High-entropy high-hardness metal carbides discovered by entropy descriptors

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High-entropy materials have attracted considerable interest due to the combination of useful properties and promising applications. Predicting their formation remains the major hindrance to the discovery of new systems. Here we propose a descriptor — entropy forming ability — for addressing synthesizability from first principles. The formalism, based on the energy distribution spectrum of randomized calculations, captures the accessibility of equally-sampled states near the ground state and quantifies configurational disorder capable of stabilizing high-entropy homogeneous phases. The methodology is applied to disordered refractory 5-metal carbides — promising candidates for high-hardness applications. The descriptor correctly predicts the ease with which compositions can be experimentally synthesized as rock-salt high-entropy homogeneous phases, validating the ansatz, and in some cases, going beyond intuition. Several of these materials exhibit hardness up to 50% higher than rule of mixtures estimations. The entropy descriptor method has the potential to accelerate the search for high-entropy systems by rationally combining first principles with experimental synthesis and characterization.

INTRODUCTION

High-entropy materials having a highly disordered homogeneous crystalline single-phase (potentially stabilized entirely by entropic contributions) continue to attract a great deal of research interest [1–3]. Remarkable properties have been reported: high strength (yield stress > 1GPa) combined with ductility [4–11], hardness [5, 12, 13], superconductivity [14], colossal dielectric constant [15], and superionic conductivity [16]. Entropy is thought to play a key-stabilizing role in high-entropy alloys [1], entropy-stabilized oxides [17, 18], high-entropy borides [19] and high-entropy carbides [20–23]. The latter three classes consist of disordered metal cation sublattices with several species at equi-concentration combined with oxide [15, 17, 18, 24], boride [19] or carbide [20–23] anion sublattices. These systems offer the potential to combine excellent thermo-mechanical properties and resilient thermodynamic stability given by entropy stabilization with the higher oxidation resistance of ceramics [25]. The resistance of disordered carbides to extreme heat [26–28], oxidation [23] and wear makes them promising ultra-high-temperature ceramics for thermal protection coatings in aerospace applications [29], and as high-hardness, relatively low density high-performance drill bits and cutting tools in mining and industry.

Super-hard transition metal carbides have been known since the 1930s to exhibit significant levels of solid solution [26, 30, 31], and to display high melting temperatures [26, 27]. Ta4Hf1−xCr displays a homogeneous solid solution across all composition ranges [28, 32, 33], with Ta4HfCr5 exhibiting one of the highest experimentally reported melting points (Tm ≈ 4263K [26, 27]). In this case, the two refractory metals randomly populate one of the two rock-salt sublattices [28]. More recent measurements indicate that the maximum melting point of 4232K occurs without Ta at the composition HfC0.98 [34]. Investigation of new carbide compositions will help elucidate the high temperature behavior of these materials, and will provide an avenue to settle the discrepancies in the experimental literature. To discover materials with even more advantageous properties, including increased thermal stability, enhanced strength and hardness, and improved oxidation resistance [23], more species and configurations have to be considered. Unfortunately, the lack of a rational, effective and rapid method to find and characterize the disordered crystalline phase makes it impossible to pinpoint the right combination of species/compositions and the discovery continues by slow and relatively expensive trial and error.

Computationally, the hindrance in in-silico disordered materials development can be attributed to entropy — a very difficult quantity to parameterize when searching through the immense space of candidates (even with efficient computational methods, e.g. Monte Carlo and ab-initio lattice energies in the Wang-Landau [35] or nested sampling [36] formalisms). CALPHAD has also been applied successfully [2, 13, 37–39], although it is dependent on the availability of sufficient experimental data. This is the perfect challenge for ab-initio high-throughput computing [40] as long as reasonable entropy descriptors — the set of parameters capturing the underlying mechanism of a materials property — can be found.

In this article, we undertake the challenge by formulating an entropy-forming-ability descriptor (EFA). It captures the relative propensity of a material to form a high-
entropy single-phase crystal by measuring the energy distribution (spectrum) of configurationally-randomized calculations up to a given unit-cell size. A narrow spectrum implies a low energy cost for accessing metastable configurations, hence promoting randomness (i.e., entropy) into the system (high-EFA) at finite temperature. In contrast, a wide spectrum suggests a composition with a high energy barrier for introducing different configurations (low-EFA), and thus with a strong preference for ordered phases. The method is benchmarked by the matrix of possible carbides. Given a set of 8 refractory metals (Hf, Nb, Mo, Ta, Ti, V, W, Zr) plus carbon, the formalism predicts the matrix of synthesizable 5-metal high-entropy carbides. Candidates are then experimentally prepared, leading to a novel class of systems. In particular, it is demonstrated that the descriptor is capable of reliably distinguishing between the compositions that easily form homogeneous single phases and the ones that do not, including identifying compositions that form single phases despite incorporating multiple binary carbide precursors with different structures and stoichiometric ratios. Note that because of the differing stoichiometries of the non-rock-salt phase binary carbide precursors Mo2C and W2C, the compositions listed in this work are nominal. There are extensive carbon vacancies in the anion sublattice in the synthesized materials, further contributing to the configurational entropy. Several of these materials display enhanced mechanical properties, e.g., Vickers hardness up to 50% higher than predicted by a rule of mixtures. Thus, this class of materials has strong potential for industrial uses where dense and wear resistant impactors are needed, particularly for extreme temperature applications. The successful outcome demonstrates the strength of the synergy between thermodynamics, high-throughput computation, and experimental synthesis.

