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***Ab-initio* study of the stability and mechanical properties of refractory metal-based high-entropy ceramics**

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A theoretical investigation of carbide (TiZrHfV)C, nitride (TiZrHfV)N, and carbonitride (TiZrHfV)_{C_{0.5}N_{0.5}} ceramics with equimolar content of refractory transition metals has been conducted using the density functional theory (DFT) method. The criteria for formability of the considered ceramics, as determined by the standard deviation of the lattice parameters of components and the enthalpy of mixing, have been applied. Thermodynamic analysis has shown that these compounds are stabilized by the configurational entropy contribution, with the estimated stabilization temperature being 1716 K for (TiZrHfV)C, 684 K for (TiZrHfV)N, and 166 K for (TiZrHfV)_{C_{0.5}N_{0.5}}. It has been determined that the considered ceramics are mechanically stable. The results of *ab-initio* calculations of their mechanical properties (Young's modulus, bulk and shear moduli, hardness, and crack resistance) are presented herein.

Keywords: high-entropy carbides, nitrides, carbonitrides, mechanical properties, density functional theory.

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Introduction

Since the synthesis of high-entropy alloys (HEAs) in the early 2000s [1], [2], high-entropy materials have attracted special attention. Soon, a new class of high-entropy systems called high-entropy ceramics (HEC) was added to HEA. High-entropy ceramic constitutes a single-phase solid solution containing at least four types of metal elements and differs from traditional ceramic materials by the presence of a high-entropy effect [3], [4]. Currently, there has been considerable effort to investigate the properties of high-entropy metal oxides [3], carbides [5]–[7], nitrides [8], diborides [9], etc. In comparison to high-entropy alloys, high-entropy ceramics exhibit a greater variety of physical and chemical properties, thereby expanding their application field in such industries as aerospace, cutting tools, microelectronics, etc. [4], [10].

This paper presents the results of a theoretical study grounded in the density functional theory (DFT) of carbide (TiZrHfV)C, nitride (TiZrHfV)N, and carbonitride (TiZrHfV)_{C_{0.5}N_{0.5}} ceramics with equimolar content of refractory transition metals. The decisive role

of the entropy factor in the stabilization of these ceramics has been demonstrated, and the stabilization temperature has been estimated. A comparison has been made of the calculated mechanical properties of ceramics and similar properties of carbides and nitrides.

I. Computation models and methods

As is well known, carbides and nitrides of refractory transition metals Ti, Zr, Hf, and V have a NaCl crystal structure [11]. Most multicomponent carbides and nitrides synthesized so far have the same structure. In this case, transition elements are placed randomly on the nodes of the cationic sublattice, while carbon and nitrogen occupy the nodes of the anionic sublattice.

We use an empirical criterion in [12] to determine the possibility of a single-phase solid solution of high-entropy ceramics. This criterion is defined by the standard deviation of the lattice parameters of transition metal carbides/nitrides that form the ceramics from the average arithmetic value of the lattice parameters:

$$\delta = \sqrt{\sum_{i=1}^N x_i [1 - a_i / (\sum_{i=1}^N x_i a_i)]^2} \quad (1)$$

where a_i is the lattice parameter of the i -th carbide/nitride, x_i is its molar concentration.

The necessary condition for the formation of a solid solution is [12] the satisfaction of the inequality $\delta < 6.6\%$. According to the values of the lattice parameters from [11], these are the values for the parameter δ : 5.25% for (TiZrHfV)C, 4.72% for (TiZrHfV)C_{0.5}N_{0.5}, and 3.86% for (TiZrHfV)N. Therefore, the necessary condition for the formation of a solid solution is satisfied for the ceramics under consideration.

To perform the calculations, a 2x2x2 cubic supercell containing 64 atoms has been designed. Using a specially developed procedure, the metals' atoms were randomly allocated to their positions in the cationic sublattice nodes. In the cases of (TiZrHfV)C and (TiZrHfV)N, the anionic sublattice is completely filled with carbon/nitrogen atoms only, while for (TiZrHfV)C_{0.5}N_{0.5}, the anionic sublattice was randomly filled with carbon and nitrogen atoms with a 0.5 probability. This model allows us to accurately reproduce the equimolar composition of the ceramics, provide a realistic representation of the solid solution disorder, and perform calculations within a reasonable computational time.

