

$(\text{CrVW})_{(1-x)}(\text{TaTi})_x$, ($x = 10$ and 20 at.%), high entropy alloys as thermal barriers for nuclear fusion reactors

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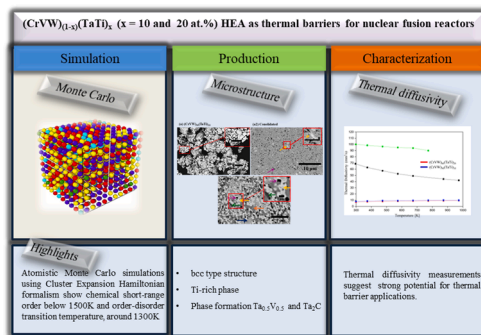
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GRAPHICAL ABSTRACT



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ABSTRACT

Due to the extreme operating temperatures in nuclear fusion reactors, current divertor monoblock materials, tungsten (plasma-facing material) and CuCrZr (heat sink), exhibit a substantial mismatch in mechanical and thermal properties. Therefore, a thermal barrier interlayer is required to guarantee continuous operation. In this work, $(\text{CrVW})_{(1-x)}(\text{TaTi})_x$ alloys ($x = 10$ and 20 at.%) were studied for application as interlayers in nuclear fusion reactors. Atomistic modeling using Monte Carlo simulations combined with a first-principles-based Cluster Expansion Hamiltonian has been performed as a function of temperature to predict the order-disorder transitions in the investigated high-entropy alloys. Moreover, the experimental alloys were prepared by mechanical alloying

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followed by spark plasma sintering. Both alloy compositions display strong negative average chemical short-range ordering below 1500 K for the W-Ta and W-Ti chemical pairs, with an estimated transition temperature around 1300 K. Atomic structures obtained from Monte Carlo simulations for $(\text{CrWV})_{80}(\text{TaTi})_{20}$ indicate that the ordering observed in this composition is stronger than that for $(\text{CrWV})_{90}(\text{TaTi})_{10}$. Moreover, both systems exhibit a bcc structure, and heat treated samples show phase growth and a four phase microstructure. The thermal diffusivity increases with temperature, reaching lower values than those of pure W and CuCrZr.

1. Introduction

Nuclear fusion is a leading candidate for large scale clean energy production, as it converts the energy released from fusion reactions into electrical energy [1]. Nevertheless, the materials used must be carefully chosen due to extreme temperatures and radiation. The divertor comprises plasma facing tungsten monoblocks [2,3], which collect the heat generated in operation and should operate at temperatures above 675 K [4]. Additionally, the heat sink CuCrZr alloy (chosen due to the thermal properties [5,6]) must operate between 423 K and 623 K [5,6] due to the fact that under irradiation, this alloy becomes brittle [7]. Furthermore, the temperature difference could lead to a Ductile-to-Brittle Transition Temperature (DBTT) in tungsten [4], ultimately resulting in mechanical failure of the divertor monoblocks. Moreover, the different coefficients of thermal expansion (CTE), $(4.6 \times 10^{-6}/\text{K})$ for tungsten and $(17.6 \times 10^{-6}/\text{K})$ for CuCrZr [7–9]. In addition to DBTT and CTE discrepancies, radiation damage will lead to material degradation and compromise reactor safety.

For this reason, an intermediate layer is required to minimize the mismatch between the plasma facing material (W) and the CuCrZr heat sink, thereby prolonging the lifespan of the reactor and its materials [10]. The selected thermal barrier should have lower thermal transport coefficients, allowing the heat sink to operate at a lower temperature. However, a strong insulating material might slow down heat flow too much, leading to W overheating and its own as well. On divertor, an expected heat flux of about 10–20 MW/m² [11,12] and the thermal barrier is expected to have low thermal conductivity ($\kappa < 15 \text{ W}\cdot\text{K}^{-1}\cdot\text{m}^{-1}$) [13] and high irradiation resistance.