RESULTS

EFA formalism. To accelerate the search in the chemical space, the entropy content of a compound is estimated from the energy distribution spectrum of metastable configurations above the zero-temperature ground-state. At finite T, any disordered state can be present with a probability given by the Boltzmann distribution and the state’s degeneracy. Note that configurations are randomly sampled up to a given unit-cell size: the larger the size, the more accurately the spectrum represents the real thermodynamic density of states.

The energy distribution (\( H_i \)) spectrum can be quantitatively characterized by its standard deviation \( \sigma \), so that the \( \sigma \) becomes the descriptor for \( S \): the smaller \( \sigma \), the larger \( S \). The descriptor for an \( N \)-species system, called the entropy forming ability (EFA), is defined as the inverse of the \( \sigma \) of the energy spectrum above the ground-state of the \( N \)-system at zero temperature:

\[
EFA(N) \equiv \{ \sigma \left[ \text{spectrum}(H_i(N)) \right]_{T=0} \}^{-1},
\]

where

\[
\sigma \left[ H_i(N) \right] = \sqrt{\frac{\sum_{i=1}^{n} g_i (H_i - H_{\text{mix}})^2}{\left( \sum_{i=1}^{n} g_i \right) - 1}},
\]

where \( n \) is the total number of sampled geometrical configurations and \( g_i \) are their degeneracies. \( H_{\text{mix}} \) is the mixed-phase enthalpy approximated by averaging the enthalpies \( H_i \) of the sampled configurations:

\[
H_{\text{mix}} = \frac{\sum_{i=1}^{n} g_i H_i}{\sum_{i=1}^{n} g_i}.
\]

The broader the spectrum, the more energetically expensive it will be to introduce configurational disorder into the system, and thus the lower the EFA. EFA is measured in (eV/atom)\(^{-1}\).

EFA calculation. A total of 56 5-metal compositions can be generated using the 8 refractory metals (8!/5!/3! = 56) of interest (Hf, Nb, Mo, Ta, Ti, V, W, Zr). For each composition, the Hermite normal form superlattices of the AFLow partial occupation (AFLOW-POCC) method \([41]\) generate 49 distinct 10-atom-cell configurations, resulting in a total of 2744 configurations needed to determine the EFA of this composition space (Methods section). The \( ab-initio \) calculated EFA values for the full set of 56 5-metal compositions are provided in Table I. Nine candidates are chosen from this list for experimental synthesis and investigation: i. the three candidates with the highest value of EFA (MoNbTaVWC\(_5\) (EFA = 125 (eV/atom)\(^{-1}\)), HfNbTaTiZrC\(_5\) (EFA = 100 (eV/atom)\(^{-1}\)), HfNbTaTiVC\(_5\) (EFA = 100 (eV/atom)\(^{-1}\)), high probability of forming high-entropy single-phases). ii. the two candidates with the lowest value of EFA (HfMoVVZrC\(_5\) (37 (eV/atom)\(^{-1}\)), HfMoTiWZrC\(_5\) (38 (eV/atom)\(^{-1}\), low probability of forming high-entropy single-phases), and iii. four chosen at random with intermediate EFA (NbTaTiVVWC\(_5\) (77 (eV/atom)\(^{-1}\)), HfNbTaTiWC\(_5\) (67 (eV/atom)\(^{-1}\)), HfTaTiWZrC\(_5\) (50 (eV/atom)\(^{-1}\)), and HfMoTaWZrC\(_5\) (45 (eV/atom)\(^{-1}\)). Figure 1(a) shows the energy distribution and EFA values obtained \( ab-initio \) from configurations generated with AFLow for the nine chosen systems. For MoNbTaVWC\(_5\), HfNbTaTiZrC\(_5\), and HfNbTaTiVC\(_5\), most of the configurations are within 20 meV/atom of the lowest energy state, and the distributions have an EFA of at least 100 (eV/atom)\(^{-1}\). Therefore, at finite temperature, most of the configura-
TABLE I. Results for the calculated entropy forming ability (EFA) descriptor, energetic distance from 6-dimensional convex hull ($\Delta H_f$) and vibrational free energy at 2000K ($\Delta F_{vib}$) for the 5-metal carbide systems, arranged in descending order of EFA.

