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First-principles study, fabrication and characterization of 
(Zr$_{0.25}$Nb$_{0.25}$Ti$_{0.25}$V$_{0.25}$)C high-entropy ceramic

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Abstract

The formation possibility of a new \((Zr_{0.25}Nb_{0.25}Ti_{0.25}V_{0.25})C\) high-entropy ceramic (ZHC-1) was first analyzed by the first-principles calculations and thermodynamical analysis and then it was successfully fabricated by hot pressing sintering technique. The first-principles calculation results showed that ZHC-1 was an entropy stabilized solid solution due to its high mixing enthalpy of 5.526 kJ/mol. The thermodynamical analysis results showed that ZHC-1 was thermodynamically stable above 959 K owing to its negative mixing Gibbs free energy. The experimental results showed that the as-prepared ZHC-1 (95.1% relative density) possessed a single rock-salt crystal structure, some interesting nanoplate-like structures and high compositional uniformity from nanoscale to microscale. By taking advantage of these unique features, compared with the initial binary metal carbides (ZrC, NbC, TiC and VC), it showed a relatively low thermal conductivity of 15.3 ± 0.3 W/(m·K) at room temperature, which was due to the presence of solid solution effects, nanoplates and porosity. Meanwhile, it exhibited the relatively high nanohardness of 30.3 ± 0.7 GPa and elastic modulus of 460.4 ± 19.2 GPa and the higher fracture toughness of 4.7 ± 0.5 MPa·m\(^{1/2}\), which were attributed to the solid solution strengthening mechanism and nanoplate pullout and microcrack deflection toughening mechanism.

Keywords: High-entropy ceramics, metal carbides, first-principles calculations, mechanical performances, thermal physical properties.
1. Introduction

Crystalline high-entropy ceramics (CHCs) are a new class of solid solutions consisted of a random arrangement of four or more elemental species, which are attracting increasing interest for their diverse properties and potential applications.\(^1,2\) Generally, in CHCs, a maximum molar configurational entropy can be produced by mixing four or more elements in equimolar concentrations.\(^3,4\) As a result, the Gibbs free energy of CHCs can be minimised and they can be thermodynamically more stable at elevated temperatures. More interestingly, much more diverse physical and chemical characteristics can be achieved in CHCs due to their four core effects including high-entropy, lattice distortion, sluggish diffusion and cocktail effect.\(^5,6\) Up to now, a variety of CHCs, including metal oxides,\(^7,8\) diborides,\(^9,10\) nitrides\(^11\) and carbides,\(^12,13\) have been successfully explored and investigated. As members of CHCs, metal carbide CHCs have attracted tremendous attention for potential applications as the structural components in extreme environments owing to their excellent physical and chemical properties including high hardness and melting point and good thermal stability and corrosion resistance.\(^14,15\) Nevertheless, only a couple of metal carbide CHCs, such as (Hf, Ta, Zr, Nb)C\(^12,13\) and (Hf, Ta, Zr, Nb, Ti)C\(^16,17\) have been successfully explored until now. Extending the state of the art for new classes of metal carbide CHCs is still a great challenge for the scientific community.

In the present work, we first analyzed the formation possibility of a new (Zr\(_{0.25}\)Nb\(_{0.25}\)Ti\(_{0.25}\)V\(_{0.25}\))C high-entropy ceramic (ZHC-1) based on the first-principles calculations and thermodynamical analysis and then successfully fabricated it by hot
pressing (HP) sintering technique for the first time. The phase evolution, microstructures and mechanical and thermal physical properties of the as-prepared ZHC-1 were investigated in detailed, as well as the related mechanisms. In addition, some mechanical properties were also further analyzed by first-principles calculations, such as hardness and elastic modulus. Most importantly, the resultant ZHC-1 exhibited the superior mechanical and thermal physical performances, which would endow ZHC-1 a promising candidate for extreme environmental applications.