High entropy alloys (HEAs) are solid solutions with simple crystal structures that exhibit excellent properties such as high hardness [1], wear [14], oxidation [10], corrosion [15], and irradiation resistance [16], as well as high thermal stability [17]. Owing to the disparate mass and size differences among some elements of the proposed compositions, strong phonon and electron scattering will result in as low thermal conductivity [18] as required for thermal barriers [19,20]. Previous publications have shown that alloys with Ti, such as $(\text{CrFeTaTi})_{70}\text{W}_{30}$ [21] and FeTiTaVW [22], revealed a complex microstructure with a Ti-rich phase. Titanium is a lightweight element with high strength and excellent oxidation resistance, which plays a crucial role in modifying the properties of high entropy alloys, thereby enhancing mechanical strength, corrosion resistance, and thermal stability. Chen, Yuhua, has shown that the addition of Ti to the CoCrFeNiMnTi_x ($x = 0, 0.25$, and $0.55 \text{ mol}\%$) alloy can change the phase from a single fcc (Fe, Ni) phase to a bcc (Ti-rich) type-structure [23]. Titanium addition increased the material's hardness from 175 HV to 253 HV and 646 HV, respectively. As well as the tensile strength of the alloy is increased from 461 MPa to 631 MPa, along with Ti ($x = 0 \text{ mol}\%$) alloy to Ti ($x = 0.25 \text{ mol}\%$) alloy, followed by a reduction to 287 MPa ($x = 0.55 \text{ mol}\%$). Due to titanium's relatively large atomic radius, grain boundary segregation or clusters in multi-principal element systems can lead to microstructural inhomogeneity, affecting mechanical properties such as hardness and wear resistance. Therefore, the binary mixing enthalpy with Ti is significantly more negative than for the other possible atomic pairs, indicating that increasing the Ti concentration will inevitably result in a thermodynamic drive towards the formation of intermetallic phases, thereby decreasing the solid solution strengthening. In this way, a reduction of the amount of Ti is explored in this paper.

This work focuses on simulation, production, and characterization of the $(\text{CrVW})_{(1-x)}(\text{TaTi})_x$, where ($x = 10$ and $20 \text{ at}\%$) high entropy alloy as a thermal barrier for nuclear fusion reactors. With this in mind, the simulation behavior of $(\text{CrVW})_{(90)}(\text{TaTi})_{10}$ and $(\text{CrVW})_{(80)}(\text{TaTi})_{20}$, applying the first-principles thermodynamic approaches, including Density Functional Theory (DFT), Cluster Expansion (CE) method, will be employed [24,25]. A detailed insight into the formation and order-disorder stability of the two HEAs will be obtained using Monte Carlo (MC) simulations of temperature-dependent properties, which will generate the atomistic structures and chemical short-range order parameters for each system [24,25]. The objective of the present atomistic and Monte Carlo simulations is thus to complement the experimentally observable thermophysical and microstructural behavior. The (Cr, V, W) base composition was selected based on each element's thermophysical and mechanical properties, and intrinsic compatibility with tungsten. Since these elements are often correlated with limited ductility, Ta and Ti were introduced, creating significant lattice distortion and phonon scattering, which is expected to reduce thermal conductivity relative to conventional refractory alloys, while also increasing the coefficient of thermal expansion (CTE) toward W and CuCrZr. The specific compositions $x = 10$ and $20 \text{ at}\%$ were chosen to maintain a refractory dominated matrix with minimal density penalty, targeting a CTE closer to tungsten while introducing measurable reductions in thermal conductivity ($x = 10 \text{ at}\%$) and at ($x = 20 \text{ at}\%$), the increased Ta/Ti content further enhances thermal/mechanical compliance and CTE, approaching values more compatible with CuCrZr, while remaining within a single-phase solid solution theoretical calculation. These compositions therefore support a practical design window for divertor interlayers.

In addition, $(\text{CrVW})_{(1-x)}(\text{TaTi})_x$ alloys ($x = 10$ and $20 \text{ at}\%$) were produced by mechanical alloying and then consolidated by spark plasma sintering (SPS). The bulk materials were characterized using Scanning Electron Microscopy (SEM), X-ray diffraction (XRD), and thermal diffusivity measurements.