| System              | EFA | $\Delta H_f$ | $\Delta F_{vib}$ | $\varepsilon$ | System              | EFA | $\Delta H_f$ | $\Delta F_{vib}$ | $\varepsilon$ | System              | EFA | $\Delta H_f$ | $\Delta F_{vib}$ | $\varepsilon$ |
|---------------------|-----|--------------|------------------|---------------|---------------------|-----|--------------|------------------|---------------|---------------------|-----|--------------|------------------|---------------|
| MoNbTaVWC$_5$       | 125 | 156          | -14              | 0.063         | HfNiTaVWC$_5$      | 67  | 110          |                  |               | TaTiVWC$_5$       | 50  | 96          |                  |               |
| HfNiTaTiZrC$_5$     | 100 | 19           | -12              | 0.094         | HfMoTaTiVWC$_5$    | 67  | 82           |                  |               | NbTiVWC$_5$       | 50  | 93          |                  |               |
| HfNiTaTiVWC$_5$     | 100 | 56           | -31              | 0.105         | HfMoNiTaZrC$_5$    | 67  | 53           |                  |               | HfMoVWC$_5$       | 50  | 96          |                  |               |
| MoNiTaTiVWC$_5$     | 100 | 82           |                  |               | HfMoNbTaZrC$_5$    | 63  | 133          |                  |               | HfMoTaVWC$_5$     | 50  | 92          |                  |               |
| NbTiTaVZrC$_5$      | 83  | 64           |                  |               | HfMoNiTaZrC$_5$    | 63  | 55           |                  |               | HfMoNiVWC$_5$     | 50  | 89          |                  |               |
| HfMoNiTaVWC$_5$     | 83  | 48           |                  |               | NbTaTiVZrC$_5$     | 59  | 61           |                  |               | MoTaVWC$_5$       | 48  | 148         |                  |               |
| NbTaTiVWC$_5$       | 77  | 72           | -19              | 0.121         | MoTaTiVZrC$_5$     | 59  | 92           |                  |               | MoTaTiWC$_5$      | 48  | 94          |                  |               |
| MoNiTaTiWC$_5$      | 77  | 111          |                  |               | MoNbTaVZrC$_5$     | 59  | 87           |                  |               | MoNbVWC$_5$       | 48  | 146         |                  |               |
| MoNiTaVWC$_5$       | 71  | 122          |                  |               | MoNbTaVZrC$_5$     | 59  | 108          |                  |               | MoNbTiVWC$_5$     | 48  | 89          |                  |               |
| MoNiTaTiZrC$_5$     | 71  | 57           |                  |               | HfNiTaVWC$_5$      | 59  | 81           |                  |               | HfNiNbVZrC$_5$    | 48  | 101         |                  |               |
| HfTaTiVZrC$_5$      | 71  | 73           |                  |               | HfNiTaVWC$_5$      | 59  | 53           |                  |               | HfTiVWC$_5$       | 45  | 99          |                  |               |
| HfNiTaVZrC$_5$      | 71  | 73           |                  |               | NbTaVZrC$_5$       | 56  | 119          |                  |               | HfNbVZrC$_5$      | 45  | 94          |                  |               |
| HfMoNiTaVZrC$_5$    | 71  | 77           |                  |               | HfTaTiVWC$_5$      | 56  | 84           |                  |               | HfMoTiVWC$_5$     | 45  | 97          |                  |               |
| HfNiTaTiZrC$_5$     | 71  | 48           |                  |               | HfMoTaVWC$_5$      | 56  | 139          |                  |               | HfMoTaVWC$_5$     | 45  | 105         | M 0.271         |               |
| HfMoNiTaZrC$_5$     | 71  | 126          |                  |               | HfMoNbVWC$_5$      | 56  | 137          |                  |               | HfTaVWC$_5$       | 43  | 97          |                  |               |
| HfMoNiTaVWC$_5$     | 71  | 99           |                  |               | HfNiNbVZrC$_5$     | 53  | 56           |                  |               | MoTaVWC$_5$       | 40  | 107         |                  |               |
| HfNiTaTiVWC$_5$     | 67  | 53           | ~0               | 0.171         | HfMoTaTiWC$_5$     | 53  | 84           |                  |               | HfMoTaVWC$_5$     | 38  | 83          | M 0.315         |               |
| MoTaTiVWC$_5$       | 67  | 128          |                  |               | HfMoNbVWC$_5$      | 53  | 81           |                  |               | HfMoVWC$_5$       | 37  | 141         | M 0.325         |               |
| HfNiTaVZrC$_5$      | 67  | 60           |                  |               | HfTaTiVZrC$_5$     | 50  | 59           | ~0               | 0.169         | HfMoTaVWC$_5$     | 45  | 105         | M 0.271         |               |

Compositions should have a high probability of being formed, so that a high level of configurational randomness is expected to be accessible in the three systems, making them promising candidates to form a high-entropy homogeneous single-phase. Achieving a similar level of configurational randomness would be progressively more difficult in NbTaTiVWC$_5$, HfNbTaTiWC$_5$, and HfTaTiVZrC$_5$ as the different configurations display a broader energy distribution, with EFAs ranging from 50 to 77 (eV/atom)$^{-1}$. A higher energy cost is needed to incorporate configurational entropy into these 3 compositions, so forming a homogeneous single-phase will be more difficult. For HfMoTaVZrC$_5$, HfMoTaTiZrC$_5$, and HfMoVZrC$_5$, the spread of energies for the configurations is very wide, with EFA values from 45 down to 37 (eV/atom)$^{-1}$. These materials would be expected to be very difficult to synthesize as a homogeneous single-phase.

Competing ordered phases. The phase diagrams for the 5-metal carbide systems were generated to investigate the existence of binary and ternary ordered structures that could compete with the formation of the high entropy single phase. First, prototypes for experimentally reported binary and ternary carbide structures [42, 43] are used to calculate the formation enthalpies of additional ordered phases for the AFLLOW database. The results are used to generate the convex hull phase diagrams for all 56 compositions using the AFLLOW-CHULL module [44]. The relevant binary and ternary convex hulls are illustrated in Supplementary Figures 1-36. The distance along the enthalpy axis of the lowest energy AFLLOW-Pocco configuration from the convex hull, $\Delta H_f$, is listed in Table I (the decomposition reaction products are summarized in Supplementary Table 2). A rough estimation of the synthesis temperature $T_s$ (see the analogous Entropy Stabilized Oxides case, Fig. 2 of Ref. 17) — can be calculated by dividing $\Delta H_f$ by the ideal configuration entropy (Supplementary Table 1, with the ideal entropy per atom evaluated as 0.5kb × log 0.2, since k_B × log 0.2 is the entropy per metal-carbide atomic pair). A precise characterization of the disorder requires more expensive approaches, such as the LTVC method [45], and is beyond the scope of this article. The highest temperature is 2254K, which is less than the synthesis temperature of 2200°C (2473K), indicating that during sintering the disordered phases are thermodynamically accessible with respect to decomposition into ordered compounds. In analogy to the formation of metallic glasses where entropic confusion obstructs crystalline growth [46, 47] once the temperature is reduced, systems with high EFA remain locked into ensembles of highly degenerate configurations, retaining the disorder achieved at high temperature. Hence, EFA provides a measure of the relative synthesizability of the disordered composition.

