First-principles study on structural mechanical and thermodynamic properties of HfMoTaTiZr

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Abstract. This study calculates the phase diagram of HfMoTaTiZr using the TCHEA1 database in Thermo-Calc software. Furthermore, it also investigates the structural and mechanical properties of HfMoTaTiZr by applying first-principles calculations. The elastic and other mechanical properties such as Young’s modulus, pugh ratio, hardness, bulk modulus was derived and discussed. These parameters were found to be in good harmony with previously available experimental reports. Vickers hardness of HfMoTaTiZr predicted from the Tians model agrees with the available experimental result. This study also investigates the thermal coefficient of linear expansion and vibrational heat capacity of the HfMoTaTiZr using the Debye–Grüneisen theory.

1. INTRODUCTION

High entropy alloys (HEAs) are unique concepts used to design metallic alloys by mixing five or more metallic elements. Almost all HEAs are strong, superconductive, and are resistant to crack fatigue, corrosion high yield strength [1]. The aerospace industry demands temperature resistant, ductile, and corrosion-resistant metallic alloys. Traditional nickel-based alloys do not fulfil such demands because they melt even in temperature below 1200 K [2], HEAs, on the other hand, have advanced as promising materials for aerospace industries based on their high melting point >17000 K[3][4].

Juan et al. [2] initially pioneered the HfMoTaTiZr. They found that BCC single crystal structure exits with Vickers hardness of 5.31 GPa. In addition, HfMoTaTiZr alloy had compression yield strengths of 1600, 1045, 855, and 339 MPa at 800, 1000, and 1200 °C, respectively. HfMoTaTiZr has been investigated by many experiments [2], [3], [5], [6], however, first-principle calculation has not been investigated yet. Therefore, the phase, mechanical and thermal properties of HfMoTaTiZr are studied and discussed in this paper.

2. COMPUTATIONAL METHODS

This study uses the TCHEA1 database of Thermo-Calc-2019 software to calculate the phase property of the HfMoTaTiZr. The first principle calculation is based on density functional theory (DFT). We employed the Vienna Ab-Initio Simulation Package (VASP) [7] installed in MedeA software. We utilized the generalized gradient approximation (GGA) as an exchange-correlation function [8] described by Perdew-Burke-Ernzerh (PBE) [9]. The convergence criterion is 0.02 eV/Ang. We further took proposed small set of ordered structure (SSOS)type 2 model proposed by Jiang group [10] to
calculate the mechanical properties. This model saves computational time and cost since it has just 5 atoms in the BCC cell. We used plane-wave cut off energy of 500 eV. The $6 \times 6 \times 3$ k mesh value comes from the requested k-spacing of 0.4 per Angstrom.

We applied the stress-strain approach to compute the elastic constants implemented in MedeA software [11]. We optimized the equilibrium super cell with high accuracy to avoid zero strain. The Voight-Reuss-Hill approximation [12] was applied to calculate bulk modulus ($B$), Shear modulus ($G$), Young’s modulus ($E$), and Poisson ratio ($\nu$) as listed by the following relations:

$$B = \frac{1}{3}(C_{11} + 2C_{12}), \quad G = \frac{1}{2}(G_V + G_R),$$

where $G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44})$ and $G_R = \frac{5}{4(S_{11}-S_{12})+3S_{44}}$, $S$ is compliance matrix.

$$E = \frac{9BG}{3B+G} \quad \text{and} \quad \nu = \frac{3B-2G}{2(3B+G)}$$

The thermodynamics calculations were performed by employing the Debye theory [13]. The internal energy-volume equation of state was used to find the Grüneisen constant $\gamma_G$.

$$E(V) = \frac{BV_0}{\frac{5}{6}\gamma_G} \left( \ln \frac{V}{V_0} - \frac{1}{\frac{5}{6}\gamma_G} \right) + E_\infty,$$

where $B$ and $V_0$ represents the bulk modulus and equilibrium volume, respectively.

After deriving the $\gamma_G$, Debye temperature is calculated as,

$$\theta_D = \frac{h}{K_B} \left( \frac{6\pi^2 q}{V_0} \right)^{\frac{1}{3}} V_m,$$

where $K_B$, $V_0$, $h$, and $q$ represents it’s are Planks and Boltzmann constant, volume, Planks constant and atoms in the unit cells, respectively.