2. Theoretical and experimental method

2.1 The first principles calculations

The first principles calculations based on density functional theory (DFT) were carried out using Vienna Ab-Initio Simulation Package (VASP).\textsuperscript{18,19} The projected-augmented-waves (PAW) with the Perdew-Burke-Ernzerhof (PBE) form of exchange-correlation potentials were adopted.\textsuperscript{20,21} It was well documented that binary transition metal carbides, such as ZrC, NbC, TiC and VC, possess two sets of face-centered cubic (FCC) sublattice,\textsuperscript{14} namely one FCC sublattice is occupied by C atoms and the other is occupied by metal atoms. As a result, it is reasonable to assume that multicomponent metal carbides would maintain the same FCC sublattice structure after forming solid solution alloys, as shown in Fig. 1, where the green balls denote C atoms while the blue ones represent metal atoms. To generate the chemical disorder in the multi-component ZHC-1, special quasi-random structure (SQS) approach was adopted.\textsuperscript{22} In the present study, the SQS supercell with 48 atoms was constructed by using the Alloy Theoretic Automated Toolkit (ATAT) code.\textsuperscript{23} For the energy
calculation on the SQS structure, plane-wave basis with energy cutoff of 500 eV was used and the calculations were performed with a k-mesh grid of \( 2\pi \times 1/60 \, \text{Å}^{-1} \) in VASP. The electronic energy convergence criterion and the ionic force convergence criterion were \( 10^{-6} \) eV and 0.01 eV/Å, respectively. The unit cell shown in Fig.1 was also used for the mechanical properties calculations on ZHC-1 and the binary carbides. In these calculations, the plane-wave cutoff energy of 800 eV was applied and the k-points Monkhorst-Pack scheme k-mesh of \( 13 \times 13 \times 13 \) was adopted in VASP. The electronic energy convergence criterion was \( 10^{-8} \) eV.\(^{24}\)

The elastic constants were further calculated by the strain-stress method and then the elastic modulus calculation was performed within the Voigt-Ress-Hill approximation.\(^{25,26}\) There were three independent elastic constants for cubic structure \( (C_{11}, C_{12} \text{ and } C_{44}) \). In general, the mechanical stability of a cubic crystal could be estimated by the generalized stability criteria which could be expressed by elastic constants: \( C_{11} - C_{12} > 0, \ C_{11} > 0, \ C_{44} > 0, \ C_{11} + 2C_{12} > 0. \)\(^{27}\) The elastic constants \( (C_{11}, C_{12} \text{ and } C_{44}) \) of ZHC-1 were 547.9 GPa, 114.9 GPa and 170.1 GPa, respectively, which satisfied the stability criteria and indicated the mechanical stability. Furthermore, the brittle-ductile behavior of materials was crucial to engineering applications and the Cauchy pressure \( (C_{12} - C_{44}) \) was often used to predict this behavior. The calculated Cauchy pressure \( (C_{12} - C_{44}) \) of ZHC-1 was negative at 0 K and 0 Pa, indicating that this system was a brittle one. On the basis of the calculated elastic constants, the “theoretical” elastic modulus and hardness were computed by the following equations: \(^{26}\)
\[ B = \frac{C_{11} + 2C_{12}}{3} \]  
(1)

\[ G = \frac{G_V + G_R}{2} \]  
(2)

\[ G_V = \frac{3C_{44} + C_{11} - C_{12}}{5} \]  
(3)

\[ G_R = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \]  
(4)

\[ E = \frac{9BG}{3B + G} \]  
(5)

\[ H_V = 2(k^2 G)^{0.585} - 3 \]  
(6)

where \( B \) is bulk modulus, \( G \) is shear modulus, \( G_V \) is Voigt shear modulus, \( G_R \) is Reuss shear modulus, and \( k \) is Pugh’s modulus ratio, defined as \( G/B \).

2.2 Preparation of ZHC-1

The commercially available ZrC, NbC, TiC and VC powders (99.9% purity, average particle size < 3 \( \mu \)m, Shanghai ChaoWei Nanotechnology Co. Ltd., Shanghai, China) were utilized as starting materials to prepare ZHC-1 by HP sintering technique in the furnace. The powders were first mixed with a ratio of 25 mol.% ZrC, 25 mol.% NbC, 25 mol.% TiC, and 25 mol.% VC, and then ball-milled for 24 h in ethanol using high-purity agate spherical media. Afterwards, they were dried, screened, and compacted into pellets of 20 mm (diameter) \( \times \) 10 mm (thickness) under a uniaxial pressure of 10 MPa. Finally, these pellets were hot-pressed inside graphite dies under a biaxial pressure of 30 MPa in vacuum at 2373 K for 30 min with a heating rate of 8 K/min.

2.3 Characterization

Nanoindentation test was performed to measure the hardness and elastic modulus of the samples by Nano-Indenter TM XP (MTS system Corp., USA) system with a
diamond Berkovich indenter with a tip radius of 20 nm. Before measurement, nanoindentation set-up was calibrated using a standard silica sample. Then the nanoindentation test was performed on the well-polished surface of the samples with a space of 10 μm between the two adjacent points under different loads (8 mN, 32 mN, 128 mN, 256 mN and 400 mN). Such an operation was repeated for 50 times. The hardness and elastic modulus of the samples were calculated by the Oliver and Pharr method based on the estimated Poisson's ratio (0.21) from the average value of four individual metal carbides. The microhardness of the samples was measured on their well-polished surface by the indentation technique using the microhardness tester with a Vickers indenter (HVS-30Z, Shanghai SCTMC Co. Ltd., China) at different loads (0.98 N, 1.96 N, 2.94 N, 4.9 N, 9.8 N, 19.6 N, 29.4 N and 49 N). Furthermore, the fracture toughness of the samples was also measured on their well-polished surface by the indentation technique using the same microhardness tester. A load of 49 N was used to generate the cracks in the sample and the fracture toughness \( K_{fc} \) was calculated by using Antis equation:\(^{30}\)

\[
K_{fc} = 0.016 \left( \frac{E}{H} \right)^{1/2} \frac{P}{c^{3/2}}
\]  

