polymeric carbon source. The polymeric carbon source undergoes preliminarily annealing to provide a uniform dispersion of metal oxide-carbon mixture, and then further heating to 1200–1500 °C to obtain pure Ta_4HfC_5 . Lu *et al.* [26] used the Hf and Ta containing polyantantahafnoxane modified with allyl-functional novolac resin to produce Ta_4HfC_5 polymer (polyantantahafnoxanesal). The resulting polyantantahafnoxanesal is subsequently solidified and pyrolyzed at 1400 °C to obtain pure Ta_4HfC_5 . These methods are very effective to prepare pure Ta_4HfC_5 with high thermal stability and chemical stability; however, these processing methods often contain complex synthesis steps leading to high-cost products. The raw materials used are also flammable and present waste disposal problems. For this reason, Gaballa *et al.* [27] have successfully prepared nano Ta_4HfC_5 by mechanical alloying for the first time. However, the formation mechanisms of the mechanical alloying derived nano Ta_4HfC_5 is still unclear,

Thus, in this work, initially, the Ta_4HfC_5 nanocrystals were prepared by the mechanical alloying method and the formation mechanism of Ta_4HfC_5 during mechanical alloying was analyzed. Then, SiBCN- Ta_4HfC_5 amorphous-nanocrystalline composite ceramic powder was prepared by the second step of mechanical alloying. Afterward, the hot-pressing sintering technology was adopted to consolidate SiBCN- Ta_4HfC_5 composite ceramics. As expected, the homogeneous distribution of nano Ta_4HfC_5 within the SiBCN ceramic matrix strongly improved the mechanical properties of the composite ceramics. The formation mechanisms of mechanical alloying

derived nano Ta₄HfC₅, and the correlation of microstructural evolution and mechanical properties of the resulting SiBCN–Ta₄HfC₅ composite ceramics were illustrated.

2 Materials and methods

2.1 Raw materials

Hexagonal boron nitride (h-BN, 99.0% purity, 0.6 µm, purchased from Advanced Technology & Materials Co., Ltd.), graphite (99.5% purity, 8.7 µm, purchased from Qingdao Huatai Lubricant Sealing S&T Co., Ltd.), cubic silicon (c-Si, 99.9% purity, 9.0 µm, purchased from China New Metal Materials Technology Co., Ltd.), hafnium carbide (HfC, 99.0% purity, 1 µm, purchased from Shanghai Puwei Applied Materials Technology Co., Ltd.), and tantalum carbide (TaC, 99.0% purity, 1 µm, purchased from Shanghai Puwei Applied Materials Technology Co., Ltd.) were used here as received.

2.2 Synthesis of Ta₄HfC₅ nanocrystals

Ta₄HfC₅ nanocrystals were prepared by the mechanical alloying method via a P4 high-energy ball-miller manufactured by FRITSCH company. Firstly, TaC and HfC mixed powders with a molar ratio of 4:1 were poured into the ball milling tanks filled with argon and then subjected to different time of milling. The ball-to-powder mass ratio was set as 20:1 and the effective ball-milling time was x h ($x = 0.5, 1, 1.5, 2, 3, 5, 10, 20, 30$). The main disc was rotated at 350 rpm and the vials were rotated at 800 rpm in reverse.

2.3 Synthesis of SiBCN–Ta₄HfC₅ powder and bulk ceramics

In this stage, c-Si, h-BN, graphite, and Ta₄HfC₅ nanocrystals were put into ball milling tanks. Among them, the molar ratio of Si:BN:C is 2:1:3, and Ta₄HfC₅ nanocrystals account for 0 wt%, 2.5 wt%, 5 wt%, 10 wt%, and 15 wt% of the total mass of powder in the ball milling tank, respectively. During the milling process, the rotation speed of the main disc was set at 350 rpm and the vials were rotated at 600 rpm in reverse. In this scene, the effective milling time of 20 h could ensure a well-defined microstructure of the mixtures [28,29]. The powders mixed, stored, and transported were conducted in high pure Ar.

SiBCN–Ta₄HfC₅ mixed powders were loaded into a graphite mould with a diameter of 36 mm and then sintered via the hot-pressing sintering system (50-250T model, AVS company, USA). The sintering was conducted at a temperature of 1900 °C and a holding time for 1 h under an axial pressure of 60 MPa. The content of Ta₄HfC₅ in SiBCN–Ta₄HfC₅ composite ceramics is 0 wt%, 2.5 wt%, 5 wt%, 10 wt%, and 15 wt%.