2. Materials and methods

In this study, Atomistic Monte Carlo (AMC) simulations were performed using the Cluster Expansion Hamiltonian (CEH) formalism, which has recently been developed to study the phase stability of compositionally complex and multicomponent systems as a function of temperature and irradiation damage in different W-based and Fe-based HEAs. The Cluster Expansion (CE) method can also be used to obtain the enthalpy of mixing values following the equation [24–30]:

$$\Delta H_{\text{mix}}^{\text{bcc}} \text{CE}(\vec{\sigma}) = \sum_{\omega} m_{\omega} J_{\omega} \langle \Gamma_{\omega}(\vec{\sigma}) \rangle_{\omega} \quad (1)$$

Where ω denotes clusters, the term m_{ω} represents the multiplicity factors, J_{ω} are effective cluster interactions derived from a set of DFT calculations applying the structure inversion approach and the term $\langle \Gamma_{\omega}(\vec{\sigma}) \rangle$ stands for the average correlation functions. Cluster function can be described as follows:

$$\Gamma_{\omega,n}^{(s)}(\vec{\sigma}) = \gamma_{j_1 K}(\sigma_1) \gamma_{j_2 K}(\sigma_2) \cdots \gamma_{j_{|\omega|} K}(\sigma_{|\omega|}) \quad (2)$$

Where $(s) = (j_1, j_2, \dots, j_{|\omega|})$ denotes the pattern of assigning point functions to the cluster. Point functions $\gamma_{j,K}(\sigma_i)$ are then defined:

$$\gamma_{j,K}(\sigma_i) = \begin{cases} 1 & \text{if } j = 0 \\ -\cos\left(2\pi \left\lfloor \frac{j}{2} \right\rfloor \frac{\sigma_i}{K}\right) & \text{if } j > 0 \text{ and odd} \\ -\sin\left(2\pi \left\lfloor \frac{j}{2} \right\rfloor \frac{\sigma_i}{K}\right) & \text{if } j > 0 \text{ and even} \end{cases} \quad (3)$$

Where $\sigma_i = (0, 1, 2, \dots, K-1)$ denotes the index of the point function. The 2-body correlation functions are then defined as a product of pair probabilities in the following manner:

$$\langle \Gamma_{2,n}^{(s)} \rangle = \langle \Gamma_{2,n}^{ij} \rangle = \sum_{a=1}^K \sum_{b=1}^K \gamma_i(\sigma_a) \gamma_j(\sigma_b) y_n^{ab} \quad (4)$$

Where y_n^{ab} represents the probability of locating two atoms, a and b , within a specific shell, indicated by the label n . The 3-body correlation functions can be defined in a similar manner as follows:

$$\langle \Gamma_{3,n}^{(s)} \rangle = \langle \Gamma_{3,n}^{ijk} \rangle = \sum_{a=1}^K \sum_{b=1}^K \sum_{c=1}^K \gamma_i(\sigma_a) \gamma_j(\sigma_b) \gamma_k(\sigma_c) y_n^{abc} \quad (5)$$

Where y_n^{abc} represents the probability of locating three atoms, a , b , and c , within a specific shell, indicated by the label n . It is worth emphasizing that the presented formulation aims to improve computational efficiency in faster finding Effective Cluster Interactions (ECI) for multi-component systems which contains >4 elements [31]. It doesn't however mean that the number of DFT training sets needs to be increased in a comparison with the conventional (not matrix) CE that normally used for binary systems. The values of ECIs remain unchanged between matrix and conventional formulations. For example, in case of HEAs with 5 element systems we did cross-check the ECIs in our study for Mo-Nb-Ta-Ti-W [25] and W-Cr-Ta-V-Ti [32] alloys to make sure that the resulting ECIs are identical from both formulations. The Effective Cluster Interactions (ECIs) are obtained through a combination of DFT calculations and the Structure Inversion Method. First, DFT calculations are performed to determine the total energies of various configurations of atoms within a structure. The total number of 682 DFT configurations which consist of training data for pure elements, binary, ternary, quaternary sub-systems and quinary W-Cr-Ta-V-Ti, has been used in the present study to map into the ECIs. More detailed description of cross-validation of enthalpy of mixing from CE in a comparison with DFT data from the least square fitting can also be found in [33]. These energies serve as a basis for deriving the interactions between clusters of atoms. The Structure Inversion Method is then applied to fit these calculated energies to a model that describes the interactions between clusters, extracting the ECIs. This approach enables the prediction of thermodynamic properties by accurately modeling interactions within the material's atomic arrangement. Canonical Exchange Monte Carlo (CEMC) is a simulation method used in computational statistical mechanics to study systems at constant temperature and constant particle number of each considered element. It is broadly used to investigate the phase transitions, structural changes, and thermodynamic properties of a given alloy composition. In this work, simulations were conducted by creating a fully disordered random configuration at 3000 K, then annealing it using the simulated annealing procedure with temperature steps of 10 K or 100 K. For each finite temperature, a series of exchanges involving neighboring atoms within the lattice was executed, and the resulting total energy of the system was calculated. If, as a result of such an exchange, the total energy has decreased, then the exchange of the atoms was accepted. In case the energy increased, the exchange was

accepted with a probability defined as $e^{\left(-\frac{\Delta E}{k_B T}\right)}$. In the next step, the energy is averaged across all exchanges, and the newly updated atomic configuration transitions to the simulations at a different temperature. The Alloy Theoretic Automated Toolkit (ATAT) package, developed by van de Walle, Asta, and Ceder, was used to carry out MC simulations