(7)

where \( P \) is the applied load, \( E \) is the elastic modulus, \( H \) is the microhardness, and \( c \) is the radial crack length (measured from center of indent). A total of 30 indentations were performed to get the average value of the fracture toughness. Thermal physical properties of the samples at room temperature were measured by the laser flash analysis (LFA-427, Netzsch, Germany) using the method introduced by Parker.\(^ {31}\) Three samples were tested and the final thermal physical properties were obtained by
the average values.

The samples were analyzed by X-ray diffraction (XRD, X’pert PRO, Almelo, Netherlands), scanning electron microscopy (SEM, supra-55; Zeiss, Oberkochen, Germany) with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM, JEM 2100, JEOL, Tokyo, Japan) with EDS. The densities of the samples were measured via the Archimedes method and the relative densities were calculated via theoretical densities that were determined by the lattice constants measured by XRD.

3. Results and discussion

The equilibrium lattice constants of ZHC-1 and the binary carbides at 0 K calculated by the first principles are listed in Table 1. It can be found that the calculated lattice constant of ZHC-1 is 4.434 Å, which is in good agreement with the calculated value of 4.421 Å from Vegard’s Law. This indicates that the equilibrium lattice constant of ZHC-1 calculated by the first principles is credible. In addition, on the basis of the energies from DFT calculations for ZHC-1 and the binary carbides at 0 K after relaxation (Table 1), we can analyze the thermodynamic stability of ZHC-1 structure. The thermodynamic stability of ZHC-1 is determined by its mixing Gibbs free energy ($\Delta G_{\text{mix}}$), which can be expressed as:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$$  \hspace{1cm} (8)

where $\Delta H_{\text{mix}}$ is the mixing enthalpy of ZHC-1, $\Delta S_{\text{mix}}$ is the mixing entropy of ZHC-1, and $T$ is the temperature. The $\Delta H_{\text{mix}}$ should be insensitive to temperature thus its variation can be negligible. As a consequence, the $\Delta H_{\text{mix}}$ of ZHC-1 can be estimated
by its value at 0 K. Specifically, the mixing enthalpy of ZHC-1 at 0 K and 0 Pa 
($\Delta H_{mix}^{0K}$) can be calculated by the following equation:

$$\Delta H_{mix}^{0K} = E_{ZHC-1} - (E_{ZTC} + E_{Nbc} + E_{TiC} + E_{Vc})/4$$

(9)

where $E$ is DFT energies of the different samples after relaxation at 0 K and 0 Pa. Using the energies from DFT calculations, the $\Delta H_{mix}^{0K}$ is calculated to be about 5.526 kJ/mol, which means that the formation of the metal sublattice with four different elements is an endothermic process. Considering a system containing two different sublattices: $h$ represents one sublattice with a number of sites $X$, and $k$ represents another sublattice with a number of sites $Y$, the mixing entropy of the ordered structure can be defined as:

$$\Delta S_{mix} = -R \left( \frac{X}{X+Y} \sum_{i=1}^{N_h} x_i^h \ln(x_i^h) + \frac{Y}{X+Y} \sum_{i=1}^{N_k} x_i^k \ln(x_i^k) \right)$$

(10)

where $R$ is the ideal gas constant, $N_h$ and $N_k$ are the elements species in the sublattice $h$ and $k$, respectively, and $x_i^h$ and $x_i^k$ are the mole fractions of the constituent $i$ in the sublattice $h$ and $k$, respectively. In our case, ZHC-1 is composed of two different sublattices including carbon sublattice ($h$) and metal sublattice ($k$). The carbon sublattice is only occupied by carbon atoms, while the metal sublattice is randomly occupied by four different equal-molar metal atoms. In other words, the value of $\sum_{i=1}^{N_h} x_i^h \ln(x_i^h)$ of carbon sublattice is equal to 0. The mixing entropy of ZHC-1 results from the disordering of metal sublattices. In addition, the values of $X$ of carbon sublattice ($h$) and $Y$ of metal sublattice ($k$) are equal to 1. As a result, the mixing entropy of ZHC-1 can be expressed as:

