High-entropy carbide-nitrides with enhanced toughness and sinterability

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ABSTRACT High-entropy ceramics (HECs) have attracted much attention due to their huge composition space, unique microstructure, and desirable properties. In contrast to previous studies, which have primarily focused on HECs with one anion, herein, we report a new family of ceramics with both multi-cationic and -anionic structures, i.e., high-entropy carbide-nitrides $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})(\text{C}_{0.5}\text{N}_{0.5})$, $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Nb}_{0.25})(\text{C}_{0.5}\text{N}_{0.5})$ and $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})(\text{C}_{0.5}\text{N}_{0.5})$. These as-synthesized HECs are mainly comprised of a face-centered cubic solid-solution phase accompanied by minor inevitable oxide phases. The formation mechanism of the solid-solution phase is discussed in terms of the lattice size difference and thermodynamic competition between configurational entropy and mixing enthalpy. It is found that the increment in the configurational entropy can effectively lower the sintering temperature and increase the fracture toughness. Particularly, the newly developed $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})(\text{C}_{0.5}\text{N}_{0.5})$ exhibits a decent fracture toughness of $8.4 \text{ MPa m}^{1/2}$ and a low sintering temperature of 1750°C , making it promising for ultra-high temperature applications. Our work not only enriches knowledge regarding the HECs categories, but also opens a new pathway for developing HECs with multi-cationic and -anionic structures.

Keywords: high-entropy ceramics, multi-cationic and -anionic structure, high-entropy effect, fracture toughness, sintering temperature

INTRODUCTION

Inspired by the unique design philosophy of high-entropy alloys (HEAs), high-entropy ceramics (HECs) were first proposed in the multicomponent metal oxides in 2015 [1]. These compositionally complex ceramics immediately attracted extensive attention due to their in-

teresting mechanical, physical and chemical properties, such as high hardness and strength, low thermal conductivity, good high-temperature structural stability and corrosion resistance. To date, a few HECs, including metal oxides [2–6], carbides [7–13], diborides [14–20], and nitrides [21], have been developed as a proof of concept, and they have great potential for application in both structural and functional fields.

Unlike HEAs, in which metal elements distribute randomly in a single lattice [22,23], the structure of HECs consists of a cationic sublattice and an anionic sublattice respectively occupied by metallic and nonmetallic elements. As a result, the compositional disorder of the cationic and anionic sites of HECs can lead to substantial increases in the molar configurational entropy (i.e., $\Delta S_{\text{conf}} = \Delta S_{\text{cation}} + \Delta S_{\text{anion}}$, where ΔS_{cation} and ΔS_{anion} are the entropies of the cationic and anionic site contributions [24], respectively). As reported for HEAs [22], an increase in the configurational entropy thermodynamically favors the formation of a single-phase solid solution structure rather than multiple-phase compounds, thus giving rise to the high-entropy effects, such as sluggish diffusion and severe lattice distortion. Recently, a few HECs containing a multi-cationic structure (i.e., involving five or more metals occupying the cationic sites) were synthesized [10,12]. To further increase the configurational entropy of HECs, however, the contribution of ΔS_{anion} should also be considered. Unfortunately, most studies in this field have mainly focused on the multi-cationic structure, while very limited work on HECs with more than one anion has been reported [25,26].

Ceramics often exhibit a low toughness and high sintering temperature [27,28], both of which seriously limit their practical applications. Recent studies have demon-

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strated that increasing the configurational entropy could be an effective pathway for toughening materials [29,30]. For instance, the L1₂-type Ni₃Al intermetallic compound is normally brittle, while the L1₂-type (Ni,Co,Fe)₃(Ti,Al,Fe) multicomponent intermetallic phase exhibited a highly enhanced ductility [29]. Moreover, increasing the configurational entropy was also found to be helpful to reduce sintering temperatures in HECs [1]. Therefore, the employment of a high-entropy concept in the design of ceramics with decent toughness and good sinterability is of great interest in the HEC community [31].