The first-principle calculations on the total energy were carried out using the QuantumEspresso software package [13]. Pseudopotentials from the QuantumEspresso library [14] with the exchange-correlation potential in the GGA-PBE approximation [15] were used. Pseudopotentials for all metals include semicore states. A study of convergence with respect to the energy cutoff parameter and the number of points in the Brillouin zone showed that for high-entropy ceramics, a cutoff energy of 44 Ry and a 6x6x6-point grid provide a total energy calculation accuracy of 3 mRy/atom. In this case, the convergence with respect to the number of k-points was < 1 mRy/atom. For cubic carbides and nitrides, the calculations were carried out for a conventional cell with a cutoff energy of 72 Ry on a 2x2x2 k-point grid. These parameters ensured a total energy convergence level of < 1 mRy/atom.

All considered structures had been optimized both in the positions of the atoms in the lattice and in its parameters. The residual forces acting on the atoms did not exceed 0.005 eV/Å after optimization.

The thermodynamic stability of (TiZrHfV)C, (TiZrHfV)C_{0.5}N_{0.5}, and (TiZrHfV)N is determined by the Gibbs free energy of mixing, ΔG_{mix} :

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}, \quad (2)$$

where ΔH_{mix} and ΔS_{mix} are the enthalpy and entropy of mixing, respectively, and T is the absolute temperature. It is possible to disregard the temperature dependence of the mixing enthalpy ΔH_{mix} [16] and take its value at 0 K for estimation.

For the considered ceramics, the enthalpy of mixing at 0 K can be calculated as follows [17]:

$$\Delta H_{mix} = E_{tot}^{HEC} - (\sum_{i=1}^N E_{tot}^i)/N \quad (3)$$

where E_{tot}^{HEC} is the total energy of the ceramic, E_{tot}^i is the total energies of the ceramic components (carbides, nitrides), $N = 4$ for (TiZrHfV)C, (TiZrHfV)N, and $N = 8$ in the case of (TiZrHfV)C_{0.5}N_{0.5}. All total energies have been calculated under the assumption of lattice parameters and atomic positions relaxation.

The considered carbide, nitride, and carbonitride ceramics consist of two different sublattices: anionic h and cationic k . The cationic sublattice is randomly filled with metal atoms of four different types with equal probability. In the case of (TiZrHfV)C/(TiZrHfV)N, the anionic sublattice is completely filled with carbon/nitrogen atoms only, and for (TiZrHfV)C_{0.5}N_{0.5}, the anionic sublattice is randomly filled with carbon and nitrogen atoms with 0.5 probability. The configurational mixing entropy of such systems, ΔS_{mix} , can be calculated by the formula [18]:

$$\Delta S_{mix} = -R \left\{ \frac{X}{X+Y} \sum_i^N x_i^h \ln(x_i^h) + \frac{Y}{X+Y} \sum_i^N x_i^k \ln(x_i^k) \right\} \quad (4)$$

where $R = 8.314462$ J/(mol*K) is the Universal Gas Constant, X, Y are the number of nodes in the sublattices h and k , respectively, N is the number of different elements in this sublattice, x_i^h, x_i^k are the mole fractions of the i -th element in the sublattices h and k , respectively.

Elastic constants of high-entropy ceramics have been calculated by the Elastic software package [19] using the strain-stress method. Using the obtained values of the elastic constants, the bulk elasticity modulus B , the moduli of shear G and Young's E , and the Poisson's ratio ν have been determined in the Voigt, Royce, and Hill approximation [20]–[22]. Vickers hardness H_V , and crack resistance K_{IC} have been calculated using the following formulas [12]:

$$H_V = 0.92(G/B)^{1.137} G^{0.708}, K_{IC} = V_0^{\frac{1}{6}} G(B/G)^{1/2}, \quad (5)$$

where V_0 is the atomic volume.

