Influence of equiatomic Zr/(Ti,Nb) substitution on microstructure and ultra-high strength of (Ti,Zr,Nb)C medium-entropy ceramics at 1900 °C

Qingqing YANG\textsuperscript{a}, Xingang WANG\textsuperscript{a,\ast}, Weichao BAO\textsuperscript{a}, Ping WU\textsuperscript{a}, Xiaofei WANG\textsuperscript{a}, Xiaojie GUO\textsuperscript{a}, Cheng ZHANG\textsuperscript{b}, Guojun ZHANG\textsuperscript{c}, Danyu JIANG\textsuperscript{a}

\textsuperscript{a}State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China
\textsuperscript{b}School of Materials Science and Engineering, Shanghai Institute of Technology, Shanghai 201418, China
\textsuperscript{c}Institute of Functional Materials, Donghua University, Shanghai 201620, China

Received: February 21, 2022; Revised: June 15, 2022; Accepted: June 16, 2022
© The Author(s) 2022.

Abstract: High-temperature mechanical properties of medium-entropy carbide ceramics have attracted significant attention. Tailoring the microstructure is an effective way to improve these high-temperature mechanical properties, which can be affected by the evolution of the enthalpy and entropy, as well as by lattice distortion and sluggish diffusion. In this study, the effects of equiatomic Zr/(Ti,Nb) substitution (Zr content of 10–40 at%) on the microstructure and high-temperature strength of (Ti,Zr,Nb)C medium-entropy ceramics were investigated. The grain size of the (Ti,Zr,Nb)C medium-entropy ceramics was refined from 9.4±3.7 to 1.1±0.4 μm with an increase in the Zr content from 10.0 to 33.3 at%. A further increase in the Zr content to 40 at% resulted in a slight increase in the grain size. At 1900 °C, the (Ti,Zr,Nb)C medium-entropy ceramics with the Zr contents of 33.3 and 40 at% exhibited ultra-high flexural strengths of 875±43 and 843±71 MPa, respectively, which were higher than those of the transition metal carbides previously reported under similar conditions. Furthermore, relatively smooth grain boundaries, which were detected at a test temperature of 1000 °C, transformed into curved and serrated boundaries as the temperature increased to 1900 °C, which may be considered the primary reason for the improved high-temperature flexural strength. The associated mechanism was analyzed and discussed in detail.

Keywords: medium entropy; mechanical property; ultra-high temperature ceramics (UHTCs); non-equimolar compositions; curved and serrated grain boundaries

1 Introduction

Ultra-high temperature ceramics (UHTCs) generally

\* Corresponding author.
E-mail: xgwang@mail.sic.ac.cn

mainly include metal carbides (MCs) [1], borides [2,3], and nitrides, which are expected to be utilized in ultra-high temperatures and ambient atmospheres above 3000 °C [4]. Among them, MC solid-solution ceramics have attracted considerable attention because of their extremely high melting points, electrical conductivities, high hardness values, and high-temperature strengths,
rendering them promising for various industrial applications [5–7]. The potential applications of these compounds can be further improved by doping [8], adding sintering aids [9], compounding multiple materials [10], and creating solid solutions [11]. The method of creating the solid solutions was inspired by the development of multi-metal solid-solution compounds. Similar to high-entropy alloys (HEAs), the ceramics with a mixing entropy not lower than 1.61R (ΔS_conf ≥ 1.61R, wherein R is the gas constant) are categorized as the high-entropy ceramics [12].

High-entropy transition MCs are considered effective and promising candidates to further improve the properties of ultra-high-temperature carbides [13]. Feng et al. [14] successfully prepared single-phase (Hf,Zr,Ti,Na,Nb)C high-entropy carbide ceramics with an average grain size of 0.9±0.3 μm via two-step hot-press sintering, and tested their flexural strength at 25–2300 °C. The flexural strength was 421±27 MPa at 25 °C. At the temperature higher than 1800 °C, the flexural strength decreased almost linearly until the temperature reached 2300 °C. Finally, a flexural strength as low as 93±10 MPa was achieved, which was attributed to an increase in the dislocation motion accompanied by a decrease in the dislocation density.