In this work, a novel class of high-entropy carbide-nitrides, (Ti_{0.33}Zr_{0.33}Hf_{0.33})(C_{0.5}N_{0.5}) (HEC-1), (Ti_{0.25}Zr_{0.25}Hf_{0.25}Nb_{0.25})(C_{0.5}N_{0.5}) (HEC-2), and (Ti_{0.2}Zr_{0.2}Hf_{0.2}Nb_{0.2}Ta_{0.2})(C_{0.5}N_{0.5}) (HEC-3), with multi-cationic and -anionic structures were synthesized *via* spark plasma sintering (SPS). The phase formation of these HECs was theoretically analyzed in terms of the lattice size difference and the thermodynamics of competition between configurational entropy and mixing enthalpy. Interestingly, the increment in the configurational entropy can effectively lower the sintering temperature and increase the fracture toughness. The newly developed HEC-3 exhibited a decent fracture toughness of 8.4 MPa m^{1/2} and a low sintering temperature of 1750°C.

EXPERIMENTAL SECTION

Synthesis of HECs

Commercially available TiC, ZrC, HfC, NbC, TaC, TiN, ZrN, HfN, NbN and TaN powders (99.5 wt.% purity, average particle size of 1–3 μm, Beijing Licheng Innovation Metal Materials Technology Co., Ltd., China) were used as starting materials to synthesize HEC-1, HEC-2, and HEC-3. The starting powders (with targeted compositions) were mixed by ball milling at 100 rpm for 10 h in stainless steel pots and milling media. Stearic acid, as a process control agent, and a ball-to-powder ratio of 1:5 were adopted during the mixing. Bulk samples with a diameter of 10 mm were synthesized by SPS (SPS-211H, Fuji Electronic Industrial Co., Ltd, Japan). For all samples, sintering was carried out in the temperature range of 1400–1850°C, with a temperature step of 50°C at a heating rate of 100°C min⁻¹ under 30 MPa uniaxial pressure for a dwell time of 5 min.

Characterizations

The microstructures of the as-synthesized samples were characterized *via* X-ray diffraction (XRD, Rigaku DMAX-RB-12KW, Cu-Kα) and scanning electron microscope

(SEM, Zeiss Supra 55) equipped with an energy dispersive X-ray spectrometer (EDX). The phase constituent and elemental distribution were identified *via* transmission electron microscopy (TEM, Tecnai G2 F30) and atom probe tomography (APT, LEAP 5000 XR). APT analyses were performed at a pulse repetition rate of 125 kHz and a target evaporation rate of 0.5% with a laser pulse energy of 600 pJ, and all the measurements were carried out at a tip temperature of 60 K. Hardness and modulus were measured by a Keysight Nano Indenter G200 with a Berkovich indenter tip under a load of 300 mN. Indentation data were analyzed according to the methods of Oliver and Pharr [32,33].

RESULTS AND DISCUSSION

The XRD patterns of the as-milled samples showed many sharp crystalline peaks corresponding to pristine structures in the mixed powders (Fig. 1), indicating that the milling process is just a mixture of powders rather than an alloying process. After the mixed powders were sintered at 1600°C for 5 min, both the peak intensity and peak number of the starting materials became suppressed, implying the alloying effect of SPS. As the sintering temperature increased to a certain value, which varied with the HEC composition, the diffraction of the shoulder peaks associated with the pristine powders disappeared, as marked by the arrows around the diffraction angle of 57°. Nevertheless, new diffraction peaks corresponding to a face-centered-cubic (FCC) lattice were developed and became dominant, which indicated the formation of HECs. In particular, the critical sintering temperatures of HEC-1 (Fig. 1a), HEC-2 (Fig. 1b) and HEC-3 (Fig. 1c) were determined to be 1850, 1800 and 1750°C, respectively, in terms of the complete disappearance of the shoulder peaks. It was noted that there were a few of oxides in all the three samples, which were introduced by the inevitable oxidation contamination during sintering under the low vacuum condition. More importantly, the higher sintering temperature led to the greater number of oxides in the HECs, as shown in Fig. 1c. These results indicate that the sintering temperature decreases with the increase in constituent elements, which will be further discussed later.

