Enhanced Hardness in High-Entropy Carbides through Atomic Randomness

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High-entropy carbides (HECs) are of great interest as they are promising candidates for ultra-high-temperature and high-hardness applications. To discover carbides with enhanced yield strength and hardness, mechanism-based design approaches are needed. In this study, dislocation core atomic randomness as a mechanism for hardness enhancement is proposed, in which the random interactions between different elements at a dislocation core make it more difficult for the dislocation to slip. The Peierls stress of an $a/2\langle 1\bar{1}0\rangle\{110\}$ edge dislocation is calculated based on density functional theory, in which atomic randomness is increased by increasing the number of elements at the dislocation core. The results show that the Peierls stress statistically increases with increasing number of elements, indicating that incorporating more elements is likely to produce higher hardness. Based on this guiding principle, three eight-cation HECs are fabricated $(\text{Ti},\text{Zr},\text{Hf},\text{V},\text{Nb},\text{Ta},\text{X},\text{Y})\text{C} (\text{X,Y} = \text{Mo},\text{W},\text{Cr},\text{Mo},\text{or}\text{Cr},\text{W})$, the composition of which is guided by ab initio calculations of their formation enthalpy and entropy forming ability. The single-phase dense ceramics all show high nanoindentation hardness of around 40 GPa. The random interactions between different elements at a dislocation core provide a mechanism for improving the hardness of structural ceramics.

1. Introduction

High-entropy carbides (HECs) are ultra-high-temperature (melting temperature $>3000$ °C) ceramics, which also display high hardness, elastic modulus, and resistance to thermal shock and chemical attack. They are promising candidates for technologies such as nuclear reactors, jet engines, hypersonic vehicles, and cutting tools. HECs contain no less than four types of transition metal cations in a rock salt structure. Generally, the cations are equimolar to maximize their configurational entropy. HECs were successfully fabricated in the form of coatings some years ago, but have only recently been reported in bulk form. Due to the emerging fundamental interest and potential applications, several compositions have been fabricated and properties such as hardness and oxidation behavior have been investigated. These compositions mainly contain refractory transition metal elements, and there is a vast potential compositional space still to explore, where compositions with advantageous properties are likely to exist.

There have been several attempts to search in high-dimensional multi-element chemical space for thermodynamically stable HECs. Generally, they used density function theory (DFT) calculations. Sarker et al. proposed “entropy forming ability” as a descriptor to predict single-phase HECs and they successfully fabricated six single-phase, five-cation HECs based on their predictions. In some other works, formation enthalpy and local lattice distortion were calculated. In addition to these successful stability predictions, we further propose that “mechanism-based design approaches” can also be utilized to identify new HECs. This approach has been adopted in the high-entropy alloy (HEA) community. For example, stacking fault energy can serve as a reliable parameter for HEA design, as it is the key thermodynamic quantity for tuning twinning or martensite formation. Maresca and Curtin screened over 600 000 high-entropy compositions in the Mo-Nb-Ta-V-W family to identify high retained strength alloys using an edge dislocation motion theory. In the current work, the Peierls stress was used as a hardness indicator for the design of HECs.

The Peierls stress measures the difficulty of moving a dislocation at zero Kelvin. For decades, the relationship between Peierls stress and solid solution strengthening has been well studied using phenomenological models. However, in HECs there are no solute or solvent atoms as all of the cations are equimolar. Mean field theory utilizing the solid solution strengthening concept has...
Figure 1. a) DFT model of $a/2(\mathbf{110})\{110\}$ type edge dislocation in four-cation high-entropy carbides. The carbon atoms (small red spheres) are on top of the big cations as the model has two atomic layers in the [001] direction. The quadrupolar configuration was used to eliminate the strain and stress fields of the surrounding dislocations due to the periodic conditions. Therefore, there are two equivalent dislocation cores. An increasing shear stress was applied and the Peierls stress was determined when the dislocations moved. The figure was created using VESTA. b) Peierls stress of mono-, binary, and high-entropy carbides with different core configurations. The yellow atoms in the inset figure correspond to the dislocation core atoms in (a), and the numbers indicate the order of the atoms in each dislocation core configuration in the main figure. In the inset, the arrows indicate the direction of the applied shear stress, $\perp$ and $\parallel$ denote the dislocation cores. c) The probability distribution function of the Peierls stress with different degrees of randomness. The curves were calculated using the stochastic Peierls–Nabarro model.