The specific heat capacity, $C_V$, is estimated as,

$$C_V(T) = 9qK_B \left( \frac{T}{\theta_D} \right)^{3} \int_0^{\theta_D} x^4 \exp x \int_0^{\exp x - 1} \frac{dx}{2}$$

where $x_D = \frac{\theta_D}{T}$ and $\theta_D$ is a Debye temperature. The thermal coefficient of linear expansion ($\alpha$) is computed as,

$$\alpha_L(T) = \frac{1}{3} \gamma_G \frac{C_V(T)}{BV_0}$$

3. RESULTS AND DISCUSSION

3.1. Structural properties

The phase formation and geometric structures of HfMoTaTiZr was predicted by computing the enthalpy of mixing ($\Delta H_{mix}$) entropy of mixing ($\Delta S_{mix}$) [14], enthalpy of mixing ($\Delta H_{mix}$) [15], atomic radius ($\delta$) [16], and valence electron concentration ($VEC$) [17] by the following, relations.
\[ \Delta S_{\text{mix}} = -R \sum_{i=1}^{n} x_i \ln x_i \]  
\[ (7) \]

\[ \Delta H_{\text{mix}} = 4 \sum_{i=1}^{n} \Delta H_{ij} \sum_{j=1}^{n} x_i x_j \]  
\[ (8) \]

\[ \delta = 100 \times \sqrt{\sum_{i=1}^{n} c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} = \sum_{i=1}^{n} x_i r_i \]  
\[ (9) \]

\[ VEC = \sum_{i=1}^{n} C_i (VEC)_i. \]  
\[ (10) \]

\[ \Delta \chi_{\text{Allen}} = \sqrt{c_i \left(1 - \frac{x_i}{\bar{x}}\right)^2} = \sum_{i=1}^{n} c_i \chi_i^{\text{Allen}} \]  
\[ (11) \]

where \( R \) is ideal gas constant, \( x_i \) and \( x_j \) are the atomic percentages of the \( i \)th and \( j \)th element respectively, \( r_i \) is the radius of the \( i \)th element, \( \bar{r} \) is averaged atomic radius, \((VEC)_i\) is the valence electron concentration of \( i \)th element, and \( \chi_i^{\text{Allen}} \) is the electronegativity of element \( i \)th and \( \bar{x} \) is the average electronegativity.

The criterion of HEA to make a stable solid phase are \( \Omega > 1.1 \) and \( \delta < 6.6\% \) [16]. Moreover, if calculated \( VEC < 6.87 \) then the HEA will form a BCC structure [17]. From our empirical calculation, it was seen that HfMoTaTiZr will form a single BCC structure.

Table 1. The values of Entropy (\( \Delta S_{\text{mix}} \)), enthalpy of mixing (\( \Delta H_{\text{mix}} \)) atomic size (\( \delta \)), and electronic parameters of the HfMoTaTiZr.

| Alloy      | \( \Delta S_{\text{mix}} \) (J/Kmol) | \( \Delta H_{\text{mix}} \) (KJ/mol) | \( \delta \) (%) | VEC  | \( \Omega \) | \( \Delta \chi_{\text{Allen}} \) | \( T_m \) (°C) |
|------------|--------------------------------------|-------------------------------------|------------------|------|----------|-----------------|--------------|
| HfMoTaTiZr | 13.38                                | -1.92                               | 5.38             | 4.6  | 7.03     | 7.6             | 2279         |

![Figure 1](image.png)

Figure 1. Calculated equilibrium phase diagrams of HfMoTaTiZr

We calculated the thermodynamic phase equilibrium of HfMoTaTiZr using thermo-calc software. Figure 1 shows HfMoTaTiZr forms a stable BCC phase over a range of temperature i.e. 1000K - 2100K. However, the hexagonal closed-packed (HCP) and C15_Laves phases are also expected to occur when the temperature becomes lower than 800 K. Previous reports on HfMoTaTiZr show existence of BCC phase only [2], [3], [6]. Yurchenko et al. [18] noted that other intermetallic phases will be formed in HEAs when \( \delta > 5\% \) and \( \Delta \chi_{\text{Allen}} > 7\% \). The results from Table 1, satisfy this criterion. However, the inter metallic phase is not detected, and BCC phase is detected in the available experiments. This shows two criteria, \( \delta > 5\% \) and \( \Delta \chi_{\text{Allen}} > 7\% \) may not be capable of predicting the Laves and HCP phases. Moreover, due to lack of annealing heat treatment during the experiments results in hiding of intermetallic phases. Therefore, we expect the future experiments will verify the
phase discrepancy of HfMoTaTiZr.