Table 1

– Thermodynamic calculations for (CrVW)₉₀(TaTi)₁₀ and (CrVW)₈₀(TaTi)₂₀ systems.

Samples	ΔH_{mix} [kJ/mol]	ΔS_{mix} [J/K.mol]	δ [%]	VEC
(CrVW) ₉₀ (TaTi) ₁₀	-2.51	13.25	4.63	5.55 (predicted bcc)
(CrVW) ₈₀ (TaTi) ₂₀	-3.73	13.63	5.19	5.43 (predicted bcc)

within this work [24–30].

Cr, V, Ta, Ti, and W powders of (99.9% nominal purity with an average particle size of 10 μm , AlfaAesar) were mixed in a non-equiatom proportion (CrVW)_(1-x)(TaTi)_x, where x ($x = 10$ and 20 at. %). The systems were mechanically alloyed in a high-energy planetary Restch EMAX milling machine using 1 cm WC balls and WC vials. The balls-to-powder mass ratio was 10:1, and milling was performed for a total of 3 hours at 350 rpm.

X-ray diffraction measurements of the powder samples were performed at room temperature using monochromatic Cu K α radiation in a Panalytical XPert Pro diffractometer with a 2 θ -step size of 0.02° from 20° to 80°. The consolidation of the powders was performed by Spark Plasma Sintering (SPS) in collaboration with Romania, using a FCT System GmbH sintering machine at a pressure of 9 kN and a temperature of 1673 K for a holding time of 5 min.

Metallographic preparation of the consolidated samples was performed by grinding with SiC paper, followed by polishing with diamond suspensions. The powders and sintered microstructures were observed using secondary electron (SE) and backscattered electron (BSE) imaging in backscattering electron (BSE) mode with a Thermo Scientific Phenom ProX G6 scanning electron microscope, equipped with a 15 keV electron beam. Thermal treatments will be performed on a tubular furnace under vacuum at 1523 K for 8 days to promote the growth of (CrVW)₉₀(TaTi)₁₀ and (CrVW)₈₀(TaTi)₂₀ phases. Moreover, the milled powder was analyzed using an Empyrean diffractometer in reflection geometry with Cu K α radiation and a step size of 0.013 degrees.

Chemical information was obtained using X-ray energy-dispersive spectroscopy (EDS). Simple thermodynamic calculations were performed to anticipate the structures resulting from the alloying process and help interpret and discuss the results, based on empirical models [34,35]. In this context, calculations of the relevant properties of (CrVW)_(1-x)(TaTi)_x, where $x = 10$ and 20 at.%, are presented. The system (CrVW)_(1-x)(TaTi)_x theoretical calculations are presented in Table 1.

3. Results and discussion

3.1. Simulation results

In this study, Atomistic Monte Carlo (AMC) simulations were performed using the Cluster Expansion Hamiltonian (CEH) formalism, which has recently been developed to study the phase stability of compositionally complex, multi-component systems as a function of temperature in various multicomponent W-based alloys. As the temperature increases, the system undergoes a transition from ordered/segregated phases to a single solid solution phase. To quantitatively characterize this transition, the Warren-Cowley short-range order (SRO) parameter and the order-disorder transition temperature (ODTT) are introduced. The Warren-Cowley SRO parameter of atom types i and j can be calculated from pair probabilities [36,37]:

$$\alpha_n^{ij} = 1 - \frac{y_n^{ij}}{c_i c_j} \quad (6)$$

In this equation, n denotes the n -th nearest neighbor, and y_n^{ij} is the probability to find the specific i - j pair in the n -th neighboring shell, which can be obtained by a matrix inversion of the correlation functions

