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

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Abstract

In this paper, 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 SiBCN-Ha4HfC5 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 nano SiC and turbostratic BN(C) phases while Ta4HfC5 retained the form of nano structure. With the in situ generation 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.

Introduction

With the development of aerospace technology, more stringent properties requirements are put forward for advanced structural-functional integration ceramic materials [1]. Among many high-temperature structural materials, SiBCN non-oxide ceramics have attracted considerable attention due to their lightweight, high specific strength, excellent thermal stability and resistance to thermal shock, oxidation and ablation [2–7].

Polymer/precursor derived ceramics (PDCs) is one of the first routes to prepare SiBCN materials. The SiBCN materials are able to remain amorphous nature at least up to 1400 °C, and do not undergo microstructural changes at this temperature [4]. The chemistry, microstructure and properties of the PDCs SiBCN can be tailored effectively by controlling the initial reagent structure, chemical reaction and processing parameters [8]. Unfortunately, this method also has some nonnegligible shortcomings that limit its wide applications. The starting materials are usually expensive and some organic solvents used are harmful to human health and the environment. This processing route is also low-yield and complex. During pyrolysis, the gases release and the mass loss are required to be carefully monitored to avoid porous structure and accurately control shrinkage (even microcracks) [9–11].

Thus, a more efficient, convenient and environment-friendly method was proposed to obtain dense nano or amorphous SiBCN monoliths and their ceramic composites, using a combination of mechanical alloying and solid-state sintering techniques (also referred as inorganic method) [10]. One of the significant advantages of this processing route is to provide centimeter-sized samples. The centimeter-sized samples are convenient for evaluating the basic mechanical and thermophysical properties [11–12]. However, the previous studies showed that the heterogeneous microstructure, which leads to poor
mechanical properties of the SiBCN ceramics, are needed to be further optimized for the real applications at high-temperatures \[13-14\].

As documented, the introduction of ultra-high temperature ceramics (UHTCs) into SiBCN ceramic matrix, is considered to be an effective strategy to improve the mechanical performance of SiBCN ceramics \[15-18\]. In previous attempts, the microstructural evolution and thermal stability of the porous PDCs ZrB\(_2\)-SiBCN and HfN-SiBCN composite ceramics have been investigated \[19-20\]. But the mechanical properties of these composite ceramics have not been evaluated because of the limitation of sample size. In another contribution, Liang et al. \[21-23\] have introduced some LaB\(_6\) into 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 and generated La\(_2\)B\(_2\)C\(_6\). Consequently, the strengthening and toughening effects of LaB\(_6\) were significantly reduced. Further, Miao et al. \[24-26\] 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; nevertheless, the particle size of the in-situ ZrB\(_2\) has grown up to a maximum value of \(~1\ \mu m\).

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

The chemically stable Ta\(_4\)HfC\(_5\), the current highest melting point compound, was theoretically forecasted by Agte et al. \[27\] and experimentally confirmed by Andrievskii et al. \[28\]. Up to present, various strategies have been used to the synthesis of the high pure Ta\(_4\)HfC\(_5\). For example, Simonenko et al. \[29\] have reported a sol-gel technology for preparing Ta\(_4\)HfC\(_5\) by using metal oxide and gel of polymeric carbon source. The polymeric carbon source was preliminarily annealing to provide a uniform dispersion of metal oxide-carbon mixture, and then further heating to 1200 ~ 1500 °C to obtain pure Ta\(_4\)HfC\(_5\). Liu et al. \[30\] used the Hf and Ta containing polytantalhafnioxane modified with allyl-functional novolac resin to produce Ta\(_4\)HfC\(_5\) polymer (polytantalhafnioxanesal). The resulting polytantalhafnioxanesal is subsequently solidified and pyrolyzed at 1400 °C to obtain pure Ta\(_4\)HfC\(_5\). These methods, of course, are quite effective to prepare pure Ta\(_4\)HfC\(_5\) with high thermal stability and chemical stability; however, these processing methods often contain complex synthesis steps, resulting in high-cost products. The raw materials used are also flammable and present waste disposal problems. For this reason, Osama et al. \[31\] have successfully prepared nano Ta\(_4\)HfC\(_5\) by mechanical alloying for the first time. However, the formation mechanisms of the mechanical alloying derived nano Ta\(_4\)HfC\(_5\) is still unclear. And the research on Ta\(_4\)HfC\(_5\)/SiBCN composite ceramics has not been reported yet.
Thus, in this work, initially, the Ta$_4$HfC$_5$ nanocrystals were prepared by an improving mechanical alloying method and then, nano Ta$_4$HfC$_5$ was introduced to the prefabricated amorphous SiBCN powders by a second stage of mechanical alloying. Afterward, the hot-pressing sintering technology was adopted to consolidate SiBCN-Ta$_4$HfC$_5$ composite ceramics. The formation mechanisms of mechanical alloying derived nano Ta$_4$HfC$_5$, the correlation of microstructural evolution and mechanical properties of the resulting SiBCN-Ta$_4$HfC$_5$ composite ceramics were illustrated. As expected, the homogeneous distribution of nano Ta$_4$HfC$_5$ within the SiBCN ceramic matrix strongly improved the mechanical properties of the composite ceramics. 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.