had some success in predicting yield strength and activation volume in HEAs, and other work highlights the importance of element interaction and interplanar potential randomness. Atomic scale DFT modeling is a powerful tool to quantify these effects and provides atomic scale details. It was used to calculate the Peierls stress of TiN and the calculated results agree with experiments. Recently the distribution of dislocation core energies and Peierls potentials in MoNbTaW HEAs were systematically investigated using DFT, and a marked effect of short-range order in elevating the Peierls potential of a screw dislocation was revealed. These results show the effectiveness and usefulness of DFT dislocation modeling, and the same approach is used in the current work, in which the Peierls stress of an edge dislocation in HECs was calculated and the influence of dislocation core structure was investigated.

2. Results

2.1. Dislocation Core Randomness and Peierls Stress

There are considered to be two main types of slip systems in rock-salt-structured transition metal carbides: for the group IV transition metal carbides it is $\langle 1\bar{1}0 \rangle \{110\}$ type with six possible slip systems, and for the group V transition metal carbides it is $\langle 110 \rangle \{111\}$ type with 12 slip systems due to an intrinsic stacking fault on the $\{111\}$ planes. For binary (Hf,Ta)C, the slip system is $\langle 1\bar{1}0 \rangle \{111\}$ even with small amounts of Ta (<15 at% of Ta on cation site), due to the promotion of intrinsic stacking faults. For (Zr,Hf,Nb,Ta)C, the operation of $\langle 1\bar{1}0 \rangle \{110\}$ was identified in micropillar experiments. In this work, only a $a/2(\mathbf{110})\{110\}$ type edge dislocation is considered to investigate the effect of atomic structure at the dislocation core on the Peierls stress. Figure 1a shows the 2D $a/2(\mathbf{110})\{110\}$ edge dislocation model used for the DFT calculations. The length of the supercell in the Burgers vector $\mathbf{b}$ direction is $(2n + 1)|\mathbf{b}|$, and $n = 9$ was chosen (Figure 1a), which means that the distance between two dislocations is 3 nm in a 456 atoms supercell. The model in Figure 1a has been widely used for dislocation modeling in metals and ceramics. For dislocation modeling of high-entropy materials, one issue is that the vast number of compositional permutations makes direct snapshot sampling intangible. To simplify the sampling, only the four atoms at the center of the dislocation core are considered, as highlighted by the red circles in Figure 1a. This is reasonable as the Peierls stress is mainly determined by the configuration of these atoms according to our DFT calculations. Figure S1, Supporting Information, shows the Peierls stress of six different supercells that have the same dislocation core configuration but with all of the other atoms randomly arranged. The variation of the Peierls stress values is very small compared with the supercells with different core configurations (Figure 1b). Therefore, only the...
dislocation core configurations are considered in the remainder of the paper.

Figure 1b shows the Peierls stress of DFT supercells with different dislocation core configurations. The Peierls stress is a range rather than a single value due to the incremental searching method used (see the Experimental Section for details). There are 16 and 256 possible dislocation core configurations for binary (Hf,Ta)C and high-entropy (Zr,Hf,Nb,Ta)C, respectively. The atomic arrangement of some configurations is listed below the Peierls stress bars according to the numbering method shown in the inset. We could not calculate all of the possible 256 configurations for (Zr,Hf,Nb,Ta)C due to computational resource limitations. Therefore, only dislocation cores with four types of elements, i.e., Zr,Hf,Nb,Ta, were calculated. Therefore, there are 4! = 24 configurations, which form a subgroup of the total 256 and can be considered as the “most random.” The monocarbides are also shown for reference. It should be commented on that the results for the binary system with dislocation core containing only one type of element are slightly different to the results for the corresponding monocarbides. This is another indication of the magnitude of the effect of the next nearest atoms to the dislocation core.