$$\Delta S_{mix} = -\frac{R}{2} \sum_{i=1}^{N_k} x_i^k \ln(x_i^k)$$

(11)
From Equation 11, the $\Delta S_{\text{mix}}$ of ZHC-1 per mole is calculated to be about 0.693R. By combining the calculated $\Delta H_{\text{mix}}$ of ZHC-1 discussed above, the $\Delta G_{\text{mix}}$ is found to be negative using Equation 8 ($\Delta G_{\text{mix}} < 0$) when the temperature is above 959 K, indicating a possible entropy-stabilized solid solution above 959 K. According to the phase formation theory in multi-component systems, however, the positive $\Delta H_{\text{mix}}$ and negative $\Delta H_{\text{mix}}$ have the same effect for restraining the solid solution formation. Only when the value of $\Delta H_{\text{mix}}$ is close to zero, the different elements can randomly distribute in the system and the solid solution phases can stably occur in the solid phase. A larger absolute value of $\Delta H_{\text{mix}}$ will make the solid solution formation more difficult and the separation or segregation of the different elements is more prone to occurring in this system. Therefore, a parameter $\Omega$ is defined for predicting the solid solution formation for various multi-component metal carbides, which can be expressed as:

$$\Omega = \frac{T_m \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|}$$

(12)

where $T_m$ is the melting temperature of ZHC-1, which can be calculated as 3502 K using the rule of mixtures:

$$T_m = \sum_{i=1}^{n} c_i (T_m)_i$$

(13)

where $(T_m)_i$ is the melting point of the $i$th component of the carbides. It should be noted that the value of $\Omega$ is positive since the value of $\Delta S_{\text{mix}}$ is always positive in the multi-component systems. If $\Omega > 1$, the contribution of the $T \Delta S_{\text{mix}}$ will exceed that of $\Delta H_{\text{mix}}$ for the solid-solution formation, and the multi-component systems will be prone to forming the solid solutions. If $0 < \Omega \leq 1$, the effects of $\Delta H_{\text{mix}}$ will become more
prominent compared with that of $T\Delta S_{\text{mix}}$, and the larger absolute value of $\Delta H_{\text{mix}}$ is, the less miscibility of the different elements occurs, that is to say, the more separations or segregations in the system can take place. To this end, the formation ability of the solid solutions can be estimated by the value of $\Omega$. The parameter $\delta$, another empirical criterion for describing the comprehensive effect of the atomic size difference in the multi-component solid solution systems, is expressed as follows:\(^3\)

$$\delta = \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2}$$  \hfill (14)

where $c_i$ is the atomic percentage of the $i$th component of the carbides, $r_i$ is the corresponding atomic radius, and here we use the lattice constants of ZHC-1 and the binary carbides as $\bar{r}$ and $r_i$, respectively. In general, a smaller atomic size difference denoted by smaller $\delta$ can help decrease the lattice distortions and the corresponding strain energy in systems. In conclusion, larger $\Omega$ and smaller $\delta$ will facilitate the formation of solid solutions. The calculated $\Omega$ and $\delta$ in ZHC-1 are 3.65 and 4.6%, respectively, which are in the range of the values of the stabilized solid solutions ($\Omega \geq 1, \delta \leq 6.6\%$).\(^3\) Therefore, it can be concluded that the formation of entropy-stabilized ZHC-1 is possible. Nevertheless, it is difficult to obtain the single-phase solid solution carbides due to the nature of strong covalent bonds and low self-diffusion coefficients. Synthesizing ZHC-1 needs ultrahigh temperatures in that the self-diffusion of the carbides typically occurs above 50% of the melting point ($T_m = 3502$ K), which is 1751 K.\(^{35}\) In other words, the synthesis of the above-mentioned ZHC-1 is challenging but worth trying.

Encouraged by the theoretical analysis, we conducted a series of experiments to
synthesize ZHC-1 by HP sintering technique under 30 MPa pressure at 2073 K, 2273 K and 2373 K, respectively. Fig. 2(a) displays XRD patterns of the phase evolution at different temperatures during HP sintering process. Initially, the initial four individual metal carbide phases merge to form two kinds of rock-salt structural solid solution of metal carbides at 2073 K. When the temperatures rise to 2273 K, those two solid solution phases dissolve into other three kinds of rock-salt structural solid solution of metal carbides. As the temperatures increase to 2373 K, a single rock-salt structural phase occurs, implying that ZHC-1 can be synthesized by HP sintering at 2373 K. As shown in Fig. 2(b), it is evident that the initial four individual metal carbide phases merge to form a single rock-salt crystal structure of metal carbides without other phases after the HP sintering at 2373 K. In addition, the lattice constant of ZHC-1 can be calculated to be 4.448 Å by Jade 6.5 software (Materials data incorporated, Livermore), which is in good agreement with the result from first-principles calculations (4.434 Å). Based on the calculated lattice constant from XRD analysis, the theoretical density of ZHC-1 can be calculated to be 6.654 g/cm³. At the same time, the measured density of the bulk ZHC-1 sample using the Archimedes method is 6.246 g/cm³. As a result, the relative density of ZHC-1 can be calculated to be 95.1%.