Materials And Methods

Raw materials

Commercial available 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.

Synthesis of Ta$_4$HfC$_5$ nanocrystals

Ta$_4$HfC$_5$ nanocrystals were prepared by 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 hours 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 h). The main disc was rotated at 350 rpm while the vials were rotated at 800 rpm in reverse.

Synthesis of SiBCN-Ta$_4$HfC$_5$ powder and bulk ceramics

In this stage, c-Si, h-BN, graphite with a molar ratio of = 2: 1: 3, and 2.5 wt%, 5 wt%, 10 wt% Ta$_4$HfC$_5$ nanocrystals were put into ball milling tanks. Before the milling process, the rotation speed of the main disc was set at 350 rpm while 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\textsuperscript{[32–33]}. The steps of mixing, storage and transportation are performed in high purity Ar.

SiBCN-Ta$_4$HfC$_5$ 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 holding time for 1 h under an axial pressure of 60 MPa. The
content of Ta$_4$HfC$_5$ in SiBCN-Ta$_4$HfC$_5$ composite ceramics is 0 wt%, 2.5 wt%, 5 wt%, 10 wt% and 15 wt%, respectively.

**Characterization**

The phase composition of the samples was measured by X’PERT X-ray diffractometer purchased from Panalytical Company of Netherlands. The scanning speed is 10°/min and the scanning range is 10°-90°. The morphologies of the samples were observed by using NanoLab 600i scanning electron microscope produced by FEI company. Tecnal G$^2$ F20 transmission electron microscope from FEI company was used to observe the microstructure of Ta$_4$HfC$_5$ and SiBCN-Ta$_4$HfC$_5$ powders. The microstructure and element distribution of the SiBCN-Ta$_4$HfC$_5$ composite ceramics were investigated by using Talos f200x transmission electron microscope produced by FEI company. The Raman spectra were collected via an inVia-Reflex testing system manufactured by RENISHAW company, with the excitation wavelength of 785 nm.

**Results And Discussion**

**Synthesis and characterization of nano Ta$_4$HfC$_5$ powder**

Prior to mechanical alloying, the powder mixture of the TaC-HfC shows sharp diffraction peaks (Fig. 1). After 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. As the milling time further raises to 1 ~ 5 h, these crystalline peaks decrease gradually and finally disappear after 10 h of milling. At this stage, the decrease of nanocrystalline peak intensities and the increase of FWHM are mainly due to the gradual solid solution of TaC and HfC. Interestingly, the single-phase Ta$_4$HfC$_5$ 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 Ta$_4$HfC$_5$ gradually decrease, implying the grain refinement of Ta$_4$HfC$_5$ (Fig. 2).

After mechanical alloying, the diffraction peaks of the as-prepared Ta$_4$HfC$_5$ shifting to the small angle direction must result from the radius difference between Hf and Ta, which can be depicted by the Vegard’s law:

$$a = a_1 c_1 + a_2 c_2$$  \hspace{1cm} (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 [34–36]. 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 TaC lattice.
TEM analyses confirm the raw materials of TaC and HfC powders both have relatively large grain size [Fig. 3(a) and (b)]. Besides, the corresponding SAED pattern displays some diffraction spots and rings of 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 [Fig. 3(d-f)]. Notably, at this milling time, mechanical alloying has induced many structural defects in both TaC and HfC, which can provide convenient channel for Hf atoms diffusing inward. With the progressing milling of 30 h, only pure Ta$_4$HfC$_5$ nanocrystals are obtained without any trace of HfC or below the limits of detection [Fig. 3(g-i)]. For pure TaC ball-milled for 30 h [Fig. 3(j-l)], SAED pattern with bright-spots and narrow-rings verifies the well-defined crystalline phase of TaC.