To investigate the microstructure and elemental distribution of the as-synthesized HECs, a series of experiments, including SEM, TEM, and APT techniques, were conducted for all the three HECs. For clarity, HEC-3 was selected as an example, since the three HECs show the same microstructure and elemental distribution features. Fig. 2a shows the typical SEM image and EDX mapping

Figure 1 XRD patterns of the as-synthesized HECs: (a) HEC-1, (b) HEC-2 and (c) HEC-3. Arrows indicate the characteristic peaks of the pristine structures of the powders, and their disappearance is an indicator of the formation of HECs.

of the as-synthesized HEC-3. It can be seen that all elements distributed randomly on a micrometer scale except for some tiny regions with the elemental segregation of O, Zr, and Hf (as marked by the white circles in Fig. 2a). The crystal structure and the nano-scaled elemental mapping were further identified *via* TEM analyses. The selected area electron diffraction (SAED) pattern of HEC-3 exhibits a typical FCC structure along the [011] zone axis (Fig. 2b), which is in good agreement with the XRD result (Fig. 1c). The distance between the two lattice planes in the high-resolution TEM (HRTEM) image of HEC-3 was measured to be 0.257 nm (Fig. 2b), which corresponds to the *d*-space of the (111) plane of the FCC structure. The typical scanning TEM (STEM) image and corresponding elemental mapping are shown in Fig. 2c. It can be seen that the Ti, Zr, Hf, Nb, and Ta elements are uniformly distributed on a nanometer scale, and no appreciable segregation is found across the three grains investigated. The homogeneous distribution of the constituent elements was also confirmed by APT analyses (Fig. 2d). Based on these data, it can be concluded that a single-phase solid solution of metal carbide-nitrides with a

uniform elemental distribution was successfully synthesized by the SPS method.

The formation mechanism of HECs is often discussed in terms of the lattice size difference, δ (Equation S1), which is similar to the atomic size difference used in HEAs [34] and essentially reflects the lattice stress. Therefore, it can also be applied to assess the formation of solid-solution HECs in terms of topological instability. In this sense, a smaller δ suggests a smaller lattice distortion, which favors the formation of HECs. Based on the lattice parameters of the starting powders (Table S1), the δ value of HEC-1, i.e., δ_1 , was estimated to be 3.6%. For HEC-2 and HEC-3, which contain NbN and TaN with a hexagonal close packing (HCP) structure, the lattice constant *c* values of NbN and TaN were used to represent the lattice parameters, because the cation-cation bonds were strained by the rigid anion net with the stronger anion-anion bonds. Gild *et al.* [35] argued that the lattice mismatch calculated by using the *c* value better reflects the average size difference than that calculated from the lattice constant *a* value for cases including the starting powders with an HCP structure. As such, the calculated

Figure 2 SEM, TEM, and APT analyses of the as-synthesized HEC-3. (a) SEM images of secondary electron and energy-dispersive X-ray spectroscopy, (b) TEM images of SAED pattern and HRTEM image, (c) STEM image and corresponding EDS compositional maps and (d) APT image.

δ_2 and δ_3 were found to be 4.7% and 12.1% for HEC-2 and HEC-3, respectively. According to the atomic size difference criterion for the formation of a solid solution in HEAs, the formation of HEC-1 and HEC-2 could be easily understood in terms of the topological instability [36]. Actually, both δ_1 and δ_2 are smaller than values reported for various HECs; however, δ_3 is quite larger than all the values reported previously for HECs [35], indicating that other factors, such as configurational entropy, play a critical role in the formation of HEC-3 rather than just the lattice size difference. In the following section, therefore, the configurational entropy of the present HECs will be estimated and discussed.

According to the modified Boltzmann equation (Equation S2) [37], the configurational entropy is $0.896R$, $1.04R$, and $1.151R$, where R is the gas constant, for HEC-1, HEC-2, and HEC-3, respectively. As mentioned before, the formation of HEC-3 is topologically instable due to

the large size difference of 12.1%. In addition, the NbN and TaN compounds involved in the formation of HEC-3 have a tendency to impede the formation of the single-phase rock-salt structure, because they have an HCP lattice and very negative formation enthalpy. After sintering, however, HEC-3 still formed the FCC rock-salt structure, suggesting that the thermodynamic equilibrium of the system at the sintering temperature of 1750°C is a dominant factor in facilitating the formation of the single solid solution structure. Therefore, it is reasonable to infer that the formation of HEC-3 is a consequence of the large mixing entropy overwhelming the mixing enthalpy, which is consistent with the calculated result of configurational entropy. In other words, the solid solution structure of HEC-3 is mainly entropy-stabilized.