Fig. 3 displays a typical polished surface SEM image and the corresponding EDS compositional maps of ZHC-1. From Fig. 3, it can be clearly seen that the compositions of ZHC-1 are perfectly uniform at the micrometer scale without evident localization of any metal elements.

TEM analysis was employed to further investigate the crystal structure and
compositional homogeneity at nanoscale. Fig. 4(a) is a representative high-resolution transmission electron microscopy (HRTEM) image of ZHC-1. It clearly exhibits a periodic lattice structure, in which a set of fringes is about 0.258 nm, corresponding to the $d$-space of (111) planes of the FCC metal carbide. Moreover, the lattice parameter can be calculated to be about 4.469 Å, close to the XRD result (4.448 Å). Selected area electron diffraction (SAED) pattern along the [112] zone axis (Fig. 4(b)) indicates that ZHC-1 is the typical FCC metal carbide structure, which is in good agreement with XRD results. Fig. 4(c) presents the typical scanning transmission electron microscopy (STEM) image and EDS compositional maps at the nanometer scale. It can be observed that Zr, Nb, Ti and V elements are uniformly distributed at nanoscale and no segregation or aggregation is found throughout the scanned area. Combined with the results from XRD and SEM, it can be concluded that a single phase solid solution metal carbide ceramic, namely $(Zr_{0.25}Nb_{0.25}Ti_{0.25}V_{0.25})C$, with good compositional uniformity from nanoscale to microscale can be prepared by HP sintering at 2373 K, which verifies the rationalization of the analysis about the formation possibility of ZHC-1.

The calculated hardness and elastic modulus of ZHC-1 and four individual metal carbides in the present and previous works along with the experimental results are listed in Table 2. As for the hardness, compared with the microhardness, the nanohardness of ZHC-1 more reflects its “theoretical hardness” due to the presence of the porosity in ZHC-1. As a consequence, in order to compare with the reported nanohardness of four individual metal carbides, the nanohardness of ZHC-1 was
measured and calculated using identical techniques and methods. As shown in Table 2, the present calculating results of the nanohardness and elastic modulus are in good agreement with other theoretical results. Although a remarkable discrepancy can be observed between the experimental and calculated elastic modulus except for ZHC-1, the experimental nanohardness is highly consistent with the calculated hardness. This indicates that the measured nanohardness and elastic modulus of ZHC-1 are relatively accurate. From Table 2, it can be clearly seen that the measured nanohardness and elastic modulus of ZHC-1 are $30.3 \pm 0.7$ GPa and $460.4 \pm 19.2$ GPa, respectively, which inherit the high hardness and elastic modulus of the binary carbides. It should be noted that the measured nanohardness of ZHC-1 is significantly higher than that of NbC and TiC, but is slightly lower than that of ZrC and VC. Meanwhile, the measured elastic modulus of ZHC-1 is significantly higher than that of most of individual binary carbides, such as NbC, TiC and VC, but is only comparable to that of ZrC. Nevertheless, the measured nanohardness and elastic modulus of ZHC-1 are still slightly higher than the “rule of mixture” value of nanohardness (29.0 GPa) and elastic modulus (425.8 GPa) from the average of four individual metal carbides. The increase in hardness and elastic modulus can be contributed to the solid solution strengthening effects. Similar solid solution strengthening effects can be found in (Hf, Ta)C solid solution\cite{44} and (Zr, Nb, Ti)C solid solution\cite{45} with the significant improvement of hardness and elastic modulus. But the solid solution strengthening effects are not significant for ZHC-1, which is due to the high mixing enthalpy of ZHC-1 (5.526 kJ/mol). In general, for most inorganic materials, there is a positive
correlation between hardness and elastic modulus. At the same time, the elastic modulus is also positive related to the internal bonding. The more negative mixing enthalpy means the larger binding force between elements.\textsuperscript{4,35} On the basis of the first-principles calculations, the mixing enthalpy of ZHC-1 is up to 5.526 kJ/mol at 0 K. This indicates that the interatomic bonding of ZHC-1 is relatively weak, which limits the increase of the hardness and elastic modulus. In addition, the nanohardness of ZHC-1 was also measured under different applied loads and the results are shown in Fig. 5(a). Obviously, the data exhibits a decrease in the nanohardness of ZHC-1 as the applied load is increased. However, the nanohardness of ZHC-1 still has a relatively high value of 23.6 ± 0.6 GPa when the applied load is increased to 400 mN. At the same time, the microhardness of ZHC-1 was measured under different applied loads. Fig. 5(b) displays the measured microhardness as a function of applied load. It can be found that the microhardness of ZHC-1 exhibits a decrease trend with the increase of applied load. The microhardness of ZHC-1 is up to 22.5 ± 0.6 GPa at an applied load of 0.98 N and then it decreases to 19.1 ± 0.5 GPa as the applied load is increased to 49 N. It’s worth noting that the measured microhardness of ZHC-1 is much lower than that of the measured nanohardness, which is primarily attributed to the presence of the porosity in ZHC-1.

