Local Lattice Distortion in High-Entropy Carbide Ceramics

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Abstract: Using the ab initio calculations, we study the lattice distortion of HfNbTaTiVC5, HfNbTaTiZrC5 and MoNbTaTiVC5 high-entropy carbide (HEC) ceramics. Results indicate that the Bader atomic radius and charge transfer in HECs is very close to those from binary carbide. The degree of lattice distortion strongly depends on the alloying element. The Bader atomic radius can excellently describe the lattice distortion in HEC. Further, the corresponding atomic radius and formation enthalpy of binary carbides may be indicators to predict the single-phase HECs.

Keywords: high-entropy carbides; lattice distortion; similar atomic environment; ab initio calculations

1. Introduction

High-entropy carbides (HECs) [1–6], as one of the high entropy materials, are being paid more attention due to their excellent properties, for instance, the high hardness, the remarkable oxidation resistance, and the adjustable range of thermal conductivity, etc. The high configuration entropy [7], as one of the key factors, is considered to induce excellent performance in high-entropy materials, including high-entropy alloys (HEAs) [8,9], high-entropy oxides (HEOs) [10], and high entropy diborides (HEBs) [11].

(Ti0.2Zr0.2Hf0.2Nb0.2Ta0.2)C powder adopts the two face-centered cubic (fcc) nested salt rock structured solid solution. It is thermodynamically more stable than its original components [1]. Using the descriptor of entropy forming ability and experimental method, Sarker et al. found the nine single phase HECs with the high hardness [12], etc. [13–17]. Herein, the cation elements are composed of refractory metals (Ti, Zr, Hf, V, Nb, Ta, Mo and W). Different from single phase equimolar quinary HEAs with $S_{\text{config}} \approx 1.61$ R, the salt-rock HEC structure has two sublattices, and the configuration entropy on the sublattice model is $\approx 0.8$ R. While in order to show the high configuration entropy of HECs, the quinary HECs have $S_{\text{config}} \approx 1.61$ R, according to the new configuration metric [18]. To study the effect of alloying elements on the properties of HECs, the (Ti0.33Zr0.33Nb0.33)C ternary carbide [19], (NbTaZr)C-based HECs [20] and (Hf0.25Ta0.25Zr0.25Ti0.25)C, (Hf0.25Ta0.25Zr0.25Nb0.25)C, (Zr0.25Ta0.25Nb0.25Ti0.25)C quaternary HECs were reported [21]. Li et al. found that in the quinary HECs, the W and/or Hf addition produces a large effect on the hardness and fracture toughness of (NbTaZr)C-based HECs [20].

As one of four core effects in HEAs, the lattice distortion is considered as a key role to enhance the performance. For HECs, these are used in the theoretical simulation to study the lattice distortion. Ye et al. found that the anion C atom severely deviates from its ideal lattice sites based on the ab initio calculations [16,22]. In this work, we propose...
the general formula to describe the local lattice distortion in HECs based on the Bader atomic radius derived from the local chemical environment. Interestingly, we find that the Bader atomic radius of MC (M = refractory metals) can be used to predict the lattice distortion and the formation of simple phases on HECs.

2. Methodology

High-entropy carbide ceramics adopt the NaCl structure, where there are two different Wyckoff position sites. Cl sites (0, 0, 0) are fully occupied by C atoms. Na positions (0.5, 0.5, 0.5) are occupied randomly by five refractory metal elements. To describe the disorder in HECs, we used the similar atomic environment (SAE) method [23,24] to construct a 3 × 3 × 5 supercell for quinary equimolar HECs based on the primary cell of the NaCl structure (a = b = c, α = β = γ = 60°) (see Figure 1). The size of the supercell was determined based on the alloying chemical composition and our available computer resources. Different from the effective medium method, the supercell method is often applied to the specific chemical composition of an alloy. The SAE method was applied to simulate the disorder and short-range order in high entropy alloys [25,26]. We took into account the number of nearest-neighboring (NN) atomic pairs up to the 7th NN distance, while the three-atom cluster is about the 3rd NN distance. The SAE supercell has 90 atoms, in which the number of C atoms is 45, and the number of atoms for each refractory metal is 9. In the support material, we list the initial and relaxed SAE structure parameter and the corresponding cartesian coordinates of atoms.