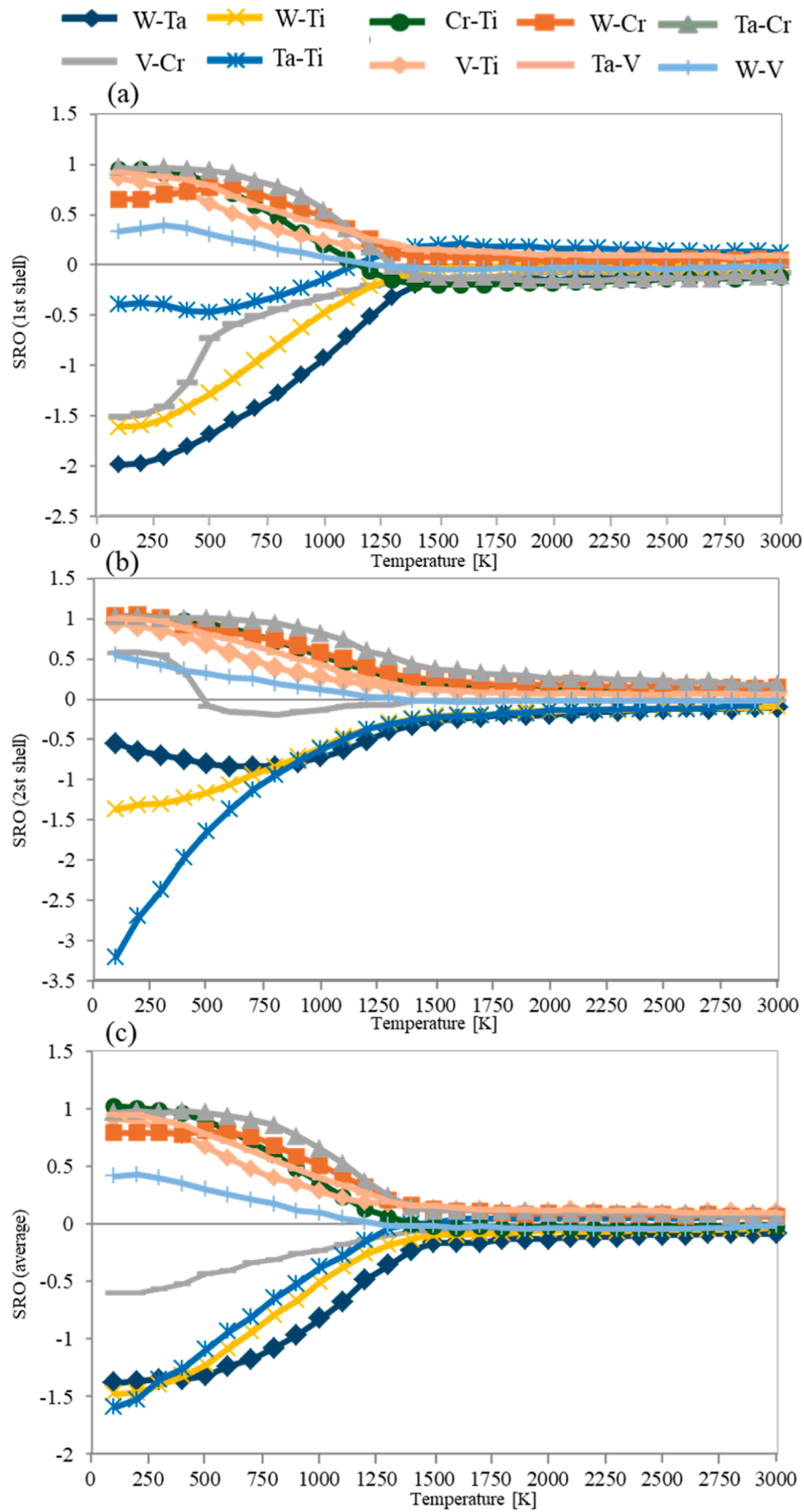


Fig. 1- Chemical short-range order parameters obtained from Monte Carlo simulations as a function of temperature for the different pairs of atoms in (a) first nearest neighbor, (b) second nearest neighbor, and (c) average in the bcc lattice for $(\text{CrWV})_{90}(\text{TaTi})_{10}$ HEA.