In Figure 1b, the foremost trend is how the distribution of Peierls stress changes from monocarbide to binary carbides to HECs. This can be better understood by comparing with the Peierls stress distributions calculated using the stochastic Peierls–Nabarro model in Figure 1c. This model introduces randomness into the χ-surface (in our DFT model this is the ⟨110⟩ plane) by using a normal distribution with different standard deviations, which corresponds to the perturbation in the interplanar potential. The results show that the standard deviation of the Peierls stress increases with increasing randomness. This means that the mean distance a dislocation moves under a certain stress decreases with increasing randomness, as more randomness means that the maximum local Peierls stress within a certain distance becomes larger, and a dislocation glides until the local Peierls stress is too large to overcome. All of this indicates that randomness has a significant effect on the yield behavior of the HECs.

The distribution of the DFT calculated Peierls stress in Figure 1b agrees with the stochastic Peierls–Nabarro model results in Figure 1c, while the DFT modeling provides more details at the atomic scale. In Figure 1b, the range of Peierls stress of (Hf,Ta)C is 5.2–8.5 GPa, which means that the randomness in binary carbides introduces a variation of the Peierls stress of ≈3 GPa. The maximum Peierls stress further increases from 8.5 GPa for the binary carbide to 9.0 GPa for the HEC. It is worth noting that the 16 dislocation core configurations with two types of elements (blue bars) form a subgroup of the 256 possible core configurations in (Zr,Hf,Nb,Ta)C, if only the four atoms at the cores are considered. Bear in mind that the dislocation cores with four types of elements (green bars) are the “most random” subgroup of the total 256 possible configurations, corresponding to a relatively high Peierls stress. This means that the range and standard deviation of the Peierls stress distributions increases from binary to HEC, with increasing randomness. The tendency of DFT simulated Peierls stresses agrees with the stochastic Peierls–Nabarro results in Figure 1c. It is also in agreement with the tendency of the yield stress values measured for TaC, HfC, and (Ta,Hf,Zr,Nb)C, for which the same slip system ⟨110⟩{110} was activated in all the three cases during micropillar compression.[23]

Based on the above results and analysis, it is reasonable to anticipate that incorporating more elements will introduce more randomness and hence it will become harder to move a dislocation. This can be understood from the viewpoints of both the bonding interactions at the dislocation core and the height of the energy barriers in the dislocation path. In the bonding picture, the dislocation movement relates to the repositioning of the atoms and hence a change of bond length and orientation, specifically of the cation–carbon bonds in the carbides. When more types of atoms are involved in this process, there is the possibility that some configurations at the dislocation core will be energetically more favorable and therefore harder to disrupt, resulting in a higher Peierls stress. In other words, a dislocation core configuration with more types of atoms is more likely to have cation–carbon bonds with different bond length/orientation and element interactions. This makes the breaking/reforming of the bonds more difficult, or equivalently in terms of the energy picture, gives rise to a higher energy barrier to dislocation movement. However, we are unable to effectively model dislocations with more elements due to the combinatorial explosion problem. Alternatively, we experimentally fabricated HECs with more types of cations to test our ideas.

In addition, it is worth noting that one advantage of DFT modeling is that detailed information at the atomic scale can be obtained. The atomic scale configuration at the dislocation core includes elemental composition and geometry features. Take the binary (Hf,Ta)C as an example as all of the possible dislocation core configurations are considered. The Peierls stress shows some dependence on composition, as cores with equimolar Hf and Ta statistically tend to have higher Peierls stress than other configurations, as can be clearly seen in Table S1, Supporting Information. This also agrees with the experimental findings that the Hf0.5Ta0.5C solid solution has the highest hardness of all Hf/Ta ratios.[24] The dependence of the Peierls stress on the geometry features, i.e., average bond length and lattice distortion, is shown in Figure S2, Supporting Information. There is no clear trend for the Peierls stress on both features. This indicates that geometry features might not be good descriptors for Peierls stress as the mechanism for dislocation movement is complex.