Recently, further studies on the HEAs with medium-entropy and non-equimolar compositions demonstrated excellent performances in terms of the mechanical properties [15–17]. Afterward, Wright et al. [18,19] proposed compositionally-complex ceramics (CCCeramics) for the first time, which included the medium-entropy (0.69R ≤ ΔS_conf ≤ 1.61R) and/or non-equimolar compositions, and demonstrated that the medium-entropy compositions can once again outperform their high-entropy counterparts [19].

Demirskyi et al. [12] successfully prepared the medium-entropy (Ti0.11,Zr0.11,Ta0.11)C (~1.10R) ceramics via the spark plasma consolidation by using commercially available carbide powders. The mean grain size and flexural strength at room temperature were 7.1±4.5 μm and 703±21 MPa, respectively. However, a gradual decrease in strength (~310 MPa) was observed with an increase in the test temperature from 1000 to 1800 °C. In our previous study, the single-phase (Ti,Zr,Hf)C medium-entropy (~1.10R) carbide with a grain size of ~1.9 μm was successfully synthesized via the carbothermal reduction at 2100 °C through the hot pressing [21]. The flexural strength at 1800 °C (614±73 MPa) was slightly higher than that at room temperature (579±62 MPa). This was attributed to the decreased grain size and high lattice parameter mismatch between TiC and ZrC, which inhibited the grain growth and enhanced the grain boundary strength. Moreover, Yang et al. [22] for the first time, reported the successful preparation of the (Ti,Zr,Ta)C medium-entropy carbide ceramics with excellent ultra-high temperature flexural strength (725±32 MPa) at 1800 °C and a grain size of approximately 1.1 μm by using core–shell structure (Ti,Zr,Ta)C medium-entropy powders.

The aforementioned studies suggest that the microstructure is one of the main factors influencing the mechanical properties of carbide ceramics. The microstructure can be affected by the evolution of the enthalpy and entropy, as well as by lattice distortion and sluggish diffusion while adjusting the configurational entropy [23]. In this study, the microstructure and high-temperature flexural strength of (Ti,Zr,Nb)C medium-entropy carbide ceramics with different Zr content were investigated. Because ZrC has a low self-diffusion coefficient and a higher melting point compared to TiC and NbC [24,25], varying the Zr content can not only adjust the configurational entropy but also enable control of the microstructure.

### 2 Experimental

TiO2 (~0.1 μm, purity of 99.99%), ZrO2 (~0.2 μm, purity of 99.95%), Nb2O5 (~3 μm, purity of 99.9%), and graphite (~2 μm, purity of 99%) were used as the original powders for the synthesis of dual-phase medium-entropy carbide powders and ceramics based on the stoichiometric amounts according to Eq. (1) and Table 1.

$$xTiO_2 + yZrO_2 + zNb_2O_5 + uC \rightarrow (Ti_xZr_yNb_z)_C + (u - 1)CO(g) \quad (1)$$

According to Eq. (1) and Table 1, the raw powders with four different compositions were mixed in a plastic bottle by using ethanol as the medium and ZrO2 balls mixing for 24 h. The obtained powder mixtures were named TZNOC-1, TZNOC-2, TZNOC-3, and TZNOC-4. Subsequently, the slurries were vacuumed

