The New Complex High-entropy Metal Boron Carbonitride: Microstructure and Mechanical Properties

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Research Article

Keywords: High-entropy ceramics, Hot-pressing sintering, Microstructure, Mechanical properties

Posted Date: June 24th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-646053/v1>

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Abstract

Dense (Ta, Nb, Hf, Zr, Ti)(BCN) ceramics (HEC-2) were successfully synthesized via hot-pressing sintering. Results show that sintering temperature and (BCN) addition have great impacts on the microstructure and mechanical properties of HEC-2 ceramics. The microstructure and phase of HEC-2 bulk ceramics were characterized by SEM, XRD and TEM. It was found that high-entropy phase, oxide phase and BN/C phase were precipitated when HEC-2119 powders were sintered at 1900 °C. In addition, the Vicker's hardness, Bending strength, Bulk density and Open porosity of HEC-2319 ceramic are 24.54 GPa, 522.00 MPa, 9.07 g/cm³ and 0.05%, respectively, whose molar ratio of metal to (BCN) is 1: 0.334. In this work, BCN high-entropy ceramics were sintered on the basis of powder preparation, as provided that sintering temperatures and components have great influences on microstructure and mechanical properties of HEC-2 ceramics.

1. Introduction

It has been about 20 years since the first article about the high-entropy alloys (HEAs) reported, and then the studies on preparations and properties of HEAs are increasing gradually [1–3]. On the basis of the research of HEAs, what prepared by doping different nonmetallic elements, such as Si, C, N, B, etc., has good mechanical properties on the advantage of light weight and great application prospects in the fields of aerospace, electronic parts, transportation and etc [4–5]. Under the studies of excellent properties of HEAs, many scholars introduced the concept of high entropy into the ceramics, expecting to design and synthesize high-performance high-entropy ceramics (HECs). In 2015, Rost et al. [6] prepared high-entropy oxide ceramics and proved the importance of entropy on phases stability for the first time. Since then, the research upsurge of high-entropy ceramics started. Previous researches on HECs mainly focused on high-entropy nitride coating [7–8], high-entropy carbides [9–11] and diborides ultra-high temperature ceramics [12–16], wear-resistant high-entropy silicides [17–18], high-entropy oxide functional materials [19–20] and other single-anion HECs [21–22]. Obviously, the hardness and creep resistance of HECs have been greatly improved than the unit and the binary ceramics, because more components are introduced into ceramics and the cation sizes are quite different which causes the solution strengthening. What's more, when solid solution is formed, it is easy to produce a lot of lattice distortion, which increases the resistance of dislocation movement and makes it very difficult for atoms to slip under external force and then limits the dislocation movement necessary for plastic deformation [23–24].

Castle E et al. [9] prepared (Hf-Ta-Zr-Ti)C and (Hf-Ta-Zr-Nb)C single-phase solid solutions by SPS sintering. It was found that lattice mismatch of monobasic carbide components was the key factor to form single-phase solid solution. Test results showed that the hardness of high-entropy carbide was 36.1 ± 1.6 GPa, which was higher than that of monobasic carbide and binary carbide of corresponding metal elements. Tallarita G et al. [14–15] prepared high-entropy diboride (Hf_{0.2}Mo_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})B₂ whose density was 92.5% by two-step method. XRD test showed that a high-entropy diboride single-phase solid solution was obtained, and the structure of diboride was similar to that proposed by Gild J [12], which was a layered structure with alternating boron atomic layers and metal layers. Performance test showed

that the hardness of high-entropy phase was 22.9 GPa which was higher than that of single diboride. It was considered that the effects of preparing powder by self-propagating method was better than that by high-energy ball-milling. Mayrhofer PH et al. [25] prepared ZrB_2 , $(\text{Zr,Ti})\text{B}_2$ and high-entropy diboride $(\text{Zr}_{0.23}\text{Ti}_{0.20}\text{Hf}_{0.19}\text{V}_{0.14}\text{Ta}_{0.24})\text{B}_2$ (HEB_2) by non-reactive magnetron sputtering physical vapor deposition. It was found that not only the hardness was gradually improved, but also the thermal stability of structural rearrangement and decomposition into binary diboride was improved with the increase of the amount of metal elements. The hardness of HEB_2 was 47.2 ± 1.8 GPa which was harder than $(\text{Zr,Ti})\text{B}_2$ ($H = 45.8 \pm 1.0$ GPa) and ZrB_2 ($H = 43.2 \pm 1.0$ GPa).