From enthalpy to entropy. It is important to consider that the metal-carbide precursors have very strong covalent/ionic bonds, and are therefore enthalpy stabilized [48]. However, the same might not be the case for their mixture. In fact, a statistical analysis of the AFLLOW.org enthalpies [44] indicates that the gain in formation-enthalpy by adding mixing species, $\Delta H_f(N + 1) − \Delta H_f(N)$, decreases with N, and can easily be over-
come by the monotonic increase in entropy-gain for the disordered systems (to go from order to complete or partial disorder). In the AFLOW analysis, the threshold between low- and high-entropy systems is around 4 mixing species. To have completely entropy-stabilized materials, 5 mixing-species are required (similar to the Entropy Stabilized Oxides [17]). For carbides in which only the metal-sublattice is randomly populated, 5 metals should be enough to achieve carbide entropy stabilization, especially at equi-composition. Notably, if other sublattices were also allowed to contain disorder, (e.g. reciprocal systems like $\text{T}_{x}\text{Hf}_{1-x}\text{C}_{1-y}$ [26, 27]), then the overall number of species might reduce. In this example, entropy was increased by introducing point defects (vacancies) — a promising strategy to improve high temperature performance. In $\text{HfC}_{1-x}$ the reduction of C to sub-stoichiometry enhances the stabilizing effect of the configurational entropy on the solid phase, offsetting its Gibbs free energy (vacancies can only exist in the solid phase) leading to an overall increase in melting point (see Ref. 28).

**Experimental results.** To validate the predictions,
FIG. 2. Experimental results for high-entropy carbides synthesis and characterization. (a) Progression of a sample of HfNbTaTiVC₅ through each processing step: hand mixing (magenta spectrum, bottom), ball milling (blue spectrum, center), and spark plasma sintering (green spectrum, top), depicting the evolution towards the desired rock-salt crystal structure ($a_{\text{exp}} = 4.42\text{Å}$). (b) Linear relationship between EFA$^{-1}$ and the distortion of experimental lattice parameters $\varepsilon$. Green circles (•) and red squares (■) indicate homogeneous high-entropy single- and multi-phase compounds, respectively. (c, d) Electron micrographs of single-phase HfNbTaTiZrC₅ and multi-phase HfMoTaWZrC₅ specimens. (e, f) Selected EDS compositional maps of the HfNbTaTiZrC₅ and HfMoTaWZrC₅ specimens. The micrographs show the presence of the secondary phase in HfMoTaWZrC₅ (circles) that is also present in XRD results, which is revealed to be a W- and Mo-rich phase. Scale bars, 10µm (c-f).
the 9 chosen carbides are experimentally synthesized and characterized (see Methods section). The chemical homogeneity of each sample is measured using energy-dispersive x-ray spectroscopy (EDS), while the crystalline structure is determined via x-ray diffraction (XRD).

An example of the evolution of a sample of composition HfNbTaTiVC₅ through each processing step is given in Figure 2(a), demonstrating the densification and homogenization into a single rock-salt structure. At least three distinct precursor phases are distinguishable in the mixed powder pattern. Following ball milling, the individual phases are still present, however the peaks are considerably broadened, which is due to particle size reduction and mechanical alloying. Following the final spark plasma sintering (SPS) step at 2200°C, the sample consolidates into a bulk solid pellet of the desired single rock-salt phase indicating the successful synthesis of a high-entropy homogeneous carbide.

Results of XRD analysis for each sample following SPS at 2200°C, presented in Figure 1(b), demonstrate that compositions MoNbTaVWC₅, HfNbTaTiZrC₅, HfNbTaTiVC₅, HfNbTaTiWVC₅, NbTaTiWVC₅, and HfTaTiWZrC₅ (the top 6) only exhibit single fcc peaks of the desired high-entropy phase (rock-salt), while HfMoTaWZrC₅, HfMoTiWZrC₅, and HfMoVWZrC₅ (the bottom 3) show multiple structures. The small peaks at 2θ = 31.7°, marked by the diamond symbol in the spectra of HfNbTaTiZrC₅, HfNbTaTiWVC₅ and HfTaTiWZrC₅ in Figure 1(b), are from the (111) plane of a monoclinic (Hf,Zr)O₂ phase that remains due to processing. The volume fraction of this phase is less than 5% and does not significantly alter the composition of the carbide phase. The distinguishable second phase in HfMoTaWZrC₅ is identified as a hexagonal phase. One and two secondary fcc phases are observed for HfMoVWZrC₅ and HfMoTiWZrC₅, respectively. Microstructure analysis and selected elemental mapping (Figure 2(c-f)) confirm that the systems displaying single-phases are chemically homogeneous, while the multi-phase samples undergo chemical segregation. For example, only grain orientation contrast is present in the HfNbTaTiZrC₅ microstructure, and no indication of notable clustering or segregation is visible in its compositional maps. On the contrary, a clear chemical phase contrast is observable in the microstructure of the multi-phase HfMoTaWZrC₅ sample, and the compositional maps demonstrate that the secondary phase, apparent in XRD, is W- and Mo-rich.