| Name   | Sample component | x   | y   | z   | u    |
|--------|------------------|-----|-----|-----|------|
| TZNC-1 | (Ti0.47,Zr0.47,Nb0.1)C | 0.45 | 0.10 | 0.225 | 3.225 |
| TZNC-2 | (Ti0.47,Zr0.47,Nb0.1)C | 0.40 | 0.20 | 0.167 | 3.167 |
| TZNC-3 | (Ti0.30,Zr0.30,Nb0.30)C | 0.30 | 0.15 | 3.15  |
to remove the ethanol by using a rotary evaporator and dried in an oven at 60 °C. The mixed powders were heated to 1700 °C for 1.5 h under a vacuum at a heating rate of 10 °C/min and cooled naturally to room temperature in a high-temperature furnace. The powders corresponding to the four compositions after the carbothermal reduction were named TZNC-1, TZNC-2, TZNC-3, and TZNC-4. The (Ti,Zr,Nb)C medium-entropy carbide powders with different Zr contents (10, 20, 33.3, and 40 at%) were loaded into a graphite die and hot-press sintered at 2100 °C with a holding time of 1 h in a graphite heated furnace. The furnace was evacuated below 10 Pa and heated at a rate of 10 °C/min up to 400 °C and at a rate of 15 °C/min from 400 to 1600 °C. Subsequently, the temperature was increased at a heating rate of 10 °C/min until 2100 °C under flowing argon (purity of 99.999%). Thereafter, the furnace was cooled at a rate of 20 °C/min to 1700 °C, followed by natural cooling to room temperature. During the heating process up to 1600 °C, the pressure was increased from 0 to 33.3 MPa at a rate of 3.33 MPa/min, and the pressure was removed until the end of the holding time. The theoretical densities of the (Ti,Zr,Nb)C samples with different Zr contents were calculated by using the lattice parameters measured by X-ray diffraction (XRD) patterns. In addition, the phase compositions of the carbide powders and ceramic samples were also analyzed by the XRD (D8, Bruker, Germany) with a Cu Kα radiation (λ = 1.54056 Å). The ultrastructural nature of the ceramic specimen element distributions and fracture surface were investigated by using the high-resolution, low-temperature conventional field emission scanning electron microscope (FESEM, Magellan 400L, FEI, USA) equipped with an electron dispersive spectroscopy (EDS, X-MAXN 80 mm², Oxford Instruments, UK), a scanning electron microscope (SEM, TM3000, Hitachi, Japan), a transmission electron microscope (TEM, JEM 2100F, JEOL, Japan), and an aberration-corrected scanning transmission electron microscope (AC-STEM, HF 5000, Hitachi, Japan). The average grain size was calculated by the image analysis method (ImageJ, National Institutes of Health, USA), and determined from approximately 200 grains. Four-point flexural strength measurements were performed by using a test bar with a dimension of 30 mm × 2.5 mm × 2 mm (length × width × height) that was polished to 0.25 µm with a diamond suspension. The four-point flexural strength was measured according to the ASTM C 1495 standard with inner and outer spans of 10 and 20 mm, respectively. The ultra-high-temperature strength testing machine (AG-X Plus, Shimadzu, Japan) was operated in a high-purity flowing Ar atmosphere at a crosshead rate of 0.5 mm/min in a temperature range of 25–1000 °C, and the crosshead rate was 2 mm/min at 1600–1900 °C. A minimum of three samples were used to calculate the flexural strength.

3 Results and discussion

The XRD patterns of the TZNC-1, TZNC-2, TZNC-3, and TZNC-4 powders synthesized via the carbothermal reduction at 1700 °C for 1.5 h are shown in Fig. 1(a). Compared with the patterns of TiC, ZrC, and NbC, the main phases were determined as Ti and Nb-rich phase (Ti,Nb(Zr)C) and Zr-rich phase (Zr(Ti,Nb)C), excluding oxides and graphite. The intensity of the diffraction peaks corresponding to the Zr(Ti,Nb)C phase increases with the Zr content increasing, which is the evidence of the increase in the Zr(Ti,Nb)C phase content.

The XRD patterns of the TZNC-1, TZNC-2, TZNC-3, and TZNC-4 powders synthesized via the carbothermal reduction at 1700 °C for 1.5 h are shown in Fig. 1(a). Compared with the patterns of TiC, ZrC, and NbC, the main phases were determined as Ti and Nb-rich phase (Ti,Nb(Zr)C) and Zr-rich phase (Zr(Ti,Nb)C), excluding oxides and graphite. The intensity of the diffraction peaks corresponding to the Zr(Ti,Nb)C phase increases with the Zr content increasing, which is the evidence of the increase in the Zr(Ti,Nb)C phase content.

The XRD patterns of the TZNC-1, TZNC-2, TZNC-3, and TZNC-4 powders synthesized via the carbothermal reduction at 1700 °C for 1.5 h are shown in Fig. 1(a). Compared with the patterns of TiC, ZrC, and NbC, the main phases were determined as Ti and Nb-rich phase (Ti,Nb(Zr)C) and Zr-rich phase (Zr(Ti,Nb)C), excluding oxides and graphite. The intensity of the diffraction peaks corresponding to the Zr(Ti,Nb)C phase increases with the Zr content increasing, which is the evidence of the increase in the Zr(Ti,Nb)C phase content.