Interestingly, it can be noted that HEC-3 exhibited the lowest critical sintering temperature among the three samples; however, it did not have the lowest melting

temperature according to the estimation of the pristine powders by the rule-of-mixtures (Table S1). This result implies that the configurational entropy of HECs might have a significant impact on the critical sintering temperatures. As shown in Fig. 3a, the critical sintering temperature (T_s) is almost linearly decreasing with the configurational entropy, which is consistent with the prediction of the Gibbs free energy formula for the cur-

rent HECs: $T_s = \frac{(\Delta H_{\text{mix}} - \Delta G_{\text{mix}})}{(\Delta S_{\text{cation}} + \Delta S_{\text{anion}})}$, where ΔH_{mix} , ΔG_{mix} , ΔS_{cation} , and ΔS_{anion} are the differences in enthalpy of mixing, Gibbs free energy, configurational entropy of cation, and configurational entropy of anions, respectively. It is seen that the critical sintering temperature is inversely proportional to the configurational entropy when the enthalpy and free energy are given. In this sense, the critical sintering temperature can be reduced effectively by enhancing the configurational entropy of the system. That is to say, we can promote the sinterability of ceramics by increasing their anionic constituents.

Based on the modified Boltzmann equation [37], we further estimated the configurational entropy of a series of ceramics with different constituents. Fig. 3b presents the configurational entropy, ΔS_{conf} , as a function of the cation number in ceramics. The black, red, and blue lines denote ceramics with one, two, and three anions, respectively. Clearly, increasing the number of anions will boost the configurational entropy significantly. In the case of ceramics with five cations, the configurational entropy boosts from 0.805R to 1.354R as the anion number increased from 1 to 3 (marked by the dashed line in Fig. 3b). With given cations, increasing the types of anions can significantly increase the configurational entropy and *vice versa*.

To understand the configurational entropy effect on the mechanical properties, we measured fracture toughness (K_{IC}) of the three HECs synthesized at 1850°C using the Vickers indentation method proposed by Niihara [38]. In the present case, the observed cracks belong to the Palmqvist crack since the ratio of the crack length to the half indentation diagonal length is less than 2.5 (Equation S3 and Table S2) [39]. As such, the fracture toughness of HEC-1, HEC-2, and HEC-3 was determined to be 5.7 ± 0.2 , 6.9 ± 0.6 , and 8.4 ± 0.6 MPa m^{1/2}, respectively, based on the hardness and modulus values (Fig. 4a), which are larger than that of conventional metal carbides or nitrides (Fig. 4b). In particular, the K_{IC} value of HEC-3 is almost three times greater than that of metal carbides and nitrides [10,40–45], which perhaps implies the beneficial effect of the multi-anionic structure on fracture toughness. To investigate the propagation behavior of cracks, HEC-3 was selected for analysis. As shown in Fig. 4c, the radial cracks propagated from the indentation corner on the well-polished surface of HEC-3. All the radial cracks exhibit a zigzag propagation path in HEC-3 (denoted by the arrows in Fig. 4c), while the radial crack from the indentation exhibits a straight propagation path in traditional single-phase structural ceramics [43,44]. To further investigate its toughening mechanism, the fracture morphology of HEC-3 was analyzed in detail. It was found that the microcrack is deflected around some ball-like particles (as indicated by the circles in Fig. 4d) which were identified to be Zr(Hf) oxides according to the corresponding EDS compositional maps (Fig. 4e). Similar phenomena were also observed in HEC-1 and HEC-2, implying that the *in-situ* formation of homogeneously distributed metal oxide particles could be a promising approach to toughening HECs. However, HEC-3 has a

Figure 3 (a) The relationship between configurational entropy and sintering temperature and (b) the configurational entropy as a function of the cation number of HECs with different anions.