Recently, on the basis of single-anion high-entropy ceramics, researchers broke the limitation of single-anion high-entropy ceramics and prepared binary or ternary-anion high-entropy ceramics [26–30]. Wen TQ et al. [26] synthesized a single rock-salt structure of metal nitride-carbides ceramic $(\text{Hf}_{0.2}\text{Zr}_{0.2}\text{Ta}_{0.2}\text{Nb}_{0.2}\text{Ti}_{0.2})(\text{N}_{0.5}\text{C}_{0.5})$ at 1773 K by the hot-pressing sintering. It showed high microhardness of 19.5 ± 0.3 GPa and nanohardness of 33.4 ± 0.5 GPa, simultaneously possessed a Bulk modulus of 258 GPa, Young's modulus of 429 GPa, Shear modulus of 176 GPa, and Elastic modulus of 572 ± 7 GPa. In addition, Wen TQ et al. [27] studied the multi-anion high-entropy aluminum-silicide $(\text{Mo}_{0.25}\text{Nb}_{0.25}\text{Ta}_{0.25}\text{V}_{0.25})(\text{Al}_{0.5}\text{Si}_{0.5})_2$. They analyzed the possibility of forming high-entropy aluminosilicate based on first-principles calculation from two aspects of chemical reaction thermodynamics and lattice size difference, and then successfully prepared high-entropy aluminosilicate at 1573 K by solid-state reaction technology. The results showed that the high-entropy aluminum-silicate had the hexagonal crystal structure of single-metal aluminum-silicate, and the distribution of all constituent elements was highly uniform. Chen H et al. [31] prepared several high-entropy ceramics powders that $(\text{Tm}_{0.2}\text{Y}_{0.2}\text{Dy}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2})_3\text{Si}_2\text{C}_2$, $(\text{Tm}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Dy}_{0.2})_3\text{Si}_2\text{C}_2$, and $(\text{Tm}_{0.2}\text{Y}_{0.2}\text{Pr}_{0.2}\text{Gd}_{0.2}\text{Tb}_{0.2})_3\text{Si}_2\text{C}_2$ and studied their electromagnetic absorption effects. The optimal absorption $\text{RL}_{\min}$ value and effective absorption bandwidth of them are -11.6 dB (3.4 mm) and 1.7 GHe, -40.7 dB (2.9 mm) and 3.4 GHe and -50.9 dB (2.0 mm) and 2.4 GHe, respectively.

Besides, the performances of high-entropy ceramics composites have been studying [32–34]. Bagdasaryan AA et al. [32] synthesized $(\text{TiZrNbTaHf})\text{N}/\text{MoN}$ nanocomposite coating by vacuum-arc deposition at various substrate biases. Research showed the coating was deposited at a higher energy condition (-200 V) with the thinnest modulation period of bilayer of 20 nm and has the maximum hardness of approximately 29 GPa. Bao WC et al. [33] synthesized a high-entropy composite $\text{M}_2\text{AlC-MC}$ ($\text{M} = \text{Ti, Zr, Hf, Nb, Ta}$) by reactive hot pressing. Compared with the MC high-entropy ceramic, M_2AlC had a larger lattice strain along with considerable amount of Al vacancies. And the Vickers hardness of the composite was measured to be 11.1 ± 1.1 GPa, but the fracture toughness was 3.7 ± 0.4 $\text{MPa}\cdot\text{m}^{1/2}$, which was lower than that of the single M_2AlC phase. But the specific mechanism of the atomic solid solution diffusion has not been studied.