The XRD patterns of the TZNC-1, TZNC-2, TZNC-3, and TZNC-4 powders synthesized via the carbothermal reduction at 1700 °C for 1.5 h are shown in Fig. 1(a). Compared with the patterns of TiC, ZrC, and NbC, the main phases were determined as Ti and Nb-rich phase (Ti,Nb(Zr)C) and Zr-rich phase (Zr(Ti,Nb)C), excluding oxides and graphite. The intensity of the diffraction peaks corresponding to the Zr(Ti,Nb)C phase increases with the Zr content increasing, which is the evidence of the increase in the Zr(Ti,Nb)C phase content.
about the size and morphology of the (Ti,Zr,Nb)C powders, the SEM analysis was performed on the TZNC-1, TZNC-2, TZNC-3, and TZNC-4 powders, and the results are shown in Fig. 2. The TZNC-1 and TZNC-2 powders exhibit a non-uniform morphology with distinct agglomerates and a wide size distribution. By contrast, TZNC-3 and TZNC-4 exhibit a uniform morphology and low agglomeration. This indicates that the Zr(Ti,Nb)C phase is beneficial to obtain the composite powders with good uniformity and dispersion.

The XRD patterns of the TZNC-1, TZNC-2, TZNC-3, and TZNC-4 ceramics sintered at 2100 °C are shown in Fig. 1(b). The XRD results confirm the formation of the single-phase solid solution of the TZNC-1, TZNC-2, TZNC-3, and TZNC-4 ceramics. The Bragg angles of (Ti,Zr,Nb)C shifted to a lower angle as the Zr content increased from 10 to 40 at%, which is mainly attributed to a larger atomic radius of Zr (1.43 Å) than those of Ti (1.32 Å) and Nb (1.34 Å). In addition, the XRD peaks broaden as the Zr content increases to 33.3 and 40 at%. According to the Williamson–Hall formulation [26], the broadening of the XRD peaks can be attributed to a decrease in the grain size.

The (Ti,Zr,Nb)C ceramics with different Zr contents were sintered at 2100 °C. The relative densities of TZNC-1, TZNC-2, TZNC-3, and TZNC-4 were 99.0%, 99.0%, 99.8%, and 99.8%, respectively. Their similar high relative density above 99% confirmed their nearly complete densification of the (Ti,Zr,Nb)C ceramics. Figure 3 shows the morphology of the polished surfaces of these samples. Remnant small pores are entrapped in large grains due to rapid grain growth during the sintering of the TZNC-1 ceramics. The higher Zr content up to 33.3 at% causes significant grain refinement in the TZNC-3 and TZNC-4 ceramics. Only a limited number of pores are apparent on the polished surface of TZNC-3 and TZNC-4. From the grain size distributions of the (Ti,Zr,Nb)C ceramics (shown in Fig. 3), it is clear that TZNC-3 has a much narrower grain size distribution compared to the other samples. The average grain size of the (Ti,Zr,Nb)C ceramics decreases from 9.4±3.7 μm for TZNC-1 to 1.1±0.4 μm for TZNC-3, and slightly increases to 1.6±0.6 μm for TZNC-4. The configuration entropy of the (Ti,Zr,Nb)C ceramics could be calculated according to Eq. (2) [27]:

\[
\Delta S_{\text{conf}} = -R \sum_{i=1}^{N} x_i \ln x_i
\]

where \(\Delta S_{\text{conf}}\) is the configuration entropy, \(R\) is the gas constant, \(x_i\) is the molar fraction of the \(i\) element, and \(N\) is the metal element specie. The configurational entropy of the (Ti,Zr,Nb)C ceramics with the Zr contents of 10, 20, 33.3, and 40 at% are 0.95\(R\), 1.05\(R\), 1.10\(R\), and 1.09\(R\), respectively. It can be concluded that the equimolar ratio of the (Ti,Zr,Nb)C ceramics with the highest configuration entropy results in their smallest grain size. The grain size of the (Ti,Zr,Nb)C ceramics can be adjusted by altering the Zr content, possibly due to the sluggish diffusion effect of increasing the configuration entropy. The flexural strength of the ceramics is closely related to their microstructures. For example, according to the Hall–Petch relationship, a fine grain size is one of the conditions beneficial to achieving an excellent ultra-high-temperature strength [28]. At the next step in this study, the flexural strength of the (Ti,Zr,Nb)C ceramics with different Zr contents was explored at 25–1900 °C.