The fracture toughness of ZHC-1 was further measured by the indentation technique, and the results are listed in Table 3. Obviously, the fracture toughness of ZHC-1 is up to 4.7 ± 0.5 MPa-m\textsuperscript{1/2}, which is larger than that of the individual binary carbide (Table 3). Although the solid solution effects can result in the increase of the
hardness and elastic modulus, it cannot lead to the increase of the toughness.\textsuperscript{15} In order to reveal the toughening mechanisms, radial crack generated by Vickers indentation were analyzed. Fig. 6(a) demonstrates a representative SEM image of Vickers indentation initiated by a load of 49 N on the well-polished surface of ZHC-1. It can be seen that the radial cracks propagated from the indentation corner, in which region the highest stresses are present. Typically, the radial crack from the indentation exhibits a straight propagation path in traditional single-phase structural ceramics, while the radial cracks all exhibit a zigzag propagation path in ZHC-1. Obviously, as indicated by the red arrows in Fig. 6(b), the microcrack showed markedly deflection near some irregular plate-like grains with the lateral sizes of 2 ~ 5 μm and then propagated along the plate-like grain boundary. This process results in an increase in the propagation path and resistance of the microcrack, which can cause ZHC-1 to be toughened, suggesting a potential microcrack deflection toughening mechanism. To further investigate the toughening mechanisms, the fracture surface of ZHC-1 was also analyzed. From Fig. 6(c), it is can be clearly seen that the fracture surface of ZHC-1 exhibits a jagged morphology with the typical transgranular fracture feature. More interestingly, plenty of the irregular nanoplates are trapped between grain boundaries and protrude from the fracture surface of ZHC-1, as shown in Fig. 6(d), indicating a potential nanoplate pullout toughening mechanism. The lateral sizes of these nanoplates are in the range of 2 ~ 5 μm, in good agreement with that of the plate-like grains, and their thickness are in the range of 100 ~ 200 nm. Fig. 6(e) displays the corresponding EDS compositional maps of Fig. 6(d). It should be noted
that the compositions of the nanoplates are the same with the surrounding matrix materials. This suggests that these nanoplates are \textit{in situ} generated in ZHC-1, which can result in the good connectivity between the matrix and the nanoplates. The formation of the nanoplates may be due to the presence of a small scale of the phase separation during the solid solution formation process.\textsuperscript{7,48,49} During the solid solution formation process, the stability of the solid solution phases will be competed by the phase separation and/or intermetallic formation.\textsuperscript{50} Generally, the larger absolute value of the mixing enthalpy is, the more phase separation and/or intermetallic formation occurs.\textsuperscript{35} This finally affects the microstructure of solid solutions. In our case, the mixing enthalpy of ZHC-1 is up to 5.526 kJ/mol. Therefore, the nanoplates will be prone to being \textit{in situ} generated in ZHC-1 when the phase separation occurs during ZHC-1 formation process. Fig. 6(f) exhibits a representative SEM image of the gaps resulting from the pullout of the nanoplates. Clearly, the widths of the gaps are in the range of 100 ~ 200 nm and their lengths are in the range of 2 ~ 5 μm, in good agreement with that of the nanoplates, which confirms the presence of a potential nanoplate pullout toughening mechanism. Therefore, owing to the presence of the good connectivity between the matrix and the nanoplates, a large part of the fracture energy can be absorbed during the microcrack deflection and nanoplate pullout, which leads to the improvement in toughness to a great extent. In other words, the enhancement of the fracture toughness of ZHC-1 should be mainly contributed to the presence of the nanoplates.