In this study, under the research of single and binary anion high-entropy ceramics, we try to prepare BCN series high-entropy ceramics with ternary anions by high-energy ball-milling [35], and synthesis

(Ta_{0.2}Nb_{0.2}Zr_{0.2}Hf_{0.2}Ti_{0.2})(BCN) (HEC-2) bulk ceramics by hot-pressing sintering. The effects of sintering temperature and molar ratio of metal to nonmetal on microstructure and mechanical properties have been studied.

2. Experimental

2.1. Powder synthesis

Commercially available Hf (99.9% purity, $D = 2-5\ \mu\text{m}$, Shanghai), Ta (99.9% purity, $D = 2-5\ \mu\text{m}$, Shanghai Shui Tian), Nb (99.9% purity, $D = 2-5\ \mu\text{m}$, Shanghai Shui Tian), Zr (99.9% purity, $D = 2-5\ \mu\text{m}$, Shanghai Shui Tian), Ti (99.9% purity, $D = 2-5\ \mu\text{m}$, Shanghai Shui Tian), W (99.9% purity, $D = 2-5\ \mu\text{m}$, Shanghai Shui Tian), h -BN (99.9% purity, $D = 0.6\ \mu\text{m}$) and graphite (99.9% purity, $D = 8-9\ \mu\text{m}$) were used as starting materials.

The preparation of powder by high-energy ball-milling is carried out in two steps, and the specific ball milling process could refer to previous reports [35]. For different systems, what is fixed is the ball-milling process, including the ball-milling time (24 h), rotation speed (600 rpm) and ball-material ratio (20: 1), and changes are corresponding metal types and nonmetal contents of the (BCN). Seven species high-entropy ceramics powders are prepared according to the Table 1.

2.2. Sintering process

The sintered powders were put in a glove box in argon atmosphere filled into a graphite mold with a diameter of 30 mm. After pre-pressing forming, the ceramic block was sintered by hot-pressing sintering. The specific sintering process is as follows: maintaining temperature and pressure for 60 min at preset temperature after heating at 20 K/min in Ar atmosphere, then releasing pressure slowly and taking it out after furnace cooling to room temperature. The specific sintering curve is shown in Fig. 1 below. We chose HEC-2 as the research object and analyze its sintering process, microstructure and mechanical characters and the specific sintering curve is shown in Table 2. What's more, in order to study the effects of BCN content on ceramics, we synthesized three ceramics with different molar ratio between metal and (BCN) as 1: 1, 1:0.5 and 1: 0.334 named HEC-21, HEC-22 and HEC-23, respectively.

2.3. Characterizations

The as-synthesized powders were analyzed by X-ray diffraction (XRD, X'PERT), scanning electron microscopy (SEM, HELIOS NanoLab 600i) equipped with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM, Tecnai G2 F30) equipped with EDS and Raman spectroscopy (inVia-Reflex).

The high-temperature thermal stability of the powder was measured by STA449C comprehensive thermal analyzer (TG-DSC) produced by NETCHI, Germany (heating rate 10 ~ 20K, heating to 1400 °C, argon atmosphere). Density is determined by Archimedes drainage method, and the sample mass is determined

by DV314C analytical balance produced by Ohaus Company of America, and its density is determined according to Eq. (1):

$$\rho_v = m_{\text{air}} \times \rho_{\text{H}_2\text{O}} / (m_{\text{air}} - m_{\text{H}_2\text{O}}) \quad (1)$$