II. Computational results and their discussion

Computed values of the total energy allow us to calculate, according to (3), the value of the mixing enthalpy for the considered ceramics. The mixing enthalpy, ΔH_{mix} , for all these compounds is found to be positive and equal to 9.892 kJ/mol for (TiZrHfV)C, 3.941 kJ/mol for (TiZrHfV)N, and 1.438 kJ/mol for (TiZrHfV)C_{0.5}N_{0.5}. However, contribution of the configurational entropy to ΔG_{mix} is negative, while its absolute value increases with temperature (see (2)). According to formula (4), the mixing entropy values for (TiZrHfV)C and (TiZrHfV)N are calculated to be $\Delta S_{mix} = 0.693R$, and for (TiZrHfV)C_{0.5}N_{0.5}, it is $\Delta S_{mix} = 1.040R$. By applying the values obtained for the enthalpy and mixing entropy, it is possible to estimate the temperature at which the Gibbs mixing energy, ΔG_{mix} , becomes negative, thus indicating the possibility of stabilization of these structures (Fig. 1).

Temperatures T_0 higher than which stabilization by the entropy contribution is possible are as follows: $T_0 = 1716$ K for (TiZrHfV)C, $T_0 = 684$ K for (TiZrHfV)N,

and $T_0=166$ K for $(\text{TiZrHfV})\text{C}_{0.5}\text{N}_{0.5}$. It must be noted that these temperatures are significantly lower than the melting points of single metal carbides and nitrides that compose ceramics. Given that the total energy of the ceramics is calculated with a relatively low degree of accuracy, and the entropy of mixing includes only the configurational contribution, it is appropriate to refer to the temperature T_0 as the estimated stabilization temperature due to configurational entropy. Thus, vanadium carbide and nitride have the lowest melting points, which are 2921 K and 2323 K, respectively [11]. Ceramic $(\text{TiZrHfV})\text{C}_{0.5}\text{N}_{0.5}$ has the lowest stabilization temperature and its formation is probable at moderate temperatures. Obtaining $(\text{TiZrHfV})\text{N}$ requires much higher temperatures. $(\text{TiZrHfV})\text{C}$ synthesis requires further higher temperatures and it is probable that obtaining a single-phase solid solution of carbide ceramics will be associated with significant difficulties.

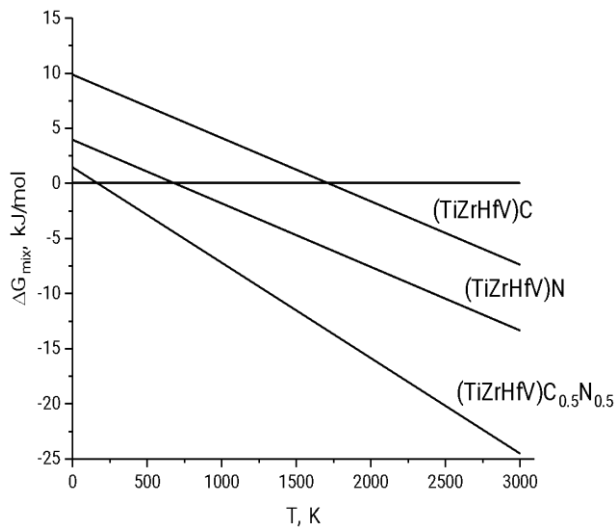


Fig. 1. Temperature dependence of the Gibbs mixing energy of high-entropy ceramics composed of $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{V}_{0.25})(\text{C}_{1-x}\text{N}_x)$ at $x = 0, 0.5, 1$.

Tables 1, 2 present the calculated and experimental values of carbides and nitrides characteristics, respectively.

The average of the moduli from [27], [28], measured in different crystallographic directions, was taken as the experimental value of the Young's modulus for ZrN, HfN, and VN in Table 2.

Calculated values of the lattice parameters of all

studied compounds practically agreed with the experimental ones with an accuracy of 0.1 – 1.3 (%) (Tables 1, 2). The discrepancies between the calculated and experimental values of Young's modulus and hardness (Tables 1, 2) are 2 – 22 (%) and 5 – 27 (%), respectively. Given that the discrepancies between the experimental values of E and H_V reported in different sources can reach 30 %, it can be argued that the calculation is generally consistent with the experiment.