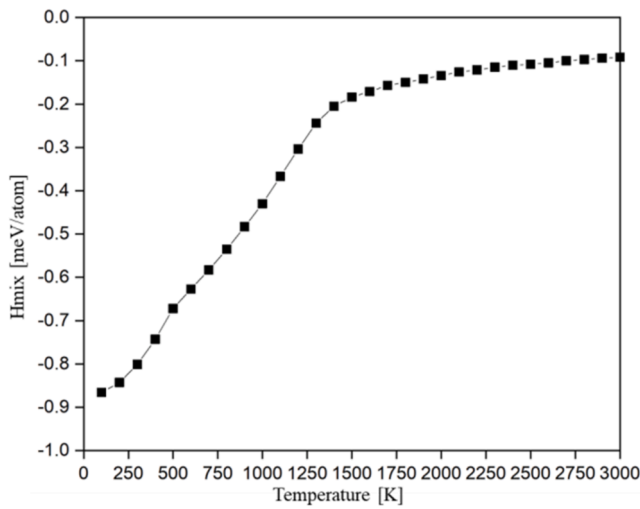


Fig. 2. - Enthalpy of mixing as a function of temperature for $(\text{CrWV})_{90}(\text{TaTi})_{10}$.

obtained from the CE, and c_i , c_j are the global concentration of atom types i and j . Here, we consider first and second nearest neighbors as well as the average (α_{avg}) SRO parameters in a BCC crystalline structure calculated as:

$$\alpha_{\text{avg}} = \frac{8\alpha_1 + 6\alpha_2}{14}, \quad (7)$$

A positive SRO parameter indicates a repulsive relationship between two different elements, while a negative SRO parameter indicates an attractive interaction. When the SRO parameter is zero, the system is in a random solid solution phase.

In Fig. 1, the SRO values for first nearest neighbor (1NN) and second nearest neighbor (2NN), as well as the average of the chemical SRO parameter for the quinary $(\text{CrWV})_{90}(\text{TaTi})_{10}$ alloy, are presented as a function of temperature. It is shown that the SROs are negative for the

chemical pairs W-Ta and W-Ti for both 1NN and 2NN, resulting in a strong negative average Chemical Short-Range Order (CSRO) below 1500 K.

It is observed that the Ta-Ti CSRO is more negatively pronounced than that between Cr-V for the alloys with low Ta and Ti compositions. Furthermore, V-Cr exhibits an average negative CSRO and a dominant positive SRO, with segregation between W-Cr, Ta-Cr, and Ta-V pairs. For the considered alloys, the average CSRO parameters between vanadium (V) and titanium (Ti) are positive.

Considering the definition of the order-disorder transition temperature (ODTT), which is defined as the temperature at which the alloy begins to become a fully disordered solid solution. In the present study, the highest temperature at which inflection points appear on the plot of enthalpy of mixing as a function of temperature is calculated for each composition. In Fig. 2, the calculated enthalpy of mixing indicates that the ODTT for $(\text{CrWV})_{90}(\text{TaTi})_{10}$ is approximately 1300 K.

Fig. 3 shows the atomistic structures for $(\text{CrWV})_{90}(\text{TaTi})_{10}$ alloy obtained from Monte Carlo simulations as a function of temperature. Segregation between W atoms (yellow) from Cr atoms (blue) is observed at low temperatures (400 and 800 K). At 1200 K and above, the stronger disordered configurations obtained are consistent with the predicted ODTT.

Figs. 4 (a) to (c) show the values for first nearest neighbor (1NN) and second nearest neighbor (2NN), for $(\text{CrWV})_{80}(\text{TaTi})_{20}$ alloy with increasing Ta and Ti concentrations and decreasing Cr, W, and V atomic concentration. The most significant change in CSRO compared to $(\text{CrWV})_{90}(\text{TaTi})_{10}$ is related to a weaker CSRO between Ta and Ti, whereas that between Cr and V becomes stronger, as exhibited in the average SRO values from Fig. 4 (c).

The competition between the SRO of Ta-Ti and those of Cr-V seems to result in an unchanging ODTT for $(\text{CrWV})_{80}(\text{TaTi})_{20}$. A comparison between the enthalpy of mixing is shown in Fig. 5, which is similar to that in Fig. 2.