In which, ρ_v is the bulk density of ceramic samples, g/cm³; $\rho_{\text{H}_2\text{O}}$ is the density of deionized water at room temperature, g/cm³; m_{air} is the mass of ceramic sample in air, g; $m_{\text{H}_2\text{O}}$ is the mass of ceramic sample in deionized water. The open porosity is calculated by Eq. (2):

$$\pi_\alpha = (m_{\text{wet}} - m_{\text{air}}) \times 100 / (m_{\text{wet}} - m_{\text{H}_2\text{O}}) \quad (2)$$

Where, π_α is the open porosity, %; m_{wet} is the weight of ceramic sample after absorbing water, g. In terms of mechanical properties test, the Vickers hardness was tested by HVS-5 microhardness tester produced by Laizhou Testing Machine Factory, Shandong Province (the load was 1 kg and the holding time was 15 s), and the Bending strength and Elastic modulus were tested by Instron-5569 electronic universal material testing machine produced by Instron Company, USA (the sample was cut into strips with a cross section of 3 mm × 4 mm and the platform span was 20 mm).

3. Results And Discussion

3.1. Microstructures of HEC powders

After high-energy ball-milling, all of seven system powders became Face-centered cubic (Fcc) solid solution as seen in Fig. 2, and the related studies on the microstructure about HEC-1, HEC-2 and HEC-3 powders have been introduced in our previous reports [35]. As far as we know, the formation of solid solution is closely related to size factor and atomic electronegativity difference. Because the radius ratios of B, C, N to metal atoms (r_x/r_M) ($X = \text{B, C, N}$; $M = \text{Ta, Nb, Hf, Zr, Ti, ...}$) are all less than 0.59, it is possible for B, C, N atoms to form interstitial compound (MX) with transition metals. Moreover, the interstitial compounds with the same structure are promoted to form infinite solid solution, because the radius differences of metal atoms are less than 15%. Specially, the solid solution process of atoms still needs further study, which is one of the key points to our next work.

According to the mixing rule and Bragg's law, HEC-6 system has the minimum average metal atom size, the minimum interplanar distance (the specific diffraction angle can be seen in Table 3) and the largest crystal plane diffraction angle, which is consistent with the XRD results in Fig. 2. The diffraction angle of (111) crystal plane decreases in the wake of the average metal atom size increasing, which can be seen from the line chart intuitively in Fig. 3. Obviously, after high-energy ball-milling, the mixed powders agglomerated, and all kinds of powders are similar to sphere as seen in Fig. 4. We have reported the similar microstructure of HEC-1 ~ 3 in the Ref. [35].

3.2. High temperature thermal stability of HEC powders

Obviously, weight loss mainly occurs in 100–200 °C and 1000–1100 °C from the TG curve of HEC-1 ~ 7 powders from RT to 1400 °C in Fig. 5. The H₂O adsorbed on the powder surface volatilized, causing a small amount of weight losses in 100 °C. When the temperature was up to 1000 °C, powders lost weight quickly, which was probably caused by the volatilization of B₂O₃ generated by oxidation of B element. Compared with the values of weight loss from HEC-1 to HEC-7, HEC-2 has the lest weight loss and the values are shown in Table 4. Therefore, we choose HEC-2 system as a specimen to study the subsequent sintering process. The specific sintering process has been introduced in Sect. 2.2.

3.3. Microstructures of HEC bulk ceramics

After hot-pressing sintering at 1900 °C, the HEC-2 mainly has a Fcc phase, followed by a small amount of oxide impurities and BN(C) phase (Fig. 6 (c)). XRD pattern shows that the crystallinity of Fcc phase increases with sintering temperature increasing, at the same time the FWHM of XRD diffraction peak decreases and the diffraction intensity increases (Fig. 6 (a), (b) and (c)). What's more, the amorphous BCN phase crystallized forming BN/C phase when heating to 1900 °C. In Ref. [35], it was found that oxides formed when the powders heated at a lower temperature (1100 °C) in argon atmosphere, because oxygen impurities were inevitably brought into the powder preparation process by adopting high-energy ball-milling. Besides, the use of high-activity metal elemental as raw material powders also made it easier to introduce oxygen impurities. With the increase of sintering temperature (> 1700 °C), the oxides have a phase transformation from monoclinic phase to high-temperature stable tetragonal phase which is consistent with the existing researches [36–37]. In addition, when the sintering temperature reached 1900 °C, a small amount of BN/C precipitated.