2.4 Characterization

The phase composition of the samples was measured by X'PERT X-ray diffractometer purchased from the Panalytical Company of Netherlands. The scanning speed is 10 (°)/min and the scanning range is 10°–90°. The morphologies of the samples were observed using the NanoLab 600i scanning electron microscope (SEM) produced by the FEI company. Tecnai G2 F20 transmission electron microscope was used to observe the microstructure of Ta₄HfC₅ and SiBCN–Ta₄HfC₅ powders. The microstructure and element distribution of the SiBCN–Ta₄HfC₅ composite ceramics were investigated using a Talos f200x transmission electron microscope (TEM) produced by the FEI company. The Raman spectra were collected via an inVia-Reflex testing system manufactured by RENISHAW company, with the excitation wavelength of 785 nm.

3 Results and discussion

3.1 Synthesis and characterization of nano Ta₄HfC₅ powder

Before mechanical alloying, the powder mixture of the 4TaC–HfC shows sharp diffraction peaks (Fig. 1). After

Fig. 1 XRD patterns of the 4TaC–HfC powder mixture after mechanical alloying for different time.

0.5 h of milling, the intensities of the corresponding diffraction peaks are reduced and the full width at half maximum (FWHM) becomes wider. This should be argued to the grain refinement of TaC and HfC [30]. As the milling time further raises to 1–5 h, TaC and HfC gradually undergo a solid solution reaction to form Ta₄HfC₅. Interestingly, the single-phase Ta₄HfC₅ solid solution is obtained after mechanical alloying for 10 h. Further prolonging the milling time to 20–30 h, the diffraction peaks of the as-prepared Ta₄HfC₅ gradually decrease, implying the grain refinement of Ta₄HfC₅.

After mechanical alloying, the diffraction peaks of the as-prepared Ta₄HfC₅ shifting to the small angle direction result from the radius difference between Hf and Ta, which can be depicted by the Vegard's law:

$$a = a_1c_1 + a_2c_2 \quad (1)$$

where a , a_1 , and a_2 represent the lattice constant of the new forming solid solution and the two starting components, respectively. The c_1 and c_2 represent the concentration of the two starting components, respectively [31–33]. The radius of the Hf is bigger than that of Ta. Thus, the short-range diffusion of Hf

atoms into the interstitial sites of Ta can lead to the expansion of the TaC lattice (Fig. 2).

TEM analysis confirms the raw materials of TaC and HfC powders both have relatively large grain size (Figs. 3(a) and 3(b)). Besides, the corresponding SAED pattern displays some diffraction spots and rings of

Fig. 2 XRD patterns of pure TaC powder and 4TaC–HfC powder mixture after mechanical alloying for 30 h, Inset is the magnified image of 65°–75°.

Fig. 3 TEM, HRTEM, and SAED images of the pure TaC powder and 4TaC–HfC powder mixture after mechanical alloying for different time. (a–c) 4TaC–HfC, 0 h; (d–f) 4TaC–HfC, 0.5 h; (g–i) 4TaC–HfC, 30 h; (j–l) pure TaC powder, 30 h.

HfC and TaC (Fig. 3(c)). After ball milling for only 0.5 h, the grain size of TaC and HfC decreases obviously and some diffraction spots of TaC and HfC have disappeared (Figs. 3(d) and 3(f)). Notably, at this milling time, mechanical alloying has induced many structural defects in both TaC and HfC, which can provide conveniently channel for Hf atoms diffused inward. With progressing milling of 30 h, only pure Ta_4HfC_5 nanocrystals are obtained without any trace of HfC or below the limits of detection (Figs. 3(g)–3(i)). For pure TaC ball-milled for 30 h (Figs. 3(j)–3(l)), SAED pattern with bright-spots and narrow-rings verifies the well-defined crystalline phase of TaC. The interplanar crystal spacing of TaC is slightly smaller than that of

Ta_4HfC_5 , which is consistent with XRD analysis results.

The SEM surface morphologies in Fig. 4(a) further ensure that the raw materials of the 4TaC–HfC powder mixture have a larger particle size. Nevertheless, after mechanical alloying for 0.5 h, the particle size of the powder mixture decreases obviously, which is mainly composed of nanoparticles (Fig. 4(b)). With the progress of mechanical alloying (1.5–30 h), these particles are continuously deformed, crushed, and cold sintered; however, the morphologies of the resulting particles are almost unchanged. The EDS maps in Figs. 4(f)–4(i) confirm that the Ta, Hf, and C atoms distribute uniformly after 30 h of milling, suggesting a good solid solubility of Hf into TaC.

Fig. 4 SEM surface images of 4TaC–HfC mixed powders after mechanical alloying for different time. (a) 0 h; (b) 0.5 h; (c) 1.5 h; (d) 20 h; (e, f) 30 h; (g–i) the corresponding element maps, and the inserted are the magnifying SEM images.