The SEM surface morphologies in Fig. 4(a) further ensure that the raw materials of TaC-HfC powder mixture have 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 nano-particles [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 Fig. 4(f)-(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.

Figure 5 shows the XRD patterns of the in situ SiBCN-Ta$_4$HfC$_5$ amorphous-nanocrystalline composite powder with different Ta$_4$HfC$_5$ content. 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$_4$HfC$_5$ were observed, and these peak intensities gradually increase with the increase of Ta$_4$HfC$_5$ content. Confidently, the nano Ta$_4$HfC$_5$ 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. 6).

The formation mechanisms of the mechanical alloying derived nano Ta$_4$HfC$_5$ are elaborated in Fig. 7. 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 can be represented by the following equation $^{[37]}$:

$$\rho_D = \frac{2\sqrt{3}(\varepsilon^2)^{\frac{1}{2}}}{D^3 b} \quad (2)$$

Where $\varepsilon$ is the microstrain, $D$ is the grain size, and $b$ is the Burgers vector. According to formula (2), larger microstrain and smaller grain size lead to higher dislocation density in the crystal. Besides, the decrease in grain size results in an increase in surface area per unit volume. Higher surface energy provides a driving force for diffusion, while more defects provide channels for atom diffusion. Therefore, a uniform solid solution of Ta$_4$HfC$_5$ was formed.
Microstructural evolution and mechanical properties of as-sintered SiBCN-Ta$_4$HfC$_5$ composite ceramics

After reactive hot-pressing sintering, SiBCN-Ta$_4$HfC$_5$ composite ceramics mainly consist of BN(C), $\beta$-SiC, $\alpha$-SiC and Ta$_4$HfC$_5$ (Fig. 8). Obviously, the intensity of the diffraction peaks of the Ta$_4$HfC$_5$ is positively correlated with the content of Ta$_4$HfC$_5$. Interestingly, with the increase of Ta$_4$HfC$_5$ content, the diffraction peaks of $\alpha$-SiC decrease while the diffraction peaks of $\beta$-SiC increase. These means that the in situ Ta$_4$HfC$_5$ affects the $\beta \rightarrow \alpha$ transition of SiC.

Figure 9 exhibits the Raman spectra of the as-sintered SiBCN-Ta$_4$HfC$_5$ composite ceramics with various Ta$_4$HfC$_5$ content. Two Raman peaks in a range of 1250–1750 cm$^{-1}$ are gradually enhanced with the increase content of the in situ Ta$_4$HfC$_5$. 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 [38].

After hot-pressing sintering, amorphous SiBCN has crystallized to product 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, while B, C and N elements are distributed in the form of BN(C) phase at SiC grain boundaries. With 2.5 wt% Ta$_4$HfC$_5$ addition, most of the Ta$_4$HfC$_5$ ~ 10 nm are distributed in BN(C) phase in the form of nanocrystals (Fig. 11). The Ta$_4$HfC$_5$ grains are thereby separated by BN(C). This structure is beneficial to the grain refinement of Ta$_4$HfC$_5$ and constrains short-range diffusion of the atoms. The EDS maps of the selective region in Ta$_4$HfC$_5$-BN(C) clearly show that the Ta, Hf and some C elements are distributed in Ta$_4$HfC$_5$ phase, while the rest of C elements are distributed in BN(C) phase (Fig. 12). With 10 wt% Ta$_4$HfC$_5$ addition, a part of nano Ta$_4$HfC$_5$ ~ 10 nm is still uniformly distributed in BN(C), while other nano Ta$_4$HfC$_5$ > 10 nm is randomly distributed in the ceramic matrix (Fig. 13). The microstructural evolution diagram of the SiBCN-Ta$_4$HfC$_5$ composite ceramics with different Ta$_4$HfC$_5$ content is displayed in Fig. 14.