Comparison of the thermal physical properties between the as-prepared ZHC-1
and the initial four binary metal carbides is shown in Table 4. The ZHC-1 shows a relatively low thermal diffusivity of $5.2 \pm 0.1 \text{ mm}^2/\text{s}$ at room temperature, and its heat capacity is measured to be about $0.49 \pm 0.04 \text{ J/(g-K)}$. As a result, the ZHC-1 exhibits a relatively low thermal conductivity of $15.3 \pm 0.3 \text{ W/(m-K)}$ at room temperature, which is much smaller than that of most of binary metal carbides, such as ZrC, TiC and VC, but is only comparable to that of NbC. But the measured thermal conductivity of ZHC-1 is much less than the “rule of mixture” value of thermal conductivity (27.7 W/(m-K)) from the average of four individual metal carbides. The decrease of the thermal conductivity of ZHC-1 may be due to the result of the interaction of solid solution effects, nanoplates and porosity. Firstly, the formation of ZHC-1 is a substitutional reaction among the four binary metal carbides. Those four kinds of the metal atoms are expected to randomly occupy the sites of the metal sublattice in the FCC structure. As a result, numerous substitutional atom defects can be introduced into the lattices, which will result in an increase in thermal resistance. The reason is that there is a positive correlation between substitutional atom defects and thermal resistance ($\tau^{-1}$), which can be given by the following equation:\textsuperscript{52}

$$
\tau^{-1} = \frac{\delta^3 \omega_D^4}{4\pi v_m^2} (\Gamma_M + \Gamma_S) 
$$

(15)

where $\delta^3$ is the atomic volume, $\omega_D$ is the Debye frequency, $v_m$ is the mean velocity of the material, and $\Gamma_M$ and $\Gamma_S$ represent the scattering parameter due to mass fluctuations and strain field fluctuations, respectively. It is evident that a large number of mass and strain field fluctuations will be created around substitutional atom defects, resulting in the increase of $\Gamma_M$ and $\Gamma_S$, which will improve the thermal resistance and
finally decrease the thermal conductivity of ZHC-1.\textsuperscript{53,54} Secondly, the presence of the nanoplates in ZHC-1 will provide a great deal of grain boundaries, which will increase the phonon scattering and thereby improve the thermal resistance. The correlation between nanoplates and thermal resistance can be expressed as:\textsuperscript{55}

\[
\tau^{-1} = \frac{v_m}{L}
\]  

Equation 16, it is evident that the presence of the nanoplates in ZHC-1 will result in the increase in thermal resistance and finally contributes to the decrease in thermal conductivity of ZHC-1. In addition to the intrinsic effects including solid solution effects and nanoplates, the presence of the porosity can also increase the phonon scattering, improve the thermal resistance and finally decrease the thermal conductivity. In our case, the relative density of ZHC-1 is only 95.1\%. This indicates the presence of a certain amount of porosity in ZHC-1, which can decrease the thermal conductivity to a certain extent. In consequence, the porosity is also a factor that causes the decrease in thermal conductivity.

4. Conclusion

In conclusion, we had theoretically demonstrated the formation possibility of a new ZHC-1 based on the first-principles calculations and thermodynamical analysis and then successfully fabricated it by HP technique for the first time. The as-prepared ZHC-1 exhibited a single rock-salt crystal structure of metal carbides, some interesting nanoplate-like structures and high compositional uniformity from nanoscale to microscale. Therefore, compared with the initial binary metal carbides
(ZrC, NbC, TiC and VC), it had the relatively low thermal conductivity due to the presence of solid solution effects, nanoplates and porosity. More importantly, it showed the relatively high hardness and elastic modulus and higher fracture toughness because of the presence of the solid solution strengthening mechanism and nanoplate pullout and microcrack deflection toughening mechanism. These superior performances would endow ZHC-1 a promising candidate for extreme environmental applications.
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Author Contributions

Y. Chu conceived and designed the experiments. Y. Chu and B. Ye performed the experiments. Y. Chu and B. Ye analyzed the data. T. Wen, M.C. Nguyen, L. Hao and C.Z. Wang performed the first-principles calculations. All authors commented on the manuscript.

Notes

The authors declare no competing financial interest.
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### Table 1. Calculated equilibrium lattice constants and DFT energies of the different systems at 0 K.

| Systems       | ZHC-1 | ZrC  | NbC  | TiC  | VC  |
|---------------|-------|------|------|------|-----|
| Lattice constants (Å) | 4.434 | 4.710 | 4.482 | 4.333 | 4.157 |
| Energies (eV/atom)    | -9.668 | -9.732 | -10.274 | -9.356 | -9.539 |

### Table 2. Comparison of the calculated (Cal) and experimental (Exp) hardness and elastic modulus of ZHC-1 and four individual metal carbides using identical methods or techniques.