The flexural strengths of the (Ti,Zr,Nb)C ceramics with different Zr contents are shown in Fig. 4(a). It can be seen that, the room temperature flexural strengths of TZNC-1, TZNC-2, TZNC-3, and TZNC-4 are comparatively close in the range of 420–460 MPa, possibly due to their similar relative densities. The flexural strength of TZNC-1 is stable throughout the temperature range, with the flexural strength of 457±9 MPa at 1900 °C. However, in a notable difference from the flexural strength of TZNC-1, those of the TZNC-2, TZNC-3, and TZNC-4 ceramics significantly increase with increasing the test temperature.

This difference in the flexural strength may be related to the grain boundary morphology at the various test temperatures. The different changing trends of the fracture surface morphology between TZNC-1 and
TZNC-3 at 25–1800 °C are shown in Fig. 5. The grain boundary morphology of TZNC-1 (Fig. 5(a)) shows a mixed fracture mode of transgranular and intergranular fractures at room temperature. Even at 1800 °C, the transgranular cleavage can still be found for TZNC-1 (depicted by the arrows in Fig. 5(c)), which explains its stable flexural strength in the entire temperature range.

The fracture surfaces of TZNC-3 ceramics exhibit primarily transgranular at room temperature, which changes to an unusual fracture behavior above 1000 °C. The fracture surface of the TZNC-3 ceramics above 1000 °C (Figs. 5(e) and 5(f)) is much rougher than that at room temperature (Fig. 5(d)), and a lot of steps appear on the fracture surface. This unusual fracture behavior could consume more energy compared to the transgranular fracture. The grains bond tightly together even at 1800 °C, indicating the higher grain boundary strength. Furthermore, the polished surface shows that the grain boundaries of the TZNC-1 ceramic were mostly flat (shown in Fig. 6(a)), but the grain boundaries of the TZNC-2, TZNC-3, and TZNC-4 ceramics changed to curved and serrated at 1900 °C (as shown in Figs. 6(b)–6(d)). The flexural strengths of the monocarbides TiC [21] and ZrC [20] reported in our previous studies and that of NbC in the present study at 25–1800 °C are shown in Fig. 4(b) for comparison. The flexural strengths of TiC, ZrC, and NbC decreased almost linearly from approximately 450 MPa at room temperature to 280–330 MPa at 1800 °C. The strength degradation at the high temperature is caused by grain boundary sliding and grain pull-out during the loading of the bar and final intergranular failure [20,21]. The grain surface
Fig. 5 Fracture surface SEM images of (a–c) TZNC-1 and (d–f) TZNC-3 ceramics at different test temperatures of (a, d) 25 °C, (b, e) 1000 °C, and (c, f) 1800 °C.

Fig. 6 Polished surface SEM images of (a) TZNC-1 ceramic with flat grain boundaries, and (b) TZNC-2, (c) TZNC-3, and (d) TZNC-4 ceramics with curved and serrated grain boundaries at 1900 °C (marked with arrows).

and grain boundaries (not shown here) are relatively smooth, with no pronounced roughness or curved/serrated grain boundary in these monocarbidies up to 1800 °C.

Notably, the flexural strengths of the TZNC-2, TZNC-3, and TZNC-4 ceramics (600±91, 729±56, and 669±114 MPa, respectively) at 1600 °C are approximately 30% higher than those at 1000 °C (463±55, 563±109, and 539±46 MPa, respectively). This is possible because the curved grain boundaries change in the morphology from relatively flat at 1000 °C to rough at 1600 °C (shown in Figs. 7(b) and 7(c)). As the temperature is increased from 1600 to 1800 °C, the flexural strengths of TZNC-2, TZNC-3, and TZNC-4 reach 611±60, 786±48, and 755±84 MPa, respectively. With a further increase in the temperature to 1900 °C, TZNC-3 and TZNC-4 demonstrated ultra-high flexural strengths of 875±43 and 843±71 MPa, respectively, higher than those of previously reported transition MCs under similar conditions [12,14,20–22]. Meanwhile, the flexural strengths of TZNC-2, TZNC-3, and TZNC-4 showed an increasing trend at 1000–1900 °C, possibly due to the evolution of the relatively smooth curved grain boundaries to curved and serrated boundaries (marked by arrows in Figs. 7 and 6(c) for the TZNC-3 samples). The curved and serrated grain boundaries not only hinder the sliding between adjacent grain boundaries, but also passivate the crack tip and inhibit the crack propagation, further enhancing the flexural strength [29,30].