As can be seen from Tables 1 and 2, carbides have lower Poisson's ratios, ν , and bulk moduli, while their values of the lattice parameter, hardness, and H_V/E ratio are higher than those of nitrides. High values of the H_V/E ratio indicate significant material hardening and resistance to plastic deformation; for example, this value for boron and diamond is close to 0.074 and 0.098, respectively [31].

The calculated physical and mechanical properties of high-entropy ceramics are presented in Table 3. The number in parentheses (Table 3) is an estimated (expected) value of some quantities determined by the mixture rule using the corresponding calculated data of carbides and nitrides of each metal from Tables 1 and 2, Δa is the distance averaged over all atoms from their positions to the nodes of the ideal lattice.

The mechanical stability of crystal lattices is the stability against small homogeneous deformations [32]. Mechanical stability criteria can be formulated in the form of various mathematically equivalent conditions that are imposed on elastic constants. In particular, the positivity of all eigenvalues of the elastic constants matrix is a necessary and sufficient condition for mechanical stability [33]. Calculation of the elastic constants and eigenvalues of the elastic constants matrix showed that all studied ceramics are mechanically stable.

Material is regarded as brittle if its Poisson's ratio is less than 0.26; otherwise, it exhibits plastic behavior [34]. The B/G ratio is also an indicator that allows for the assessment of material fracture nature [35]. Materials for which $B/G > 1.75$ are classified as ductile. In Fig. 2, b, these values are scaled so that for brittle materials they appear below the horizontal line. According to these criteria, VN and $(\text{TiZrHfV})\text{N}$ are considered ductile, while the rest are considered brittle (Tables 1 – 3 and Fig. 2, b).

According to [36], the formation of the crystal lattice is significantly influenced by the most refractory components. These are hafnium carbide and nitride, which have melting points of 4163 K and 3273 K, respectively, and have higher than average lattice parameters (Tables 1–

Table 1.

Physical and mechanical properties of carbides					
Compound	TiC	ZrC	HfC	VC	Source
a , Å	4.3178	4.6828	4.6395	4.1180	[11]
	4.3275	4.7081	4.6243	4.1524	calculation
E , GPa	451	348	352	421	[11]
	430.1	390.3	445.0	538.1	calculation
B , GPa	257.1	224.9	246.6	316.4	calculation
G , GPa	176.1	161.2	185.5	221.2	calculation
ν	0.22	0.21	0.20	0.22	calculation
H_V , GPa	21.6; 32.0	26	25.3; 32.0	25	[11], [23]–[25]
	23.3	23.2	26.9	28.0	calculation
H_V/E	0.054	0.059	0.060	0.052	calculation

Table 2.

Physical and mechanical properties of nitrides					
Compound	TiN	ZrN	HfN	VN	Source
a , Å	4.249	4.537	4.500	4.136	[11]
	4.2417	4.5946	4.5042	4.1147	calculation
E , GPa	463	392	515.5	396	[26]–[28]
	470.8	379.7	423.6	429.2	calculation
B , GPa	287.3	252.0	278.1	325.4	calculation
G , GPa	191.9	152.0	170.0	167.6	calculation
ν	0.23	0.25	0.25	0.28	calculation
H_V , GPa	20.5	18	19	21	[23], [29], [30]
	24.0	18.1	19.9	16.3	calculation
H_V/E	0.051	0.048	0.047	0.038	calculation

Table 3.