The formation mechanisms of the mechanical alloying derived nano Ta_4HfC_5 are elaborated in Fig. 5. During the mechanical alloying process, the sample particles are continuously deformed, crushed, and cold sintered under mechanical impact conditions, which led to grain refinement and microstrain occurring in the crystal grains. The dislocation density (ρ_d) can be represented by the following equation [34]:

$$\rho_d = 2\sqrt{3} \frac{(\varepsilon^2)^{\frac{1}{2}}}{Db} \quad (2)$$

where ε is the microstrain, D is the grain size, and b is the Burgers vector. According to Eq. (2), larger microstrain and smaller grain sizes lead to higher dislocation density in the crystal. Besides, the decrease in grain size increases the surface area per unit volume. Higher surface energy provides a driving force for diffusion, and more defects provide channels for atom diffusion. Therefore, a uniform solid solution of Ta_4HfC_5 was formed.

Figure 6 shows the XRD patterns of the *in situ* SiBCN– Ta_4HfC_5 amorphous-nanocrystalline composite powder with different Ta_4HfC_5 contents. After 20 h of mechanical alloying, the lattice structure of c-Si, h-BN, and graphite was destroyed to form amorphous SiBCN. Besides, the broad diffraction peaks of Ta_4HfC_5 were observed, and these peak intensities gradually increase with the increase of Ta_4HfC_5 content. Confidentially, the nano Ta_4HfC_5 does not react with other components of SiBCN and still presents the form of nanocrystals (3–5 nm) in the amorphous matrix after mechanical alloying (Fig. 7).

Fig. 5 Formation mechanisms of the nano Ta_4HfC_5 during mechanical alloying.

Fig. 6 XRD patterns of *in situ* SiBCN– Ta_4HfC_5 amorphous-nanocrystalline composite powder with different Ta_4HfC_5 contents.

Fig. 7 TEM and HRTEM images of the (a, b) SiBCN amorphous powder and (c, d) SiBCN– Ta_4HfC_5 amorphous-nanocrystalline composite powder.

3.2 Microstructural evolution and mechanical properties of as-sintered SiBCN– Ta_4HfC_5 composite ceramics

After reactive hot-pressing sintering, SiBCN– Ta_4HfC_5 composite ceramics mainly consist of BN(C), β -SiC, α -SiC, and Ta_4HfC_5 (Fig. 8). The intensity of the diffraction peaks of the Ta_4HfC_5 is positively correlated with the content of Ta_4HfC_5 . With the increase of Ta_4HfC_5 content, the diffraction peaks of α -SiC decrease and the diffraction peaks of β -SiC increase. This means that the *in situ* Ta_4HfC_5 affects the $\beta \rightarrow \alpha$ transition of SiC.

Figure 9 exhibits the Raman spectra of the as-sintered SiBCN– Ta_4HfC_5 composite ceramics with various Ta_4HfC_5 content. Two Raman peaks in a range of 60–260 cm^{-1} are gradually enhanced with the increased content of the *in situ* Ta_4HfC_5 . The emergence of Raman peak at 1374 cm^{-1} results from the D-side peak edge of graphite and the scattering peak of h-BN [5]. However, the generation of Raman peak at 1588 cm^{-1} should be assigned to the G-side peak of graphite [35].

Fig. 8 XRD patterns of the as-sintered SiBCN-Ta₄HfC₅ composite ceramics with different Ta₄HfC₅ contents.

Fig. 9 Raman spectra of the as-sintered SiBCN-Ta₄HfC₅ composite ceramics with different Ta₄HfC₅ contents.

After hot-pressing sintering, amorphous SiBCN has crystallized and transformed into turbostratic BN(C) and nano SiC (Fig. 10). For pure SiBCN, BN(C) phase is distributed at the grain boundaries of SiC grains. Besides, the Si elements are mainly distributed in SiC grains, and B, C, and N elements are distributed in the form of the BN(C) phase at SiC grain boundaries. With a 2.5 wt% Ta₄HfC₅ addition, most of the Ta₄HfC₅ (~10 nm) are distributed in the BN(C) phase in the form of nanocrystals (Fig. 11). The Ta₄HfC₅ grains are thereby separated by BN(C). This structure is beneficial to the grain refinement of Ta₄HfC₅ and constrains short-range diffusion of the atoms. The EDS maps of the selective region in Ta₄HfC₅-BN(C) clearly show that the Ta, Hf, and some C elements are distributed in the Ta₄HfC₅ phase, and the rest of the C elements are distributed in BN(C) phase (Fig. 12). With 10 wt% Ta₄HfC₅ addition, a part of nano Ta₄HfC₅ (~10 nm) is still uniformly

distributed in BN(C), and another nano Ta₄HfC₅ >10 nm is randomly distributed in the ceramic matrix (Fig. 13). The microstructural evolution diagram of the SiBCN-Ta₄HfC₅ composite ceramics with different Ta₄HfC₅ contents is displayed in Fig. 14.