2.2. Design and Synthesis of Eight-Cation HECs

Figure 2a shows the formation enthalpy and entropy formation ability (EFA) of the 190 possible compositions of eight-cation HECs. We fixed the six elements (blue elements in Figure 2b inset) in order to reduce the vast high-dimensional compositional space. The other two elements out of the eight were chosen from the transition metals (20 yellow elements in Figure 2b inset), which reduces the number of possible compositions to 20!/18!2! = 190. For each composition, 21 different 16-atom supercells (see Experimental Section) were used to calculate the formation enthalpy and EFA. The upper-left part in Figure 2a shows the formation enthalpy. Most of the compositions have a negative formation enthalpy, and generally the compositions containing Sc or Y have the lowest formation enthalpy. Compositions
containing Ag, Au, or Pt tend to have relatively high positive formation enthalpy, indicating that these elements are inactive. The lower-right part shows the EFA. Only a few compositions have high EFA as indicated by the red color, and generally these compositions contain Mo and W. The compositions with the highest EFA also contain Rh, Ir, Pd, or Pt. One possible reason for this is that these elements are inactive and do not have preferred neighbor cations, and hence different atomic arrangement in different supercells tend to give similar energies, which results in a small standard deviation and high EFA.

To identify compositions for experimental fabrication, the EFA values were plotted against enthalpy of formation in Figure 2b. The line is estimated according to the experimental results for previously reported five-cation HECs (details in Figure S3, Supporting Information), and it can be understood from the view point of the Gibbs free energy, i.e., low enthalpy and high entropy favor stability. First, nine compositions were selected containing at least one element of Mo and W (green dots), which have the highest EFA or lowest enthalpy. In these compositions, Sc reduces enthalpy and Rh/Ir/Pd/Pt increase EFA, following the same trend shown in Figure 2a. However, when considering the feasibility of synthesis, currently only the composition with Mo-W is possible, as for the monocarbide precursors for the other compositions are currently unavailable. We additionally chose two other compositions with Cr-Mo and Cr-W (shown in red) because they are just below the blue line and the monocarbide precursors are available. Therefore, three compositions were selected for further experimental synthesis, and hereafter they are referred to as HEC8-MoW, HEC8-CrMo, and HEC8-CrW.

It is worth noting that there will be carbon nonstoichiometry as the starting powder of Cr3C2 and Mo2C introduces carbon vacancies.

Figure 2c shows X-ray diffraction (XRD) patterns of the three eight-cation HECs. All of the three compositions show a single-phase rock-salt structure without other phases. Figure 2d shows scanning electron microscopy (SEM) images and the corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping results for HEC8-MoW (see Figure S4, Supporting Information, for HEC8-CrMo/CrW), in which all of the elements are distributed uniformly at the micro level. Table S2, Supporting Information, displays the EDS compositional results, and the content of all of the metal elements are similar (11–14 At%) except for Cr (only 6 At%). As the Cr atoms distribute homogenously without any segregation or aggregation (Figure S4, Supporting Information), this may due to the
loss of Cr$_3$C$_2$ during the spark plasma sintering (SPS) process when the sintering temperature was higher than the melting temperature of Cr$_3$C$_2$ (1895 °C). All of the samples have high relative density (> 97%) and large grain size 20–40 μm, which made it easier to perform the nanoindentation test as it was less likely that indentation would be near pores or on the grain boundaries.

### 2.3. Hardness of Eight-Cation HECs

Table 1 shows the hardness and other related properties of the three HEC8 compositions. The high-entropy (Zr,Hf,Nb,Ta)C$_{\text{C}}$, binary, and monocarbides are also shown for comparison. All of the carbides were fabricated using the same SPS sintering route used in previous work involving the same authors or in the present work.[4,23,26,27] The mechanical testing was performed under identical nanoindentation testing conditions, and average hardness and Young’s modulus were taken from the region of penetrations of 100–300 nm. The SEM images of the indents in HEC8-MoW (Figure S6, Supporting Information), as a typical example, show that the majority of the indents did not exhibit cracking, and the shape of the indents have a regular triangular shape, which suggests that no pile-up occurred around them and hence the measured nanoindentation data were correctly evaluated by the Oliver–Pharr method.[28] The eight-cation HECs exhibit an enhanced hardness compared to the other carbides (Table 1). A significant enhancement in hardness of ≈25% is found by comparing the measured indentation hardness values with the rule of mixtures (ROM) values from the measured (DFT calculated for CrC and MoC) values of the component monocarbides with rock salt structure. The hardness values do not show a dependence on the average valence electrons concentration (VEC) and lattice distortion (the difference between the lattice parameter from XRD and the ROM of lattice parameters of monocarbides), indicating that these descriptors may be over simplified and uninformative. Alternatively, dislocation core randomness may play some role in the hardness behavior, as found from the DFT modeling results. It is reasonable to suggest that the incorporation of a number of different metallic elements into a single-phase solid solution causes local nonuniformities in the lattice structure that further impede the motion of dislocations.