Physical and mechanical properties of high-entropy ceramics composed of $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{V}_{0.25})(\text{C}_{1-x}\text{N}_x)$, $x = 0, 0.5, 1$, calculated from the results of its *ab-initio* study

Compound	(TiZrHfV)C	(TiZrHfV) $\text{C}_{0.5}\text{N}_{0.5}$	(TiZrHfV)N
a , Å	4.4720 (4.4531)	4.4339 (4.4084)	4.3940 (4.3638)
Δa , Å	0.1163	0.1543	0.1456
B , GPa	237.7	249.8	258.8
G , GPa	168.3	173.2	143.5
E , GPa	408.6 (450.9)	422.1 (438.4)	363.4 (425.8)
ν	0.21	0.21	0.27
B/G	1.41	1.44	1.80
H_V , GPa	23.4 (25.4)	23.3 (22.5)	15.8 (19.6)
K_{IC} , $\text{MPa}\cdot\text{m}^{1/2}$	2.99	3.10	1.86
H_V/E	0.057 (0.056)	0.055 (0.051)	0.043 (0.046)

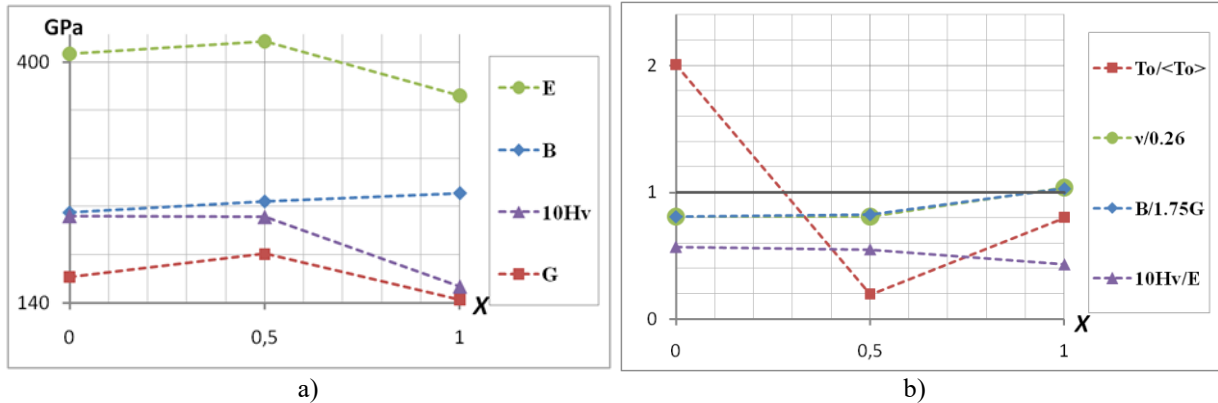


Fig. 2. A comparison of elastic moduli, hardness (a) and ratios $T_0/\langle T_0 \rangle$ ($\langle T_0 \rangle$ – arithmetic average of the three ceramics), $\nu/0.26$, $B/1.75G$, $10H_V/E$ (b) of high-entropy ceramics composed of $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{V}_{0.25})(\text{C}_{1-x}\text{N}_x)$ at $x = 0, 0.5, 1$.

3). Indeed, the lattice parameters of all three studied ceramics turned out to be higher than the expected (average) values, Table 3, which most likely lead to a decrease in Young's moduli compared to the expected (average) ones [36].

As seen from Table 3 and Fig. 2, a, nitride ceramics have the highest bulk modulus, and $(\text{TiZrHfV})\text{C}_{0.5}\text{N}_{0.5}$ has the highest Young's and shear moduli. The hardness, crack resistance, Poisson's ratio, and H_V/E ratio of $(\text{TiZrHfV})\text{C}$ and $(\text{TiZrHfV})\text{C}_{0.5}\text{N}_{0.5}$ ceramics have similar values, while the corresponding values for $(\text{TiZrHfV})\text{N}$ are much lower, which can be explained by the greater ductility of the latter (Table 3 and Fig. 2).

The highest entropy of mixing of the $(\text{TiZrHfV})\text{C}_{0.5}\text{N}_{0.5}$ ceramic has led to the lowest temperature T_0 (Fig. 1, 2, b). The calculations have shown

that this ceramic has the highest values of Young's modulus and shear, the largest average deviations of atomic positions from lattice nodes, and its hardness and H_V/E ratio turned out to be higher than the expected ones (Table 3, Fig. 2).