Fig. 10 TEM and HEM images of the pure SiBCN ceramics. (a, b) Bright-field images; (c-h) HAADF-STEM image and corresponding EDS maps.

Fig. 11 TEM and HRTEM images of the SiBCN-Ta₄HfC₅ composite ceramics with 2.5 wt% Ta₄HfC₅. (a, b) Bright-field images; (c) magnifying TEM image of area A; (d) HRTEM image of area A.

Fig. 12 Selective EDS maps of Ta_4HfC_5 distributed within BN(C) region for composite ceramics with 2.5 wt% Ta_4HfC_5 .

Fig. 13 TEM images and EDS maps of the SiBCN– Ta_4HfC_5 composite ceramics with 10 wt% Ta_4HfC_5 . (a) Bright-field TEM image; (b) STEM image; (d–j) EDS maps.

Fig. 14 Schematic illustrating the microstructure evolution of Ta_4HfC_5 distribution in composite ceramics with different Ta_4HfC_5 addition.

Fig. 15 Flexural strength and fracture toughness of the as-sintered SiBCN– Ta_4HfC_5 composite ceramics with different contents of Ta_4HfC_5 .

The flexural strength and fracture toughness of the as-sintered SiBCN– Ta_4HfC_5 composite ceramics are shown in Fig. 15. The introduction of Ta_4HfC_5 nanocrystals has effectively improved the flexural strength and fracture toughness of the SiBCN ceramics. For pure SiBCN ceramics, they only show flexural strength of 156.1 MPa and the fracture toughness of $1.82 \text{ MPa}\cdot\text{m}^{1/2}$. With 10 wt% Ta_4HfC_5 addition, the composite ceramics possess optimized flexural strength reaching 344.1 MPa, and the composite ceramics with 5 wt% Ta_4HfC_5 obtain fracture toughness of $4.52 \text{ MPa}\cdot\text{m}^{1/2}$.

4 Conclusions

In this study, SiBCN– Ta_4HfC_5 composite ceramics were prepared by two-step mechanical alloying combined with reactive hot-pressing sintering. After the above analysis, the following conclusions can be drawn:

1) In the initial step of mechanical alloying of 30 h, the 4TaC–HfC powder mixture is crushed, cold sintered, and interdiffused, finally forming Ta₄HfC₅ nanocrystalline. After the second step of milling for 20 h, a hybrid structure of amorphous SiBCN and nano Ta₄HfC₅ can be obtained. The lattice structures of C–Si, h-BN, and graphite were destroyed to form amorphous structures. However, Ta₄HfC₅ is uniformly distributed in amorphous powder in the form of nanocrystals.

2) After reactive hot-pressing sintering, SiBCN–Ta₄HfC₅ composite ceramics mainly contain Ta₄HfC₅, BN(C), β-SiC, and α-SiC. The Ta₄HfC₅ still exists in the form of nanocrystalline and does not react with the SiBCN matrix composition. With only 2.5 wt% Ta₄HfC₅ addition, nano Ta₄HfC₅ is preferentially distributed in BN(C) phase; however, it tends to both distribute in BN(C) phase and ceramic matrix when 10 wt% Ta₄HfC₅ is adopted.

3) The introduction of the Ta₄HfC₅ nanocrystals can effectively improve the flexural strength and fracture toughness of SiBCN ceramics due to the grain refinement and uniform distribution of nano Ta₄HfC₅. SiBCN ceramics with 10 wt% Ta₄HfC₅ present optimized flexural strength of 344.1 MPa, and composite ceramics with 5 wt% Ta₄HfC₅ obtain fracture toughness of 4.52 MPa·m^{1/2}.

Acknowledgements

We appreciate the financial support from the National Natural Science Foundation of China (52002092, 51621091, 51472059, 51225203, and 51272300), the National Key Research and Development Program (2017YFB0310400), the Postdoctoral Innovative Talents Support Program (BX20190095), and the China Postdoctoral Science Foundation (Grant Nos. LBH-Z19141 and 2019M660072). This work was also funded by Advanced Space Propulsion Laboratory of BICE and Beijing Engineering Research center of Efficient and Green Aerospace Propulsion Technology (No. LabASP-2019-08).

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