The TEM and HRTEM images of the TZNC-3 ceramic sample after the flexural test at 1900 °C are shown in Fig. 8. Stripes with an equal thickness of approximately 100 nm arranged in a rough parallel band can be observed at the grain boundary of TZNC-3 (Fig. 8(a)), confirming the presence of curved and serrated boundaries in the grains. Meanwhile, a coherent boundary is also

Fig. 7 Grain boundary morphology SEM images of polished surfaces of TZNC-3 ceramic samples after testing at (a) 25 °C, (b) 1000 °C, (c) 1600 °C, and (d) 1800 °C (marked with arrows).
detected in the curved and serrated grain boundaries of TZNC-3 at 1900 °C (Fig. 8(b)), indicating the strong interfacial bonding strength between the (Ti,Zr,Nb)C grains. The grain boundaries have a significant effect on the mechanical properties of ceramics [31]. The flexural strength of TZNC-3 at 1000–1900 °C is higher than those of TZNC-1, TZNC-2, and TZNC-4, possibly due to its high density of interfaces and grain boundary strength.

The load–displacement curves of the (Ti,Zr,Nb)C ceramics at 1800 and 1900 °C are shown in Fig. 9. TZNC-1, TZNC-2, TZNC-3, and TZNC-4 exhibit a linear-elastic behavior to failure from room temperature (not shown here) to 1800 °C (Fig. 9(a)) at a crosshead rate of 0.5–2 mm/min. TZNC-1 still maintains the linear-elastic behavior at 1900 °C at a crosshead rate of 2 mm/min (Fig. 9(b)). However, at the same crosshead rate, the nonlinear behavior was observed for TZNC-2, TZNC-3, and TZNC-4 at 1900 °C (Fig. 9(b)). Feng et al. [14] reported that the (Hf,Zr,Ti,Ta,Nb)C high-entropy ceramics exhibited a significant deviation from the linear behavior at 2200–2300 °C, even at a high displacement rate of 3.0 mm/min. The flexural strength of (Hf,Zr,Ti,Ta,Nb)C decreased almost linearly from 318±21 MPa at 2000 °C to 93±10 MPa at 2300 °C [14]. Liu et al. [32] also reported that the flexural strength of the HfB2–SiC ceramics decreased and the nonlinear behavior occurred during the bending test at 1600 °C.

To compare the effect of different crosshead rates, the TZNC-3 ceramics were also analyzed at a crosshead rate of 4 mm/min at 1900 °C to avoid the effect of slow crack growth and/or creep at elevated temperatures [33]. TZNC-3 exhibited the linear-elastic behavior (Fig. 9(c)) at 1900 °C at the rate of 4 mm/min. The flexural strength of TZNC-3 was 811±82 MPa (the average of the two specimens), which was slightly lower than that at 2 mm/min (875±43 MPa). According to ASTM C1465-08, the strength degradation is observed at low-stress rates and high temperatures for some materials [34]. In these cases, creep damage occurs in the form of creep cavities, and micro- or macro-cracks are formed on the tensile surface. Certain ceramics may also demonstrate a strength enhancement at low-stress rates because of crack healing or crack tip blunting. The increase in the flexural strength of TZNC-3 from 1000 to 1900 °C may be related to the crack healing or crack tip blunting owing to its unique grain boundary morphology. The effect of the appreciable plastic deformation, which could cause blunt crack tips, is also a potential contribution for the excellent strength at 1900 °C [35]. The ultra-high strength of (Ti,Zr,Nb)C medium-entropy ceramics at 1900 °C and the effects of the crosshead rate on the flexural strength will be investigated further in the future.