| Samples | Source   | Nanohardness ($H_n$, GPa) | Elastic Modulus ($E$, GPa) | Load (mN) |
|---------|----------|---------------------------|---------------------------|-----------|
| ZrC     | Exp$^{36,37}$ | 32.5                      | 464.0                     | 10        |
|         | Cal(current) | 23.1                      | 383.0                     |           |
|         | Cal$^{38,39}$ | 24.1 ~ 26.0               | 390.7 ~ 402.2             |           |
|         | Exp$^{40}$ | 24.5                      | 406.0                     | 10        |
| NbC     | Cal(current) | 22.2                      | 472.5                     |           |
|         | Cal$^{38,41}$ | 24.5 ~ 25.4               | 496.3 ~ 501.9             |           |
|         | Exp$^{42}$ | 25.6                      | 397.3                     | 13        |
| TiC     | Cal(current) | 23.5                      | 425.5                     |           |
|         | Cal$^{38,39}$ | 25.4 ~ 25.9               | 435.0 ~ 441.5             |           |
| VC      | Exp$^{43}$ | 33.3                      | 436                       | 9         |
|         | Cal(current) | 28.5                      | 531.8                     |           |
| ZHC-1   | Exp(current) | 30.3 ± 1.2                | 460.4 ± 19.3              | 8         |
|         | Cal(current) | 26.2                      | 452.9                     |           |
Table 3. Comparison of the fracture toughness of ZHC-1 with three individual metal carbides.

| System | Fracture toughness ($K_Ic$, MPa·m$^{1/2}$) | Load (N) | Equation | Ref |
|--------|---------------------------------|---------|----------|-----|
| ZrC    | 2.1 ± 0.2                       | 19.6    | Anstis   | 41  |
| NbC    | 2.9 ± 0.2                       | 98      | Lawn     | 46  |
| TiC    | 3.3 ± 0.1                       | 9.8     | Anstis   | 47  |
| ZHC-1  | 4.7 ± 0.5                       | 49      | Present work | |

Table 4. The measured thermal diffusivity, heat capacity and thermal conductivity of ZHC-1 and the reported four individual metal carbides (relative density: 100%) at room temperature.$^{16,51}$

| Samples | Thermal Diffusivity [mm$^2$/s] | Heat Capacity [J/(g·K)] | Thermal Conductivity [W/(m·K)] |
|---------|--------------------------------|-------------------------|--------------------------------|
| ZrC     | 15.2                           | 0.37                    | 33.5                           |
| NbC     | 6.1                            | 0.57                    | 16.3                           |
| TiC     | 8.3                            | 0.19                    | 22.2                           |
| VC      | 13.4                           | 0.51                    | 38.9                           |
| ZHC-1   | 5.2 ± 0.1                      | 0.49 ± 0.04             | 15.3 ± 0.3                     |
Figure captions

Fig. 1. A simple schematic illustration of the atomic structure that does not take the lattice distortion into account of ZHC-1.

Fig. 2. XRD characterization of the different samples: (a) XRD patterns of the as-prepared samples at different temperatures and the mixture of four metal carbide powders; (b) enlargement of (a): A is ZHC-1, B is the mixture of four metal carbide powders, and C is the standard diffraction peaks from (111) planes of four metal carbides.

Fig. 3. SEM image of the polished surface of ZHC-1 and the corresponding EDS compositional maps.

Fig. 4. TEM analysis of ZHC-1: (a) HRTEM image; (b) SAED pattern; (c) STEM image and the corresponding EDS compositional maps.

Fig. 5. The measured nanohardness and microhardness of ZHC-1 as a function of applied load.

Fig. 6. SEM characterization of ZHC-1: (a) SEM image of Vickers indentation initiated by a load of 49 N on the well-polished surface of ZHC-1; (b) high magnification of (a) indicates the presence of the crack deflection toughening mechanism; (c) SEM image of the fracture surface of ZHC-1; (d) high magnification of (c) indicates the presence of the nanoplate pullout toughening mechanism; (e) EDS compositional maps of (d); (f) high magnification of (c) confirms the presence of the nanoplate pullout toughening mechanism.
Figures

Fig. 1. A simple schematic illustration of the atomic structure that does not take the lattice distortion into account of ZHC-1.
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A new \((\text{Zr}_{0.25}\text{Nb}_{0.25}\text{Ti}_{0.25}\text{V}_{0.25})\text{C}\) high-entropy ceramic (ZHC-1) with a single rock-salt crystal structure of metal carbides, some interesting nanoplate-like structures and high compositional uniformity from nanoscale to microscale was fabricated and investigated in detailed and it exhibited the superior mechanical and thermal physical performances, which would endow ZHC-1 a promising candidate for extreme environmental applications.