Homogeneity analysis. Peak broadening in XRD patterns (Figure 1(b)) is used to quantify the level of structural homogenization achieved in the samples. According to the Williamson-Hall formulation [52], broadening in XRD is principally due to crystallite size \((\propto 1/\cos \theta, \theta = \text{Bragg angle})\) and lattice strain \((\propto 1/\tan \theta)\). For multi-component systems, significant broadening is expected to occur due to local lattice strains and variations in the interplanar-spacings throughout the sample [53]. The latter can be attributed to the inhomogeneous distribution of the elements, the extent of which can be evaluated by applying the analysis to a multi-component system, which has only a single lattice structure and is assumed strain-free [53].

The lattice distortion of the rock-salt phase in the single-phase materials (or the most prevalent in the multi-phase ones) is determined by using the relationship between broadening \(\beta_S\) and Bragg angle \(\theta\) (Methods section):

\[
\beta_S \cos \theta = 4 \varepsilon \sin \theta + \frac{K\lambda}{D},
\]

where \(\varepsilon\) is the lattice strain or variation in interplanar-spacing due to chemical inhomogeneity, \(K\) is a constant (dependent on the grain shape), \(\lambda\) is the incident x-ray wavelength, and \(D\) is the crystallite size. Since materials are assumed strain free, \(\varepsilon\) — obtained by inverting Equation (4) — represents the relative variation of the lattice parameter due to inhomogeneity. Thus, \(\varepsilon\) is both a measure of homogeneity and of the effective mixing with respect to the ideal scenario. The results for the EFA descriptor, the experimental characterization, as well as the values for \(\varepsilon\) for all 9 carbides compositions are given in Table I. The values for \(\varepsilon\) range from 0.063% for MoNbTaVWC₅ and 0.094% for HfNbTaTiZrC₅ (the most homogeneous materials) to 0.325% for HfMoVWZrC₅ (the least homogeneous material). Overall, the experimental findings agree well with the predictions of EFA descriptor, validate its ansatz and indicate a potential threshold for our model of 5-metal carbides: EFA \(~ 50\ (eV/atom)^{-1}\)\) homogeneous disordered single-phase (high-entropy).

High-entropy synthesizability. The comparison between the EFA predictions and the homogeneity of the samples is analyzed in Figure 2(b). Although the Williamson-Hall formalism does not provide particularly accurate absolute values of \(\varepsilon\), it is effective for comparing similarly processed samples, determining the relative homogeneity. The lattice distortion \(\varepsilon\) (capturing homogeneity) decreases linearly with the increase of EFA. The Pearson (linear) correlation of EFA\(^{-1}\) with \(\varepsilon\) is 0.97, while the Spearman (rank order) correlation is 0.98. As such, the EFA takes the role of an effective high-entropy synthesizability descriptor.

Three facts are relevant. i. Intuitively, several of the carbide compositions that easily form a highly homogeneous phase, particularly HfNbTaTiVC₅ and HfNbTaTiZrC₅, come from binary precursors having the same structure and ratio of anions to cations as the final high-entropy material. ii. Counterintuitively, the highest-EFA and most homogeneous phase MoNbTaVWC₅ is made with two precursors having different structures and stoichiometric ratios from the high-entropy material, specifically orthorhombic \(\alpha\)-Mo₂C and...
hexagonal α-W₂C, leading to a final sub-stoichiometric MoNbTaVWC₅₋ₓ. The additional disorder provided by the presence of vacancies in the C-sublattice is advantageous: it allows further entropy stabilization, potentially increasing the melting point vis-à-vis the stoichiometric composition [28]. An investigation of the effect of carbon stoichiometry is clearly warranted, although it is outside of the scope of this study. iii. For tungsten and molybdenum, metal-rich carbides are used because of the difficulties in obtaining molybdenum monocarbide (MoC) powder, or tungsten monocarbide (WC) powder in the particle sizes compatible with the other precursors, hindering consistent mixing, sintering and homogenization. It should be noted that additional samples of MoNbTaVWC₅ were also synthesized using hexagonal WC with a smaller particle size, and the homogeneous rock-salt phase was again successfully obtained (see Supplementary Figure 37). The existence of phase-pure MoNbTaVWC₅ indicates that, similar to the rock-salt binary carbides, the multi-component carbide is stable over a range of stoichiometry. From experimental/phenomenological grounds, the formation of such a phase is surprising. The equi-composition binary carbides MoC and WC have hexagonal ground-states, and their rock-salt configurations have significantly higher formation enthalpy [54]. Considering these facts, there are no experimental indications that adding Mo and W would contribute to stabilizing the most homogeneous rock-salt 5-metal carbide that was predicted by the EFA and later validated experimentally. The arguments demonstrate the advantage of a descriptor that quantifies the relative entropy forming ability over simple empirical/phenomenological rules, in that it correctly identifies this composition as having a high propensity to form a single phase, while simultaneously correctly predicting that several other systems having both Mo and W subcomponents undergo phase separation.