![Figure 1. The similar atomic environment supercell containing 90 atoms for HEC, enlarged by the 3 × 3 × 5 primitive rock-salt structure.](image)

To obtain the optimized structures of HECs, we employed the Vienna ab initio simulation package (VASP) to perform the electronic density of state [27]. The exchange–correlation potentials were treated by using the Perdew-Burkey-Ernzerh functional in the framework of the generalized gradient approximation [28]. The ion–electron interactions were performed by using the projector augmented wave (PAW) method [29]. The valence electron configuration of element is 3s^23p^63d^2 for Ti, 3s^23p^63d^2 for V, 4s^24p^64d^5 for Zr, 4s^24p^64d^5 for Nb, 4s^24p^64d^5 for Mo, 5p^66s^2 for Hf, and 5p^66s^2 for Ta. The Brillouin zone sampling was performed using the special k points generated by the Monkhorst–Pack scheme with a density parameter of 0.2 Å⁻¹. The plane wave energy cutoff of 400 eV provided accurate results. The tolerances of energy and maximum force were set to 1.0 × 10⁻⁵ eV and 2.0 × 10⁻² eV Å⁻¹, respectively. Constant pressure and full relaxations with Methfessel–Paxton smearing (with a width of 0.2 eV) were used. With the Bader method [30], the atomic radius and charge transfer were extracted from the ab initio electronic density of state.
3. Results and Discussion

Considering that the MC binary carbides (M is the refractory metals, except for MoC and WC) have the same crystal structure as HECs, we first compare the atomic radius and charge transfer in MC and HECs. Herein, we employed the Wigner–Seitz (WS) radius to describe the complex bonding topology of each alloying element in HECs. Figure 2 shows the Bader WS radius of MC (M = Hf, Mo, Nb, Ta, Ti, V, Zr). We can see that the atomic radius of carbon strongly depends on the bonding in MC, with a change from 1.269 to 1.433 Å. Among the MC carbides, the carbon in VC has the smallest atomic radius, while the atomic radius of carbon is the largest for ZrC. With the increase in atomic number, the atomic radius difference between carbon and the refractory metal becomes large. Taking the MC carbide as the reference ground structure, we calculated the formation enthalpy $\Delta H_1$ of HECs listed in Table 1. $\Delta H_2$ was calculated based on the energy of graphite, HCP Ti, Zr, Hf and BCC V, Nb, Ta, and Mo. Experimentally, it has been found that the enthalpy of graphite is 0.019 eV lower than the enthalpy of diamond. To obtain $E(C)$, we calculated the energy of diamond and shifted it by applying the experimental difference value. Compared to $\Delta H_2$, $\Delta H_1$ has a less negative value, which is close to the range of the single phase HEAs [31].

![Figure 2. The Bader WS radius (Å) for MC (M = Hf, Mo, Nb, Ta, Ti, V, Zr).](image)

**Table 1.** Listed are the formation enthalpy $\Delta H_1$ (in KJ/mol), average radial displacement $\Delta d$ (in Å) for individual alloy components, total radial displacement $\Delta d_{\text{tot.}}$, and atomic misfitting difference $\delta$ in the considered HECs. The available experiments are from Reference [12]. $\Delta H_1 = E_{\text{HEC}} - \sum c_i E_{\text{MC}}$, with $E_{\text{MC}}$ for the energy of binary carbides, $\Delta H_2 = E_{\text{HEC}} - \sum c_i E_{\text{i}}$, with $c_i$ for the composition and $E_{\text{i}}$ for the energy of ground state of elements (graphite for HCP, Hf, Ti, Zr, BCC for Mo, Nb, Ta, V).

| HECs       | $\Delta H_1$ | $\Delta H_2$ | $\Delta d$ | $\delta$ | Exp. |
|------------|--------------|---------------|------------|---------|------|
|            | C | Hf | Mo | Nb | Ta | Ti | V | Zr | tot. |      |
| HfNbTaTiVc | 1.330 | -- | 0.062 | 0.045 | -- | 0.065 | 0.039 | 0.050 | 0.084 | -- | 0.059 | 4.514 | 0.107 |
| HfNbTaTiZrC | -0.902 | -- | 0.062 | 0.039 | -- | 0.033 | 0.038 | 0.027 | -- | 0.037 | 0.048 | 3.884 | 0.094 |
| MoNbTaTiVc | -1.276 | -- | 0.049 | -- | 0.102 | 0.046 | 0.044 | 0.043 | 0.105 | -- | 0.060 | 4.223 | --     |