### 2.4. Discussions on Randomness and Hardness

In this paper, we propose dislocation core randomness as a mechanism for hardness enhancement, and it is useful to add some comments on the relationship between dislocation core randomness and solid solution strengthening. These two share the same concept that local nonuniformities impede the motion of dislocations, while the former is more complex, as the equimolar composition of HECs means that a vast number of dislocation core configurations must be considered in a combinatorial or statistical way. In that sense, solid solution strengthening, where the solute is a minority component and is well defined, can be regarded as a simpler case of dislocation core randomness strengthening. The mechanism of dislocation core randomness also agrees with the mathematical stochastic Peierls–Nabarro model, in which randomness gives rise to an increase in the interplanar potential. Here, by using DFT calculations, which provide atomic scale information of the dislocation, we show that the randomness originates from different dislocation core configurations.

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Table 1. Hardness ($H$, VEC, lattice constants, and indentation modulus of HECs. DFT calculated values are presented for the carbides in italic. The theoretical hardness values of rock-salt CrC$^{[40]}$ and MoC$^{[41]}$ and experimental hardness value of rock-salt WC$^{[42,43]}$ are taken from the literature. The distortion was calculated using the percentage difference between the experimental value of the solid solution and the average lattice constants of the components. The experimental lattice constants were determined using XRD refinement (Figure S5, Supporting Information).

| Sample          | $H$ [GPa] | $H_{\text{ROM}}$ [GPa] | VEC | Lattice constant [Å] | Distortion | Indentation modulus [GPa] |
|-----------------|-----------|------------------------|-----|----------------------|------------|--------------------------|
| HEC8-MoW        | 39.5 ± 1.2| 29.8                   | 8.875| 4.436                | 1.77%      | 569                      |
| HEC8-CrMo       | 41.2 ± 1.0| 30.4                   | 8.875| 4.446                | 2.01%      | 570                      |
| HEC8-CrW        | 40.9 ± 1.3| 31.2                   | 8.875| 4.440                | 2.69%      | 579                      |
| (Zr,Hf,Nb,Ta)C   | 36.1 ± 1.6| 29.0                   | 8.5 | 4.553                | 3.79%      | 598                      |
| (Hf,Ta)C$^{*}$  | 32.9 ± 1.8| 26.10                  | 8.5 | 4.536                | 3.05%      | 559                      |
| TiC             | 39.8 ± 1.3| –                      | 8   | 4.336$^{\text{DFT}}$| –          | 577                      |
| ZrC             | 34.7 ± 1.3| –                      | 8   | 4.725$^{\text{DFT}}$| –          | 530                      |
| HfC$^{*}$       | 31.5 ± 1.3| –                      | 8   | 4.651$^{\text{DFT}}$| –          | 552                      |
| VC              | 34.4 ± 1.6| –                      | 9   | 4.162$^{\text{DFT}}$| –          | 538                      |
| NbC             | 29.5 ± 1.0| –                      | 9   | 4.506$^{\text{DFT}}$| –          | 563                      |
| TaC$^{*}$       | 20.6 ± 1.2| –                      | 9   | 4.482$^{\text{DFT}}$| –          | 579                      |
| CrC             | 31.7$^{[40]}$| –                     | 10  | 4.708$^{\text{DFT}}$| –          | –                        |
| MoC             | 21.2$^{[41]}$| –                     | 10  | 4.383$^{\text{DFT}}$| –          | –                        |
| WC              | 27$^{[42,43]}$| –                     | 10  | 4.385$^{\text{DFT}}$| –          | –                        |

$^{*}$These carbides were reported in ref.[4] previously.
The strengthening mechanism can be either intrinsic or extrinsic.[29] The intrinsic mechanism is related to the bond strength in the ideal lattice, and the extrinsic mechanism is related to the interaction of dislocations with lattice imperfections such as solute or grain boundaries. The “dislocation core randomness” mechanism proposed in this paper is an extrinsic strengthening mechanism, where dislocations interact with many different randomly distributed atoms. It is worth noting that, due to the core randomness, the dislocation cores are different from each other, i.e., have different elemental compositions and atomic configurations.