**Mechanical properties.** The Vickers hardness, Hᵥ, and elastic modulus, E, of both the binary carbide precursors and the synthesized 5-metal single-phase compositions are measured using nanoindentation, where the properties are extracted from load-displacement curves (see Supplementary Figure 38(a)). The binary precursor samples for these measurements are prepared and analyzed using the same protocol to ensure the validity of the comparisons (see Methods section for more details). The results for the 5-metal compositions are in Table II, while those for the binary carbides are listed in Table III (Methods section). It is found that, for the 5-metal compositions, the measured Hᵥ and E values exceed those predicted from a rule of mixtures (ROM) based on the binary precursor measurements. The enhancement of the mechanical properties is particularly strong in the case of HfNbTaTiZrC₅, where the measured E and Hᵥ exceed the ROM predictions by 10% and 50%, respectively (see Supplementary Figure 38(b) for a comparison between the Hᵥ results obtained from calculation, experiment, and ROM). Mass disorder is one possible source of the enhanced hardness: deformation is caused by dislocation movements and activation energy is absorbed and released at each lattice step. An ideal ordered system can be seen as a dislocation-wave-guide with matched (uniform) impedance along the path: propagation occurs without any relevant energy reflection and/or dispersion. This is not the case for disordered systems: mass inhomogeneity causes impedance mismatch, generating reflections and disturbing the transmission by dispersing (scattering) its group energy. Macroscopically the effect is seen as increased resistance to plastic deformations — more mechanical work is required — i.e. increase of hardness. Other possible causes of increased hardness include solid solution hardening [5, 13, 20], where the atomic size

| system          | MoNbTaVWC₅ | HfNbTaTiZrC₅ | HfNbTaTiWC₅ | HfNbTaTiW₅C | NbTaTiW₅C | HfTaTiW₅ZrC |
|-----------------|------------|--------------|-------------|-------------|-----------|-------------|
| AFLOW (ROM)     |            |              |             |             |           |             |
| exp. (ROM)   | (321)     | (267)        | (279)       | (296)       | (305)     | (274)       |
| G             | 278        | 235          | 267          | 252         | 253       | 246         |
| exp. (ROM)   | (183)     | (165)        | (196)        | (186)       | (189)     | (178)       |
| E             | (495)     | (455)        | (476)        | (459)       | (400)     | (458)       |
| AFLOW (ROM) | 28         | 27           | 27           | 26           | 29         | 25          |
| exp. (ROM)   | (-)       | (-)          | (-)          | (-)          | (-)       | (-)         |
| Hᵥ, Chen      | 20         | 27           | 27           | 26           | 29         | 25          |
| exp. (ROM)   | (20)      | (25)         | (25)         | (26)         | (26)      | (21)        |
| Hᵥ, Teter     | 20         | 32           | 27           | 26           | 31         | 27          |
| exp. (ROM)   | (28)      | (28)         | (25)         | (30)         | (29)      | (27)        |
| Hᵥ, Tian      | 20         | 27±2         | 27±2         | 26±2         | 28±2      | 33±2        |
| exp. (ROM)   | (20)      | (27±2)       | (27±2)       | (26±2)       | (28±2)    | (33±2)      |
mismatch results in lattice distortions, limiting the motion of dislocations necessary for plastic deformation; and changes in the slip systems and the ease with which slip can occur [20, 55].

Elastic properties are calculated using AFLOW [41, 56] for the 5-metal compositions MoNbTaVWC$_5$, HfHfTaTiZrC$_5$, HfNbTaTiVC$_5$, NbTaTiWVC$_5$, and HfTaTiWZrC$_5$ (Table II) and their precursors. In general, results are within the experimentally reported ranges for the binary carbides (Table III in the Methods section). $H_V$ values are estimated from the bulk and shear moduli using the models introduced by Chen et al. [49], Teter [50], and Tian et al. [51]. Computational models do not consider plastic deformation mechanisms in inhomogeneous systems and thus $H_V$ predictions underestimate experiments, leading to results consistent with the ROM of binary carbides (Table II). The outcome further corroborates that the experimentally observed enhancement of the mechanical properties is due to disorder.

**Vibrational contribution to formation free energy.**

The vibrational contributions to the formation Gibbs free energy, $\Delta F_{\text{vib}}$, at 2000K are listed in Table I for the 6 compositions synthesized as a single phase. The vibrational free energies, $F_{\text{vib}}$, are calculated using the Debye-Grüneisen model implemented in the AFLOW-AGL module [57], using the Poisson ratio calculated with AFLOW-AEL [56]. The average $F_{\text{vib}}$ for the 5-metal compositions are calculated, weighted according to the Boltzmann distribution at 2000K. The vibrational contribution to the formation Gibbs free energy, $\Delta F_{\text{vib}}$, for each composition is obtained from the difference between its average $F_{\text{vib}}$ and the average $F_{\text{vib}}$ of its component binary carbides. $\Delta F_{\text{vib}}$ at 2000K ranges from $\sim 0 \text{meV/atom}$ for HfHfTaTiWVC$_5$ to $\sim 31 \text{meV/atom}$ for HfNbTaTiVC$_5$, which are significantly less than the total entropy contribution (mostly configurational plus vibrational) required to overcome the values of 50meV/atom to 150meV/atom for the formation enthalpy $\Delta H_f$. These results are in agreement with previous observations that the vibrational formation entropy is generally an order of magnitude smaller than the configuration entropy [39, 58].