Figure 4 (a) Vickers hardness and Young's modulus of HECs with the standard deviation of the error bar; (b) fracture toughness of HECs and the data reported in the literature [10,38–43] with the standard deviation of error bar; (c) SEM image of Vickers indentation initiated by a load of 98 N on the well-polished surface of HEC-3; (d) SEM image of the fracture surface of HEC-3, indicating the presence of the ball-like particle boundary; (e) EDS compositional maps of (d).

higher fracture toughness than the others, which could be attributed to the higher content of oxides resulting from the higher configurational entropy in HEC-3. Detailed investigation regarding the effects of entropy and oxides on toughness is ongoing. The unique combination of decent fracture toughness and good structural stability renders the newly-developed HECs promising applications in aerospace engineering domains, such as scramjet propulsion and hypersonic aerospace vehicles.

CONCLUSIONS

In summary, we developed a new class of HECs with multi-cationic and -anionic structures, i.e., (Ti_{0.33}Zr_{0.33}-

Hf_{0.33})(C_{0.5}N_{0.5}), (Ti_{0.25}Zr_{0.25}Hf_{0.25}Nb_{0.25})(C_{0.5}N_{0.5}) and (Ti_{0.2}Zr_{0.2}Hf_{0.2}Nb_{0.2}Ta_{0.2})(C_{0.5}N_{0.5}), and investigated the effects of configurational entropy on the sinterability and mechanical properties. It was found that ΔS_{conf} has an important impact on both the formation and fracture toughness of HECs. Moreover, an increase in ΔS_{conf} can promote the sinterability of ceramics by reducing the sintering temperature and improve the fracture toughness by deflecting crack propagation. As a result, HEC-3, which possesses the highest ΔS_{conf} among the three newly developed HECs, exhibited the lowest sintering temperature of 1750°C and the largest K_{IC} value of 8.4 MPa m^{1/2}. This finding not only enriches knowledge

regarding the categories of HECs, but also opens a new pathway for developing high-performance HECs with multi-cationic and -anionic structures.

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Author contributions Liu X and Zhang P conceived the idea. Liu X and Lu Z supervised the project. Zhang P synthesized the samples and characterized the structural and mechanical properties. Zhang P, Liu X and Lu Z wrote the manuscript. All the authors analyzed the data and commented the manuscript.

Conflict of interest All authors declare that they have no conflict of interest.

Supplementary information Experimental details and supporting data are available in the online version of the paper.

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具有高断裂韧性和易烧结性的高熵碳氮化物陶瓷

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摘要 高熵陶瓷由于具有巨大的成分空间、独特的微观结构和良好的性能而倍受关注。与现有高熵陶瓷研究主要集中在以单个阴离子和多个阳离子组成的混合结构不同, 本文报道了一系列具有多阴离子和多阳离子混合而成的新型高熵陶瓷: $(\text{Ti}_{0.33}\text{Zr}_{0.33}\text{Hf}_{0.33})-(\text{C}_{0.5}\text{N}_{0.5})$, $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{Nb}_{0.25})(\text{C}_{0.5}\text{N}_{0.5})$ 和 $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})(\text{C}_{0.5}\text{N}_{0.5})$ 。这类高熵陶瓷主要由面心立方固溶体相组成, 同时伴随着少量不可避免的氧化物相。从晶格尺寸差、构型熵和混合焓的竞争关系对其形成机制进行了分析讨论。由于多阴离子带来的高熵效应, 新开发的高熵陶瓷材料具有良好的断裂韧性和易烧结性。特别是, $(\text{Ti}_{0.2}\text{Zr}_{0.2}\text{Hf}_{0.2}\text{Nb}_{0.2}\text{Ta}_{0.2})(\text{C}_{0.5}\text{N}_{0.5})$ 的断裂韧性高达 $8.4 \text{ MPa m}^{1/2}$, 具有作为超高温防护材料的应用前景。该工作不仅丰富了高熵陶瓷的种类, 而且为开发具有多阴离子和阳离子结构的高熵陶瓷提供了新的思路。