The microcracks and holes on the ceramic surfaces indicate that the ceramics are not completely dense (Fig. 7). It can be seen from the fracture morphology of the ceramics that when the sintering temperature is 1700 °C, the ceramics are composed of nano-sized small particles, and no obvious cracks or holes appear on the fracture section and particles are intact on section in Fig. 8. When the sintering temperature is up to 1800 °C, small particles connect and there are clearly cracks on section. When sintering temperature is 1900 °C, there is obvious lamellar phase in ceramics. According to XRD analysis, the lamellar substance is BN/C phase, and the fracture surface has obvious traces of lamellar tearing and large particles pulling out with sintering temperature increasing.

In order to further analyze the microstructures characteristics, HEC-2119 ceramic after hot-pressing sintering was tested by TEM (Fig. 9). Based on the electron diffraction spots, the position 1, 2, 3 and 4 are the Fcc phase, the oxide phase, the mixture of amorphous phase and nanocrystalline and the BN/C phase, respectively. It can be seen from the EDS patterns that all elements in the Fcc high-entropy phase are uniformly distributed, but the solid solubility of N in the high-entropy phase is far less than others, whose atomic size is the smallest and which mainly concentrates in BN phase. One of the reasons for that situation is probably that besides atomic size, electronegativities of atoms also have a great

influence on solubility. Compared with C and B, the electronegativity difference between N and transition metal is the largest, causing the smallest solubility.

We speculate that oxides are solid solutions composed of hafnium, niobium, zirconium and oxide based on the EDS results, which can be expressed as $(\text{Hf}, \text{Nb}_x, \text{Zr}_y)\text{O}_z$. By compared the content of metal atoms between oxide phase and high-entropy phase, it can be found that the hafnium and zirconium contents of former are higher than latter, while it is opposite for Nb elements. By studying the oxidation sequence of elements in subgroup Ⅴ and Ⅵ under the condition of high entropy, Backman L et al [38] found that the predatory ability to oxygen of metal element is $\text{Hf} > \text{Zr} > \text{Ti} > \text{Ta} > \text{Nb}$, so Hf and Zr atoms are oxidized first. However, Nb atoms with the least oxidation tendency are oxidized, which may be due to the great solubility of oxygen. Due to the limitation of oxygen content, Nb atoms are not oxidized into the most stable Nb_2O_5 , but exist in the form of NbO_2 . According to the principle of similar compatibility, HfO_2 , ZrO_2 and NbO_2 are dissolved into single solid-solution oxides because of the same crystal structure. It is worth noting that ZrO_2 has a phase transformation from monoclinic-phase to tetragonal-phase when temperature is higher than 1170 °C [39], and changes to monoclinic-phase back when the temperature decreases. But that phenomenon is not observed during the sintering process of HEC-21 powders, we speculate that the formation of oxide phase is based on HfO_2 structure. It proves once again that HEC-21 is a multiphase ceramic mixed with high-entropy phase, oxides and BN/C phase sintered at 1900 °C, 60 MPa in argon atmosphere.

3.4. Effects of nonmetal content on phase and microstructure

The addition amount of BCN has a certain influence on phase and microstructure. Besides high-entropy phase and oxides phase, hexagonal phase M_6B_2 was precipitated with the decrease of BCN, while the diffraction peak of BN/C phase disappeared (Fig. 6 (c), (d) and (e)). It can be seen from the fracture morphology that the lamellar BN/C gradually decreases with the decrease of BCN, and there is basically no lamellar phase in HEC-23, which is consistent with the results of XRD patterns (Fig. 6 (e)). Although there is a small amount of layered phase in HEC-22, it is not shown in Fig. 6 (d) because of its little content.