The guiding principle of “randomness increases hardness” should be understood in a statistical way. In other words, the hardness of compositions with more elements is statistically higher than that with less elements, according to the DFT modeling results. This does not mean that the hardness of every composition must be higher than its constituents. Hardness is determined by many factors including different slip systems and cross slip. The dislocation core randomness might not be a deterministic factor, but is a contributing mechanism, which is supported by the DFT modeling of the Peierls stress.

3. Conclusion

In summary, by DFT modeling of a a/2(110){110} type edge dislocation in HECs, we show that incorporating more elements into a dislocation core statistically increases the Peierls stress, which can be attributed to “dislocation core randomness.” Based on this guiding principle that more elements may be beneficial for higher hardness, eight-cation HECs were designed based on both the enthalpy and entropy descriptors using DFT calculated data. Three HECs (Ti,Zr,Hf,V,Nb,Ta,X,Y)C (X,Y = Mo,W or Cr,Mo or Cr,W) were successfully fabricated as dense single-phase ceramics with homogenously distributed atoms. All three HECs show high nanoindentation hardness of around 40 GPa, higher than any of their constituents. This work shows that mechanism-based design together with stability prediction utilizing DFT modeling could accelerate the design of high-entropy materials with enhanced properties for a wide range of different technological applications.

4. Experimental Section

Dislocation Modeling: The quadrupolar configuration was adopted following previous studies.[19,33] In this configuration, the dislocation core was not affected by the extra strain and stress fields of the surrounding dislocations. The special quasi-random structures model implemented in the Alloy Theoretic Automated Toolkit (ATAT)[35] was used to generate the supercell. In some supercells, the types of atoms at the dislocation core were modified manually to obtain desired atomic configurations. Then both the lattice parameters and atomic positions were relaxed. Shear stress was introduced manually by changing the x component of the b lattice vector with a value ∆x, and then the atomic positions of the supercell with modified b lattice vector were relaxed. With increasing ∆x, the shear stress increased, and when the shear stress became larger than the Peierls stress, the dislocation moved in the atomic relaxation procedure. Hence, the range of the Peierls stress could be determined. Instead of the incremental method used in the previous work,[14] in this work a half-interval search algorithm was used and searching stopped when the range of the Peierls stress was less than 0.5 GPa. The correction due to the periodic image interactions was not applied as the trend rather than the exact values of the Peierls stress was important in this work.

Entropy and Enthalpy Calculations: There were 20!182! = 190 possible compositions for eight-cation HECs [Ti,Zr,Hf,V,Nb,Ta,X,Y]C (X,Y = Mo,W or Cr,Mo or Cr,W). The chosen elements were the common transition metals from Groups III–VI in the periodic table (yellow elements in Figure 2b inset). Every composition contained Ti, Zr, Hf, V, Nb, Ta, and two other elements from the rest of the chosen transition metals. A 2 × 2 × 2 supercell of the rock-salt unit cell was used to calculate the EFA and formation enthalpy of all of the compositions. The supercell had eight carbon atoms and eight cation atoms, i.e., one atom for each type of cation element. This gave 210 different configurations (i.e., distinct arrangement of atoms considering symmetry), which were generated using the SUPERCCELL program. 10% of the 210 configurations (i.e., 21 configurations) was randomly chosen to calculate the EFA. The EFA is defined as the inverse of the standard deviation of the energy distribution spectrum of all the configurations at zero temperature:

\[
\text{EFA} = \frac{\langle \sigma(\text{spectrum}(H(N))) \rangle - \sigma^{-1}}{\sigma}
\]

where the sum runs over all of the geometrical configurations and \( g_i \) are their degeneracies. \( H_{\text{mix}} \) is the average formation enthalpy of all the sampled configurations:

\[
H_{\text{mix}} = \sum_{i=1}^{N} g_i H_i
\]

The stability prediction was based on the values of EFA and \( H_{\text{mix}} \).