4 Conclusions

In summary, the ternary (Ti,Zr,Nb)C medium-entropy ceramics with various Zr contents were prepared by using self-synthesized carbide powders sintering. The Zr content (10–40 at%) in the (Ti,Zr,Nb)C medium-entropy ceramics could be adjusted to effectively suppress the rapid grain coarsening and enhance the
high-temperature strength. In the temperature range of 1000–1800 °C, the flexural strengths of the four (Ti,Zr,Nb)C medium-entropy ceramics were in the following descending order: TZNC-3 (560–790 MPa) > TZNC-4 (530–760 MPa) > TZNC-2 (460–610 MPa) > TZNC-1 (~430 MPa). At 1900 °C, the flexural strengths of TZNC-2, TZNC-3, and TZNC-4 were 672±132, 875±43, and 843±71 MPa, respectively, which may have resulted from the appearance of curved and serrated grain boundaries that could effectively passivate the crack tip and inhibit the crack propagation. However, the flexural strength of TZNC-1 with a flat grain boundary was 457±9 MPa at 1900 °C. The (Ti,Zr,Nb)C ceramics with an equal molar ratio has significant mechanical properties at ultra-high temperatures, which could be attributed to the synergistic effects of the high density and high boning strength of interfaces, and the curved and serrated grain boundaries. Therefore, our findings provide a new approach for the future design of high-performance carbide ceramics for high-temperature structural applications.

Acknowledgements

Financial supports from the National Natural Science Foundation of China (Nos. 52172076, 52032001, 11575275, and 52102081) and the State Key Laboratory of High Performance Ceramics and Superfine Microstructure are greatly appreciated.

Declaration of competing interest

The authors have no competing interests to declare that are relevant to the content of this article.

References

[1] Liu JX, Shen XQ, Wu Y, et al. Mechanical properties of hot-pressed high-entropy diboride-based ceramics. J Adv Ceram 2020, 9: 503–510.
[2] Dai FZ, Sun YJ, Wen B, et al. Temperature dependent thermal and elastic properties of high entropy (Ti0.2Zr0.2Hf0.2Nb0.2Ta0.2)B2: Molecular dynamics simulation by deep learning potential. J Mater Sci Technol 2021, 72: 8–15.
[3] Liu D, Liu HH, Ning SS, et al. Chrysanthemum-like high-entropy diboride nanoflowers: A new class of high-entropy nanomaterials. J Adv Ceram 2020, 9: 339–348.
[4] Zhang Y, Sun SK, Guo WM, et al. Optimal preparation of high-entropy boride–silicon carbide ceramics. J Adv Ceram 2021, 10: 173–180.
[5] Ye BL, Chu YH, Huang KH, et al. Synthesis and characterization of (Zr1/3Nb3/3Ti1/3)C metal carbide solid-solution ceramic. J Am Ceram Soc 2019, 102: 919–923.
[6] Cedillos-Barraza O, Grasso S, Nasiri NA, et al. Sintering behaviour, solid solution formation and characterisation of TaC, HfC and TaC–HfC fabricated by spark plasma sintering. J Eur Ceram Soc 2016, 36: 1539–1548.
[7] Xiang HM, Xing Y, Dai FZ, et al. High-entropy ceramics: Present status, challenges, and a look forward. J Adv Ceram 2021, 10: 385–441.
[8] Wan DT, He LF, Zheng LL, et al. A new method to improve the high-temperature mechanical properties of Ti3SiC2 by substituting Ti with Zr, Hf, or Nb. J Am Ceram Soc 2010, 93: 1749–1753.
[9] Lu K, Liu JX, Wei XF, et al. Microstructures and mechanical properties of high-entropy (Ti0.2Zr0.2Hf0.2Nb0.2Ta0.2)C ceramics with the addition of SiC secondary phase. J Eur Ceram Soc 2020, 40: 1839–1847.
[10] Squire TH, Marschall J. Material property requirements for analysis and design of UHTC components in hypersonic applications. J Eur Ceram Soc 2010, 30: 2239–2251.
[11] Wang XG, Liu JX, Kan YM, et al. Effect of solid solution formation on densification of hot-pressed ZrC ceramics with MC (M = V, Nb, and Ta) additions. J Eur Ceram Soc 2012, 32: 1795–1802.
[12] Demirskyi D, Nishimura T, Suzuki TS, et al. High-temperature toughening in ternary medium-entropy (Ta0.3Ti0.3Zr0.3)C carbide consolidated using spark-plasma sintering. J Asian Ceram Soc 2020, 8: 1262–1270.
[13] Chen L, Zhang W, Tan YQ, et al. Influence of vanadium content on the microstructural evolution and mechanical properties of (TiZrHVNaTa)C high-entropy carbides processed by pressureless sintering. J Eur Ceram Soc 2021, 41: 60–67.
[14] Feng L, Chen WT, Fahrenholtz WG, et al. Strength of single-phase high-entropy carbide ceramics up to 2300 °C. J Am Ceram Soc 2021, 104: 419–427.
[15] Gali A, George EP. Tensile properties of high- and medium-entropy alloys. Intermetallics 2013, 39: 74–78.
[16] Gludovatz B, Hohenwarter A, Thurston KVS, et al. Exceptional damage-tolerance of a medium-entropy alloy CrCoNi at cryogenic temperatures. Nat Commun 2016, 7: 10602.
[17] Li ZM, Raabe D. Strong and ductile non-eutectic high-entropy alloys: Design, processing, microstructure, and mechanical properties. JOM 2017, 69: 2099–2106.
[18] Wright AJ, Wang QY, Huang CY, et al. From high-entropy ceramics to compositionally-complex ceramics: A case study of fluorite oxides. J Eur Ceram Soc 2020, 40: 2120–2129.
[19] Wright AJ, Wang QY, Ko ST, et al. Size disorder as a descriptor for predicting reduced thermal conductivity in medium- and high-entropy pyrochlore oxides. Scripta Mater 2020, 181: 76–81.
[20] Shen YB, Wang XG, Zhang GJ, et al. Strong ZrC ceramics at high temperatures with the addition of W. J Am Ceram Soc 2019, 102: 3090–3096.
[21] Wang XF, Wang XG, Yang QQ, et al. High-strength medium-entropy (Ti,Zr,Hf)C ceramics up to 1800 °C. *J Am Ceram Soc* 2021, **104**: 2436–2441.