From the fracture section (Fig. 10), the fracture morphology of HEC-21 ceramic is composed of a large number of randomly oriented lamellar BN/C and a small number of intact particles covered by lamellar. The fracture morphology of HEC-22 ceramic is mainly composed of intact particles and a small number of lamellar BN/C. The fracture morphology of HEC-23 ceramic with the least BCN content is composed of a large number of intact grains and a small number of grains with tearing characteristic, and there is substantially no lamellar phase. Compared with the grain size, it is found that with the decrease of BCN content, the grain size increases gradually. The main reason is that BN/C distribution among particles can effectively hinder grain growth.

3.5. Mechanical properties of HEC-2 bulk ceramics

With the sintering temperature increasing, the density and flexural strength increase gradually, and the surface porosity decreases. The specific values are in Table 5. After sintering at 1900 °C, the flexural strength of HEC-2119 is as high as 495.82 MPa. In addition, the Vickers hardness increases first and then decreases with the increase of sintering temperature (Fig. 11). The Vickers hardness of HEC-2118 ceramic is 7.57 GPa, and the hardness of HEC-2119 is 5.56 GPa. The reason for this variation tendency is that the ceramic form lamellar BN/C at 1900 °C that is easy to slip between lamellae, leading to the decrease of Vickers hardness. With the decrease of BCN content, the density, hardness and bending strength increase, but the surface porosity decreases. To a certain extent, the decrease of porosity indicates the increase of density, which is due to the high BCN content in HEC-21 ceramic, which effectively hinders the grain growth. The decrease of BCN content in HEC-22 ceramic makes the grain size larger than the former, and the increased grain squeezes lamellar to increase its density. There is no lamellar BN/C phase in HEC-23 ceramic to hinder the grain growth, which makes the grain size of this system the largest. The Vickers hardness, bending strength and open porosity of HEC-2319 are 24.54 GPa, 522.00 MPa and 0.05%, respectively. When BCN content decreases, the precipitation amount of lamellar BN/C phase decreases, and the proportion of high-entropy phase increases, which effectively improves its Vickers hardness and bulk density, and the specific change of hardness is shown in Fig. 12.

From the fracture section (Fig. 8 and Fig. 10), the change of phase and structure leads to the change of fracture mode. The fracture modes of HEC-21 ceramics are mainly lamellar tearing and intergranular fracture. The fracture modes of HEC-22 ceramics are lamellar pull-out and intergranular fracture. The fracture modes of HEC-23 ceramics with the least BCN content are intergranular fracture and transgranular fracture. In addition, compared with sintering temperature, BCN content has less influence on the bending strength.

4. Conclusions

Compact high-entropy metal boron carbonitride HEC-21 ceramics were prepared at 1700 °C, 1800 °C and 1900 °C, respectively. Besides the face-centered cubic high-entropy phase, there are oxides and lamellar BN/C phases in HEC-2119. As the temperature increases, the particle size, bending strength and density increase, but the hardness increases at first and then decreases. The mechanical properties of HEC-2 ceramic sintered at 1900 °C and 60 MPa show that the hardness, density and bending strength increase as the BCN content decreases.

Declarations

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (Grant no. 52002092 and 51832002), National Key Research and Development Program of China (Grant no. 2017YFB0703200 and 2017YFB0310400), Postdoctoral Innovative Talents Support Program (Grant no.

BX20190095), and Chinese Postdoctoral Science Foundation (Grant no. 2019M660072 and LBH-Z19141).

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Tables

Table 1

Ingredients of HEC-1~7 powders.