DFT Calculations: The DFT calculations for geometry optimization were performed using the Quantum-ESPRESSO package.[37] The Garrity–Bennett–Rabe–Vanderbilt high-throughput pseudopotential library was used.[38] The Perdew–Burke–Ernzerhof functional was used along with ultrasoft pseudopotentials for all of the atoms. For EFA calculations, both the lattice parameters and atomic positions were relaxed using a 5 × 5 × 5 k-mesh.

Sample Synthesis: HfC, TaC, Mo2C, and VC powders from ABCR, ZrC, TiC, and NBC powders from American Elements, and WC and Cr2C powders from Alfa Aesar were chosen to synthesize the HECs because of their high purity and small particle size. The purity of all of the starting powders was higher than 99%, and the average particle size was lower than 45 μm except for the ZrC powder, which had a particle size of <150 μm. The powders were weighed in equimolar proportions, and mixed by ball milling at 150 rpm for 24 h (5 min milling, 5 min pause) in WC pots with WC milling balls (ball-to-powder ratio is 10:1). A small amount of stearic acid was used as a process control agent. All of the handling and ball milling performed in an argon atmosphere. After ball milling, 9 g of each powder mixture was loaded into a 20 mm diameter graphite die, and then sintered using SPS (FCT HPD 25, FCT System GmbH, Rauenstein, Germany). The samples were produced following a sintering and pressure profile that was optimized in previous work[4] on the (Hf,Ta)C and (Zr,Hf,Nb,Ta)C single phase systems, which employed a two-step heating profile at 1800 and 2300 °C. The dwell time at 2300 °C had to be adjusted to 10 min to obtain a desirable large grain size (≈10–50 μm) for the micromechanical testing. During sintering, heating, and cooling, rates of 25–100 °C min⁻¹ were employed. In order to minimize the degradation of the graphite dies at high temperature, a continuous stream of Ar was introduced into the furnace chamber (with the vacuum pump running) to maintain a pressure of around 1200 Pa throughout all of the processing. In order to check whether there was WC contamination during the ball
milling, the surface of the balls was observed by optical microscopy, and they were found to still be smooth and glossy after milling. The EDS results in Table S2 in the Supporting Information also indicate that there was no significant WC contamination.

**Structure Characterization:** The crystal structure was characterized using XRD (PanalyticalX’Pert Pro diffractometer, Cu-kα source, The Netherlands). The sintered samples were investigated using SEM (FEI Inspect-F field emission gun scanning electron microscope, FEG-SEM, USA) and EDS. The density of the samples was measured using the Archimedes method in water.

**Mechanical Properties Measurement:** The mechanical properties of the prepared monocarbide samples and optimized high-entropy samples were measured using an Agilent/Keysight G200 Nanoindenter equipped with a diamond Berkovich tip. Indents were arranged in arrays of 8 × 8 (i.e., 64 indentations per sample) using a continuous stiffness measuring mode with a maximum penetration depth of 300 nm and a distance between the indents of 10 μm. The indents were positioned sufficiently far from each other to neglect the influence of the residual stress field of adjacent indents and to incorporate measurements across several grains of different orientation. To minimize inconsistencies in measurements due to the interaction of the residual stress field of the indents with grain boundaries, pores, etc., grains were chosen that were far larger (≥10–50 μm) than the size of the indents (≥2 μm). After testing, indentations were analyzed using SEM (Zeiss – Auriga) to filter out those that were located at grain boundaries or close to any inclusions (e.g., pores) and to study their morphology. The arrangement of the Berkovich indents is illustrated as an example for HEC8-MoW in Figure S5, Supporting Information; similar characteristics were observed for all of the carbide samples.

**Supporting Information**
Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**
The authors declare no conflict of interest.

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DFT calculations, dislocation modeling, hardness, high-entropy carbides

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