**DISCUSSION**

In this article, an entropy forming ability descriptor has been developed for the purpose of capturing synthesizability of high-entropy materials. The framework has been applied to refractory metal carbides, leading to the prediction and subsequent experimental discovery of homogeneous high-entropy single-phases. The method is able to quantitatively predict the relative propensity of each composition to form a homogeneous single-phase, thus identifying the most promising candidates for experimental synthesis. In particular, the experiments validate the prediction that the composition MoNbTaVWC$_5$ should have a very high propensity to form a homogeneous single-phase, despite incorporating both Mo$_2$C and W$_2$C, which have different structures (hexagonal and/or orthorhombic instead of rock-salt) and stoichiometric ratios from the 5-metal high-entropy material.

Furthermore, it is demonstrated that disorder enhances the mechanical properties of these materials: HfHfTaTiZrC$_5$ and HfTaTiWZrC$_5$ are measured to have hardness of 32 GPa (almost 50% higher than the ROM prediction) and 33 GPa, respectively, suggesting a new avenue for designing superhard materials. The formalism could become the long-sought enabler of accelerated design for high-entropy functional materials with enhanced properties for a wide range of different technological applications.

**METHODS**

**Spectrum generation.** The different possible configurations required to calculate the energy spectrum are generated using the AFLOW-POCC algorithm [41] implemented within the AFLOW computational materials design framework [54, 63, 64]. The algorithm initially generates a super-lattice of the minimum size necessary to obtain the required partial occupancies within some user-specified accuracy. For each unique supercell, the AFLOW-POCC algorithm then generates the complete set of possible supercells using Hermite normal form matrices [41]. Non-unique supercell combinations are eliminated from the ensemble by first estimating the total energies of all configurations using a Universal Force Field [41, 65] based method, and then identifying duplicates from their identical energies.

**Structure generation.** In the case of the high-entropy carbide [17] systems investigated here, the AFLOW-POCC algorithm starts with the rock-salt crystal structure (spacegroup: $Fm\bar{3}m$, #225; Pearson symbol: cF8; AFLOW Prototype: AB$\text{cF8}$225.a.b [66]) as the input parent lattice. Each anion site is occupied with a C atom (occupancy probability of 1.0), while the cation site is occupied by 5 different refractory metal elements, with a 0.2 occupancy probability for each. The AFLOW-POCC algorithm then generates a set of configurations (49 in total in the case of the rock-salt based 5-metal carbide systems, once structural duplicates are excluded), each containing 10 atoms: one atom of each of the metals, along with 5 carbon atoms. This is the minimum cell size necessary to accurately reproduce the required stoichiometry. All configurations have $g_i = 10$, except for one where $g_i = 120$, so that $\sum_{i=1}^{n} g_i = 600$ for the rock-salt based 5-metal carbide systems. Note that computational demands increase significantly with the number of elements: AFLOW-POCC generates 522, 1793 and 7483 for 6-, 7- and 8-metal carbide compositions, respectively.

**Energies calculation.** The energy of each configuration is calculated using density functional theory (VASP [67]) within the AFLOW framework [63] and the standard settings [64]. Each configuration is fully relaxed using the PBE parameterization of the GGA exchange-correlation functional [68], PAW potentials, at least 8000 k-points per reciprocal atom (KPPRA), and a plane-wave cut-off of at least 1.4 times the cut-off values of constituent species’ pseudopotentials [64]. The formation enthalpy ($H_f$) of each configuration along with the
link to AFLOW.org entry page is provided in Supplementary Tables 4-10.

**Mechanical properties.** Elastic properties are calculated using the Automatic Elasticity Library (AEL) module [56] of the AFLOW framework, which applies a set of independent directional normal and shear strains to the structure, and fits the resulting stress tensors to obtain the elastic constants. From this, the bulk: B, and shear: G, moduli are calculated in the Voigt, Reuss and Voigt-Reuss-Hill (VRH) approximations, with the average being used for the purposes of this work. The elastic or Young’s modulus: $E$ is calculated using the approximation $E = 9BG/(3B + G)$, which can be derived starting from the expression for Hooker’s Law in terms of $B$ and the Poisson ratio, $\nu$: $\nu_{11} = 1/\sqrt{E [\sigma_{11} - \nu (\sigma_{22} + \sigma_{33})]}$ [69], and similarly for $\nu_{22}$ and $\nu_{33}$. For a cubic system, $\nu_{11} = S_{11} + S_{12} + S_{13}$ (similarly for $\nu_{22}$ and $\nu_{33}$), where $S_{ij}$ are the elements of the elastic compliance tensor, so that $1/E = S_{11}$ and $-\nu/E = S_{12}$. For a cubic system, the bulk modulus is $B = 1/[3(S_{11} + 2S_{12})] = E/[3(1 - 2\nu)]$. The Poisson ratio can be written as $\nu = (3B - 2G)/(6B + 2G)$, and combining with the expression for $B$ and rearranging gives the required $E = 9BG/(3B + G)$.

The elastic properties for the 5-metal compositions are first calculated for each of the 49 configurations generated by AFLOW-POCC. The VRH approximated values of $B$ and $G$ for these configurations are listed in Supplementary Table 3, along with the AFLOW-POCC ensemble averaged electronic density of states (see Supplementary Figure 39). The average elastic moduli are then obtained, weighted according to the Boltzmann distribution at a temperature of 2200°C (the experimental sintering temperature). These calculated values are compared to those obtained using a rule of mixtures (ROM, average of the binary components, weighted according to fractional composition in the sample).