However, the atomic structures obtained from Monte Carlo simulations at four different temperatures: 400 K, 800 K, 1200 K, and 1800 K for $(\text{CrWV})_{80}(\text{TaTi})_{20}$, shown in Fig. 6, indicate that the ordering here is

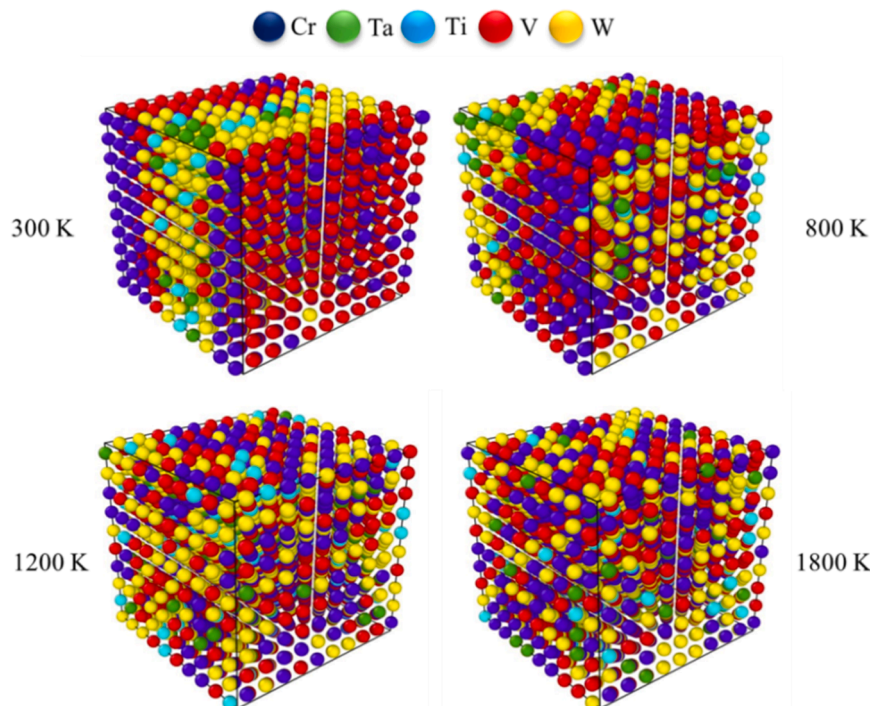


Fig. 3-. Atomic structures obtained from Monte Carlo simulations for a $10 \times 10 \times 10$ bcc-supercell at four different temperatures: 400 K, 800 K, 1200 K, and 1800 K for $(\text{CrWV})_{90}(\text{TaTi})_{10}$.