The flexural strength and fracture toughness of the as-sintered SiBCN-Ta$_4$HfC$_5$ composite ceramics are shown in Fig. 15. Apparently, the introduction of Ta$_4$HfC$_5$ 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 fracture toughness of 1.82 MPa$\cdot$m$^{1/2}$, respectively. With 10 wt% Ta$_4$HfC$_5$ addition, the composite ceramics possess optimized flexural strength reaching to 344.1 MPa, while the composite ceramics with 5 wt% Ta$_4$HfC$_5$ obtain fracture toughness of 4.52 MPa$\cdot$m$^{1/2}$.

Conclusion

In this study, SiBCN-Ta$_4$HfC$_5$ 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, TaC-HfC powder mixture are crushed, cold sintered and interdiffused, and finally form Ta$_4$HfC$_5$ nanocrystalline. After the second step of milling for 20 h, a hybrid structure of amorphous SiBCN and nano Ta$_4$HfC$_5$ can be obtained. The lattice structures of C-Si, h-BN and graphite were destroyed to form amorphous structures. However, Ta$_4$HfC$_5$ is uniformly distributed in amorphous powder in the form of nanocrystals.

(2) After reactive hot-pressing sintering, SiBCN-Ta$_4$HfC$_5$ composite ceramics mainly contain Ta$_4$HfC$_5$, BN(C), β-SiC and α-SiC. The Ta$_4$HfC$_5$ still exists in the form of nanocrystalline and does not react with the SiBCN matrix composition. With only 2.5 wt% Ta$_4$HfC$_5$ addition, nano Ta$_4$HfC$_5$ is preferentially distributed in BN(C) phase; however, it tends to both distribute in BN(C) phase and ceramic matrix when 10 wt% Ta$_4$HfC$_5$ is adopted.

(3) The introduction of the Ta$_4$HfC$_5$ nanocrystals can effectively improve the flexural strength and fracture toughness of SiBCN ceramics due to the grain refinement and uniform distribution of nano Ta$_4$HfC$_5$. SiBCN ceramics with 10 wt% Ta$_4$HfC$_5$ present optimized flexural strength of 344.1 MPa, while composite ceramics with 5 wt% Ta$_4$HfC$_5$ obtain fracture toughness of 4.52 MPa•m$^{1/2}$.

**Declarations**

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Figures
Figure 1
The XRD patterns of the TaC-HfC powder mixture after mechanical alloying for different time.
Figure 2

The XRD patterns of pure TaC powder and TaC-HfC powder mixture after mechanical alloying for 30 h, inserted is the magnifying picture.
Figure 3

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

The SEM surface images of TaC-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, the inserted are the magnifying SEM images.

Fig 4 The SEM surface images of TaC-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, the inserted are the magnifying SEM images.
Figure 5

The XRD patterns of in situ SiBCN-Ta4HfC5 amorphous-nanocrystalline composite powder with different Ta4HfC5 content.
Figure 6

The TEM and HRTEM images of the (a-b) SiBCN amorphous powder and (c-d) SiBCN-Ta4HfC5 amorphous-nanocrystalline composite powder.
The formation mechanisms of the nano Ta4HfC5 during mechanical alloying.

Figure 7

The formation mechanisms of the nano Ta4HfC5 during mechanical alloying.
Figure 8

The XRD patterns of the as-sintered SiBCN-Ta4HfC5 composite ceramics with different Ta4HfC5 content.
The Raman spectra of the as-sintered SiBCN-Ta4HfC5 composite ceramics with different Ta4HfC5 content.

**Figure 9**

The Raman spectra of the as-sintered SiBCN-Ta4HfC5 composite ceramics with different Ta4HfC5 content.
Figure 10

The TEM and HEM images of the pure SiBCN ceramics. (a-b) Bright-field images; (c)-(j) HAADF-STEM image and corresponding EDS maps.
Figure 11

The 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.
Figure 12

The selective EDS maps of Ta4HfC5 distributed within BN(C) region for composite ceramics with 2.5 wt% Ta4HfC5.
Figure 13

The TEM images and EDS maps of the SiBCN-Ta4HfC5 composite ceramics with 10 wt% Ta4HfC5. (a) Bright-field TEM image; (b) STEM image; (d)-(j) EDS maps.
**Figure 14**

The schematic illustrating the microstructure evolution of Ta4HfC5 distribution in composite ceramics with different Ta4HfC5 addition.
Figure 15

The flexural strength and fracture toughness of the as-sintered SiBCN-Ta4HfC5 composite ceramics with different content of Ta4HfC5.