Three different models are used for predicting the Vickers hardness based on the elastic moduli: Chen et al. ($H_v = 2(k^2G)^{0.585} - 3$; $k = G/B$) [49], Teter ($H_v = 0.151G$) [50], and Tian et al. ($H_v = 0.92k^{0.137}G^{0.708}$; $k = G/B$) [51]. Note, however, that these models are based on the elastic response of the materials, and do not take into account phenomena such as plastic deformation, slip planes, and lattice defects.

**Sample preparation.** Initial powders of each of the eight binary precursor carbides (HIC, NbC, TaC, TiC, Mo2C, VC, W2C, ZrC) are obtained in greater than 99% purity and −325 mesh (< 44μm) particle size (Alfa Aesar). Samples are weighed out in 15 g batches and mixed to achieve the desired 5-metal carbide compositions. To ensure adequate mixing, each sample is ball milled in a shaker pot mill for a total of 2 hours in individual 30-minute intervals intersected by 10-minute rest times to avoid heating and consequent oxide formation. All milling is done in tungsten carbide lined stainless steel milling jars with tungsten carbide grinding media.

Bulk sample pellets are synthesized via solid-state processing routes. The field assisted sintering technique (FAST), also called spark plasma sintering (SPS), is employed to simultaneously densify and react the compositions into single-phase materials. For all samples, sintering is done at 2200°C with a heating rate of 100°C/min, 30 MPa uniaxial pressure, and a 5-minute dwell at temperature. Samples are heated in vacuum atmosphere to 1300°C followed by flowing argon to 2200°C. All sintering is done in 20 mm graphite die and plunger sets with graphite foil surrounding the samples to prevent reaction with the die.

**Sample analysis.** Elemental analysis is performed using an FEI Quanta 600 SEM equipped with a Bruker e-Flash EDS detector at an accelerating voltage of 20 kV. Microstructural SEM imaging is carried out using an FEI Apreo FE-SEM equipped with a Bruker e-Flash EDS detector at an accelerating voltage of 20 kV. Microstructural SEM imaging is carried out using an FEI Apreo FE-SEM equipped with a Bruker e-Flash EDS detector at an accelerating voltage of 20 kV. Microstructural SEM imaging is carried out using an FEI Apreo FE-SEM equipped with a Bruker e-Flash EDS detector at an accelerating voltage of 20 kV.

**Bulk sample sintering.** All sintering is done in 20 mm graphite die and plunger sets with graphite foil surrounding the samples to prevent reaction with the die.
of $\theta$, and $x$ is a constant between 1.0 and 2.0. In the current analysis, $x$ is set to 2.0 due to the Gaussian-like shape of the instrument peaks, as this value leads to the lowest standard deviation of linear fits to the peak broadening data.

Both crystallite size and lattice strain contribute to $\beta_S$ [52, 71, 72]:

$$\beta_S = 4\varepsilon \tan \theta + \frac{K\lambda}{D \cos \theta},$$

(6)

where $\varepsilon$ is the lattice strain or variation in interplanar spacing due to chemical inhomogeneity, $K$ is a constant (dependent on the grain shape), $\lambda$ is the incident x-ray wavelength and $D$ is the crystallite size. Rearranging Equation (6) gives:

$$\beta_S \cos \theta = 4\varepsilon \sin \theta + \frac{K\lambda}{D}$$

(7)

The slope of a linear fit to the plot of $\beta_S \cos \theta$ against $\sin \theta$ is equal to the strain, or lattice distortion, while the $y$-intercept of a linear fit with zero slope determines the crystallite size.

**Mechanical Testing.** Mechanical properties of each of the single-phase compositions are tested using a Keysight NanoIndenter G200 with a Berkovich indenter tip. To rule out indentation size effects, testing is carried out at loads of both 50 mN and 300 mN, and no significant deviation in hardness or modulus is observed. To allow valid cross-comparison, each of the HECs is compared to the binary carbides, which were hot-pressed and indentation tested under identical conditions. For the reported values, tests are carried out according to the standard method outlined in ISO 14577 using a maximum load of 50mN. Values are calculated as an average of 40 indents, and are reported with errors of plus or minus one standard deviation. A fused crystal silica standard is used in each sample is vibratory polished using 0.05 $\mu$m colloidal silica and 12 hours to ensure minimal surface roughness. All tests are carried out at a temperature of 27°C $\pm$ 0.5°C. Indentation data is analyzed according to the methods of Oliver and Pharr [73, 74]. The elastic (i.e. Young’s) modulus is determined using $1/E_{\text{eff}} = (1 - \nu^2)/E + (1 - \nu_1^2)/E_1$, where $E_{\text{eff}}$ is the effective modulus (sometimes called the reduced modulus) obtained from nano-indentation, $E$ and $\nu$ are the Young’s modulus and Poisson’s ratio, respectively, for the specimen, while $E_1$ and $\nu_1$ are the same parameters for the indenter. A Poisson’s ratio for each of the binary carbides is obtained from literature [75] where available. For 5-metal carbide samples where data for each of the constituents is available, the value used for Poisson’s ratio is taken as the average of the constituent binaries. If this average is unavailable (i.e. when Mo and/or W are present), Poisson’s ratio is assumed to be equal to 0.18.

**Data availability.** All the *ab-initio* data are freely available to the public as part of the AFLLOW online repository and can be accessed through AFLLOW.org following the REST-API interface [63] and AFLUX search language [76].

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