We show in Figure 3 the Bader WS radius and charge transfer of each element for HECs. From the right panel in Figure 3, we can find that the charge transfer between elements in HECs is consistent with that of per element in binary carbides. The charge transfer mainly occurs between carbons and refractory metal elements. The carbons obtain about $-1.2$ average charge from the refractory metal elements, while the refractory metal elements have the discrete values of charge transfer. It suggests that the charge transfer
on refractory metals is sensitive to the local chemical environment (different bonding lengths), but the average value of charge transfer on refractory metals in HECs is very close to that in MC. Similarly, we can see from the left panel in Figure 3 that the Bader atomic radius of carbon is a small deviation range of 0.02 Å, whereas the Bader atomic radius of refractory metals depends on the local chemical environment. The present HECs all contain Nb, Ta and Ti refractory elements, but the Bader atomic radius is about the range of 1.385–1.522 Å for Nb in HfNbTaTiVC, while the change of range region is only 0.022 Å for Nb in MoNbTaTiVC. The average Bader WS radius of each element in HECs is close to the corresponding radius in MC. From Figure 3, we can see that the change of the Bader atomic radius is consistent with the charge transfer. Further, one may use the atomic radius and charge transfer of MC binary alloys to represent the corresponding information of HECs. For example, the formula of the atomic radius difference is defined as

\[
\delta = \frac{1}{N} \sum_{i} (r_i - \bar{r})
\]

where \(N\) is the number of atoms, and \((x_i, y_i, z_i)\) and \((x'_i, y'_i, z'_i)\) are the reduced coordinates of the ideal and distorted positions of each atom for individual alloy component. The local lattice distortion of some individual alloy components depends on the alloy system, for instance, the local lattice distortion of Ti is 0.050 Å in HfNbTaTiVC, whereas 0.027 Å in MoNbTaTiVC. From Table 1 and Figure 4, we find that Hf, Ta and Zr have small local lattice distortion. While C, Mo and V have severe lattice distortion. The large change of atomic coordinate induces the severe lattice distortion of 0.059 Å for HfNbTaTiVC and
0.060 Å for MoNbTaTiVC₅. Although the local lattice distortion of carbon is up to 0.062 Å, and other alloy components have small lattice distortion, it results in small lattice distortion of HfNbTaTiZrC₅. We can find that Δd is consistent with experiments based on the peak broadening in XRD patterns [12]. The local lattice distortions of Nb, Ta, and Ti strongly depend on the nearest chemical environment (see Figure 4). For example, the Nb atoms in HfNbTaTiVC₅ have large lattice distortion with respect to those in MoNbTaTiVC₅ and HfNbTaTiZrC₅. Note that the severely local lattice distortion of V and Mo does not only occur in the first nearest neighboring shell but also in other nearest neighboring shells.

![Figure 4](image_url)

Figure 4. The number of atomic pairs as a function of the radial distribution distance for the present HEC with lattice distortion. The black vertical dot lines stand for the ideal lattice position of different nearest neighboring atomic pairs.

Table 2 lists the lattice parameters of the present HECs with and without lattice distortion. Interestingly, the lattice parameter is not sensitive to the local lattice distortion. The calculated lattice parameters are consistent with the available experiments (the difference is within 0.8%). However, our calculation was performed at 0 K. Considering the temperature effect on the lattice thermal expansion, our results are larger than experiments. One possible reason is our exchange-correlation potential of PBE. It often overestimates the lattice parameter of a material. Another possible reason is the carbon vacancy that existed in the present HECs. The vacancy results in a decrease in the lattice parameter in the experiment, whereas our calculations are based on the ideal carbon composition.
Table 2. The converted lattice parameter $L$ of the equilibrium state (Å), the available experiments, lattice parameters ($a$, $b$, $c$ and $\alpha$, $\beta$, $\gamma$) of the SAE supercell for the high entropy carbides (HECs) with/without distortion.

| HECs              | $L$  | Exp. | LLD | Ideal |
|-------------------|------|------|-----|-------|
| HfNbTaTiVCs       | 4.432| 4.415| 9.403| 4.415 | 15.677  |
|                  |      |      | 9.402| 59.966| 60.012  |
|                  |      |      | 9.420| 9.420 | 15.700  |
| HfNbTaTiZrCs      | 4.519| 4.500| 9.589| 9.591 | 15.973  |
|                  |      |      | 9.585| 9.585 | 15.975  |
| MoNbTaTiVCs       | 4.375| --   | 9.282| 9.278 | 15.461  |
|                  |      |      | 9.285| 9.285 | 15.475  |

4. Conclusions

In summary, we have employed the ab initio calculation based on density functional theory in combination with the similar atomic environment to study the local lattice distortion of the HfNbTaTiVCs, HfNbTaTiZrCs, and MoNbTaTiVCs high-entropy carbide ceramics. The binary carbide has a similar Bader radius and charge transfer between C and refractory metals to the present HECs. Based on the physical parameter of the binary carbides, the formation enthalpy and classical atomic radius difference can be used to predict the single-phase formation and lattice distortion. HfNbTaTiZrCs has a larger local lattice distortion than HfNbTaTiVCs and MoNbTaTiVCs. The alloying element V and Mo show the large local lattice distortion in their first nearest neighboring shell and other neighboring shells.

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