As can be seen from Table 3 and Fig. 2, the dependence of the studied properties of high-entropy ceramics of the composition $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{V}_{0.25})(\text{C}_{1-x}\text{N}_x)$ on x (the atomic fraction of nitrogen in the anionic sublattice) is generally nonlinear, and for T_0 , G , E , and K_{IC} the dependence is not monotonic. This kind of dependence expands the possibilities of adjusting the properties of carbide-nitride ceramics by varying the parameter the atomic fraction of nitrogen in the anionic sublattice.

Conclusions

It has been shown that the calculation methods provide a high degree of agreement with the available experimental data for transition metal (Ti, Zr, Hf, V) carbides and nitrides.

An estimation of T_0 , the stabilization temperature due to configurational entropy, was carried out for the studied carbide, nitride, and carbonitride equimolar ceramics $(\text{TiZrHfV})(\text{C}_{1-x}\text{N}_x)$, $x = 0, 0.5, 1$. The T_0 values are as follows: $T_0 = 1716$ K for $(\text{TiZrHfV})\text{C}$, $T_0 = 684$ K for $(\text{TiZrHfV})\text{N}$, and $T_0 = 166$ K for $(\text{TiZrHfV})\text{C}_{0.5}\text{N}_{0.5}$.

It has been found that nitride ceramics $(\text{TiZrHfV})\text{N}$ can be attributed to plastic materials, its Poisson's ratio $\nu = 0.27$, hardness $H_V = 15.8$ GPa, crack resistance $K_{IC} = 1.86$ MPa·m^{1/2}, and ratio $H_V/E = 0.043$. It has the highest bulk modulus, 258.8 GPa, and the lowest Young's and shear moduli, 363.4 and 143.5 (GPa), respectively.

It has been shown that both ceramics $(\text{TiZrHfV})\text{C}$ and $(\text{TiZrHfV})\text{C}_{0.5}\text{N}_{0.5}$ are brittle materials with a number of properties that are practically identical: $\nu = 0.21$,

$H_V \sim 23$ GPa, $K_{IC} \sim 3$ MPa·m^{1/2}, and $H_V/E \sim 0.06$.

It has been concluded that the $(\text{TiZrHfV})\text{C}_{0.5}\text{N}_{0.5}$ ceramic with the highest entropic contribution has the lowest temperature T_0 , the highest values of Young's and shear moduli, 422.1 and 173.2 (GPa), respectively, and the largest average deviations of atomic positions from lattice nodes. Its hardness and H_V/E ratio turned out to be higher than those calculated by the mixture rule.

The dependency on x of the properties of high-entropy ceramics composition $(\text{Ti}_{0.25}\text{Zr}_{0.25}\text{Hf}_{0.25}\text{V}_{0.25})(\text{C}_{1-x}\text{N}_x)$ is nonlinear, thereby expanding the possibilities of regulating the properties of carbide-nitride ceramics by varying the atomic fraction of nitrogen in the anionic sublattice.

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***Ab-initio* дослідження стабільності та механічних властивостей високоентропійних керамік на основі тугоплавких металів**

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На основі методу функціоналу густини (DFT) теоретично досліджено карбідну (TiZrHfV)C, нітридну (TiZrHfV)N і карбонітридну (TiZrHfV)C_{0.5}N_{0.5} кераміки з еквімолярним вмістом тугоплавких перехідних металів. Застосовано критерії можливості формування розглянутих керамік за середньоквадратичним відхиленням параметрів ґраток складових та за ентальпією змішування. Термодинамічний аналіз показав, що дані сполуки стабілізуються за рахунок вкладу конфігураційної ентропії, при цьому оціночна температура стабілізації дорівнює 1716 К для (TiZrHfV)C, 684 К для (TiZrHfV)N, 166 К для (TiZrHfV)C_{0.5}N_{0.5}. Встановлено, що розглянуті кераміки є механічно стабільними. Представлено результати *ab-initio* розрахунків їх механічних властивостей (модуля Юнга, об'ємного та зсувного модулів, твердості, тріщиностійкості).

Ключові слова: високоентропійні карбіди, нітриди, карбонітриди, механічні властивості, теорія функціоналу густини.