Sample	Component
HEC-1	(Ta, Nb, Hf, Zr, W)(BCN)
HEC-2	(Ta, Nb, Hf, Zr, Ti)(BCN)
HEC-3	(Ta, Nb, Ti, Zr, W)(BCN)
HEC-4	(Ta, Nb, V, Zr, Ti)(BCN)
HEC-5	(Ta, Nb, V, Zr, W)(BCN)
HEC-6	(Ta, Nb, V, Ti, W)(BCN)
HEC-7	(Ta, W, V, Zr, Ti)(BCN)

Table 2

Sintering parameter of HEC ceramics

Sample	Temperature/°C	Pressure/MPa	Molar ratio of metals and (BCN)
HEC-2117	1700	60	0.2: 0.2: 0.2: 0.2: 0.2: 1
HEC-2118	1800	60	0.2: 0.2: 0.2: 0.2: 0.2: 1
HEC-2119	1900	60	0.2: 0.2: 0.2: 0.2: 0.2: 1
HEC-2219	1900	60	0.2: 0.2: 0.2: 0.2: 0.2: 0.5
HEC-2319	1900	60	0.2: 0.2: 0.2: 0.2: 0.2: 0.334

Table 3

Diffraction angles of (111) crystal plane.

Sample	HEC-1	HEC-2	HEC-3	HEC-4	HEC-5	HEC-6	HEC-7
AS/Å	1.4804	1.4922	1.4534	1.4494	1.4376	1.4054	1.4338
DA/°	34.6440	34.6060	34.9521	35.1149	35.1204	35.7702	35.4337
*AS: Average metal atom size; DA: Diffraction angle.							

Table 4

Weight loss of HEC ceramics heated to 1400 °C

Sample	Mass change/%
HEC-1	-4.37%
HEC-2	-1.21%
HEC-3	-6.83%
HEC-4	+1.46%
HEC-5	-10.12%
HEC-6	-15.1%
HEC-7	-7.94%

Table 5

Mechanical properties of HEC-2 bulk ceramics sintered at different temperatures.

Sample	σ /MPa	H_V /GPa	ρ_V /g/cm ³	Π_a , %
HEC-2117	194.61	3.64	5.52	1.47
HEC-2118	339.16	7.57	5.99	0.14
HEC-2119	495.82	5.56	6.13	0.09
HEC-2219	508.53	18.22	8.22	0.05
HEC-2319	522.00	24.54	9.07	0.05

Figures

Figure 1

The hot-sintering curves for the HEC powders.

Figure 2

XRD patterns of the as-synthesized HEC powders after two-step of high-energy ball-milling.

Figure 3

The variation trend between average metal atom sizes (AS) and diffraction angles (DA) of the (111) crystal plane.

Figure 4

SEM characterizations of the as-synthesized HEC powders after two-step of milling: (a) HEC-4 (b) HEC-5; (c) HEC-6; (d) HEC-7.

Figure 5

TG curves of HEC-1~7 powders with different components.

Figure 6

XRD patterns of HEC-2 bulk ceramics with different molar ratios and sintered at different temperatures: (a), (b) and (c) are HEC-2 sintered at 1700 oC, 1800 oC and 1900 oC; (d) and (e) are HEC-22 and HEC-23 sintered at 1900 oC, respectively.

Figure 7

Surface morphologies of the HEC-21 ceramics after hot-pressing sintering at different temperatures: (a) 1700 °C; (b) 1800 °C; (c) 1900 °C.

Figure 8

Fracture surfaces of the HEC-21 ceramics after hot-pressing sintering after single-edge notched beam tests at different temperatures: (a) 1700 °C; (b) 1800 °C; (c) 1900 °C.

Figure 9

TEM images, SAED spots and scanning transmission electron microscopy-energy dispersive X-ray elemental mapping analyses of HEC-2119 bulk ceramics.

Figure 10

Fracture surfaces of bulk ceramics with different molar ratios after single-edge notched beam tests: a) HEC-2119; b) HEC-2219; c) HEC-2319.

Figure 11

Vicker's Hardness of HEC-21 ceramics sintered at different temperatures.

Figure 12

Vicker's Hardness of HEC-2 ceramics with different BCN contents.