[22] Yang QQ, Wang XG, Wu P, et al. Ultra-high strength medium-entropy (Ti,Zr,Ta)C ceramics at 1800 °C by consolidating a core–shell structured powder. *J Am Ceram Soc* 2022, **105**: 823–829.

[23] Mishra RS, Haridas RS, Agrawal P. High entropy alloys—Tunability of deformation mechanisms through integration of compositional and microstructural domains. *Mater Sci Eng A* 2021, **812**: 141085.

[24] Sci Si D, Guicciardi S, Nygren M. Spark plasma sintering and mechanical behaviour of ZrC-based composites. *Scripta Mater* 2008, **59**: 638–641.

[25] Wang D, Mirovoy YA, Burlachenko AG, et al. Structure formation in equimolar mixture of HfC–ZrC–TiC–NbC carbides. *Russ Phys J* 2021, **64**: 1191–1197.

[26] Williamson GK, Hall WH. X-ray line broadening from filed aluminium and wolfram. *Acta Metall* 1953, **1**: 22–31.

[27] Yeh JW. Physical metallurgy of high-entropy alloys. *JOM* 2015, **67**: 2254–2261.

[28] Zou J, Ma HB, Liu JJ, et al. Nanoceramic composites with duplex microstructure break the strength-toughness tradeoff. *J Mater Sci Technol* 2020, **58**: 1–9.

[29] McQueen HJ, Ryan ND, Konopleva EV, et al. Formation and application of grain boundary serrations. *Can Metall Q* 1995, **34**: 219–229.

[30] Wu SW, Yang T, Cao BX, et al. Multicomponent Ni-rich high-entropy alloy toughened with irregular-shaped precipitates and serrated grain boundaries. *Scripta Mater* 2021, **204**: 114066.

[31] Ji W, Rehman SS, Wang WM, et al. Sintering boron carbide ceramics without grain growth by plastic deformation as the dominant densification mechanism. *Sci Rep* 2015, **5**: 15827.

[32] Liu JX, Zhang GJ, Xu FF, et al. Densification, microstructure evolution and mechanical properties of WC doped HfB_2–SiC ceramics. *J Eur Ceram Soc* 2015, **35**: 2707–2714.

[33] Choi SR, Salem JA. 'Ultra'-fast fracture strength of advanced ceramics at elevated temperatures. *Mater Sci Eng A* 1998, **242**: 129–136.

[34] ASTM C1368-18. Standard test method for determination of slow crack growth parameters of advanced ceramics by constant stress-rate flexural testing at elevated temperatures. ASTM International, 2018.

[35] Kim YW, Jang SH, Nishimura T, et al. Microstructure and high-temperature strength of silicon carbide with 2000 ppm yttria. *J Eur Ceram Soc* 2017, **37**: 4449–4455.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/.