3.2. Mechanical properties

Table 2. Theoretically calculated, lattice constant \(a\) (Å), elastic constants (GPa); \(C_{11}\); \(C_{12}\); \(C_{44}\), bulk modulus \(B\) (GPa), shear modulus \(G\) (GPa), Young’s modulus \(E\) (GPa), Poisson’s ratio \(\nu\), Pugh’s ratio \(B/G\), Vickers hardness \(H_v\) (GPa) at zero pressure and Kelvin, respectively.

| Alloy          | \(a\) | \(C_{11}\) | \(C_{12}\) | \(C_{44}\) | \(C_{11}-C_{12}\) | \(B\)  | \(G\)  | \(E\)  | \(\nu\) | \(B/G\) | \(\rho\) | \(H_v\) |
|---------------|-------|------------|------------|------------|-----------------|-------|-------|-------|--------|--------|--------|--------|
| HfMoTaTiZr    | 3.37  | 196        | 84         | 42         | 79              | 124   | 53    | 139   | 0.31   | 2.35   | 10.2   | 5.79   |
| Exp. [2] [3]  | 3.37  | -          | -          | -          | -               | -     | -     | -     | 133    | 0.33   | 10.21  | 5.31   |

Table 2 presents the comparison between the calculated mechanical properties of HfMoTaTiZr and those reported by available experiments. HfMoTaTiZr satisfies the mechanically stable conditions from elastic constants calculation as explained by Born Rule [19] \((C_{11} + 2C_{12} > 0, C_{11} - C_{12} > 0, C_{44} > 0, C_{11} > |C_{12}|)\). Pugh’s criterion proposes ductile nature for materials with \(B/G > 1.75\) and brittle nature for materials with \(B/G < 1.75\) [20]. We found \(B/G\) ratio of HfMoTaTiZr to be greater than 1.75, thus is likely to be ductile nature. The available experiment allattice constant, Young’s modulus, and Poisson ratio are in good harmony with the prediction by the SSOS model as shown in Table 2. Vickers hardness of HfMoTaTiZr calculated using Tian’s model [21] was observed to be 5.54 GPa. This is in accord with the experiment reports of 5.32 GPa [2]. As per the author's knowledge, experimental values related to the elastic constants, shear modulus, and bulk modulus are not available. We expect future experiments to confirm our prediction. Therefore, the first-principle calculation can be used to predict the mechanical properties of high entropy alloys [1], [4], [20], [22], [23].

3.3. Thermal properties

![Figure 2](image1.png)  ![Figure 3](image2.png)

**Figure 2.** Thermal coefficient of linear expansion \((\alpha)\) of HfMoTaTiZr against the temperature

**Figure 3.** Specific heat capacity of HfMoTaTiZr as against the temperature

The mean velocity of sound and Debye temperature were estimated to be 2536 m/s and 282K, respectively for HfMoTaTiZr. Figure 2 shows the thermal coefficient of linear expansion \((\alpha)\) of HfMoTaTiZr as a function of temperature. At low temperature, (i.e. below 250 K), \(\alpha\) of HfMoTaTiZr notices a quick increase, however, it becomes constant with the rise in temperature. Moreover, Figure 3 shows specific heat capacity \((C_v)\) of HfMoTaTiZr as a function of temperature. The \(C_v\) of HfMoTaTiZr was rises linearly at low temperature (0-600 K) but becomes linear as temperature increases. This increment is caused by the lattice vibration in the solid due to increase in temperature. Such linear increment is mostly caused by the lattice vibration and at higher temperature, it reaches the Dulong Petit limit. To best of our findings, no published experimental study is available on the
thermal properties of HfMoTaTiZr. Hence this study appears as a pioneer attempt in predicting thermal properties of HfMoTaTiZr.

4. CONCLUSION

We applied the first-principle theory to study phase, mechanical and thermodynamic properties of HfMoTaTiZr. The present calculations confirm that the BCC phase exists over a various range of temperatures for HfMoTaTiZr. The calculated lattice parameters, density, Young modulus, Poissons ratio, Vickers hardness of HfMoTaTiZr are in good agreement with the available experimentally measured values. The thermal expansion of coefficient and Debye temperature of HfMoTaTiZr at room temperature was observed to be $10.31 \times 10^{-6}/K$ and 214 K, respectively. The present computational predictions could provide systematic guidance in future works related to HfMoTaTiZr based HEAs.

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