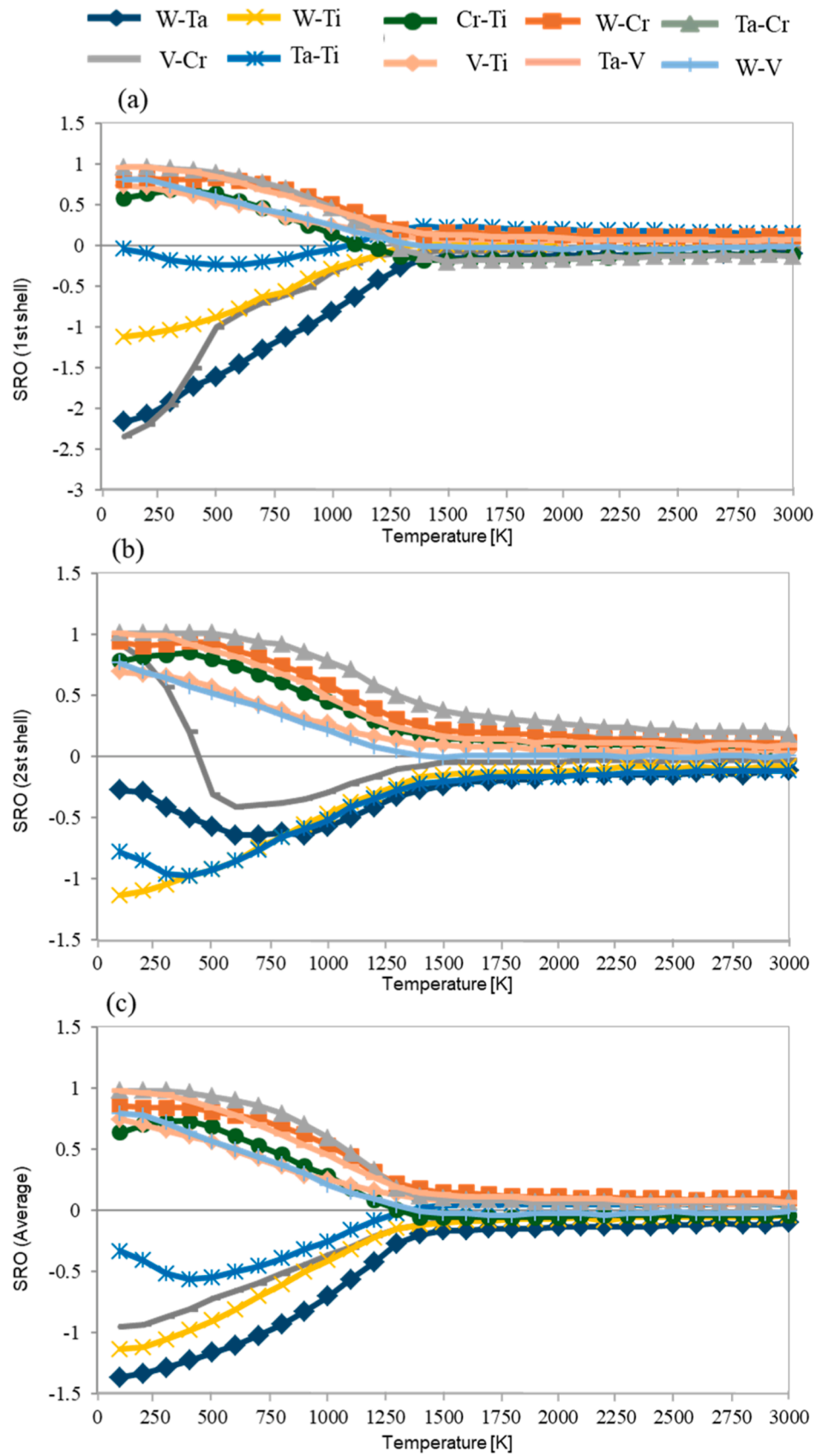


Fig. 4. – Chemical short-range order parameters obtained from Monte Carlo simulations as a function of temperature for the different pairs of atoms in (a) first nearest neighbor, (b) second nearest neighbor, and (c) average in the bcc lattice for $(\text{CrWV})_{80}(\text{TaTi})_{20}$ HEA.

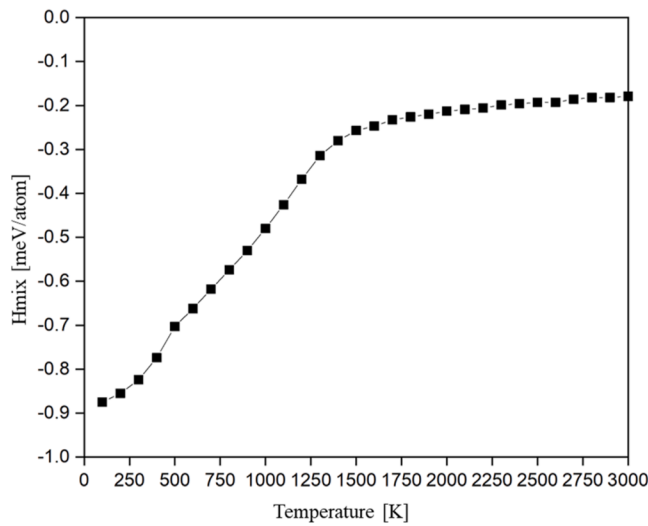


Fig. 5. - Enthalpy of mixing as a function of temperature for $(\text{CrWV})_{80}(\text{TaTi})_{20}$.

stronger than observed in a comparison with the case for $(\text{CrWV})_{90}(\text{TaTi})_{10}$.

To cross-check the ODTT, larger Monte Carlo simulations were performed in HEAs using $30 \times 30 \times 30$ bcc supercell sizes. The results are shown in Fig. 7 for a comparison between the two investigated HEAs, $(\text{CrWV})_{90}(\text{TaTi})_{10}$ (top) and $(\text{CrWV})_{80}(\text{TaTi})_{20}$ (bottom), at three different temperatures: 400 K, 800 K, and 1200 K. It is now clearer that, in the thermodynamic limit, alloys with higher Ta and Ti concentrations exhibit a more substantial segregation effect, reflecting the driving force between W and Cr. It can be concluded that the ODTT (around 1400 K) is higher in $(\text{CrWV})_{80}(\text{TaTi})_{20}$ compared to $(\text{CrWV})_{90}(\text{TaTi})_{10}$.

3.2. Powder characterization

Fig. 8 (a1) and (b1) show the experimental diffractograms for (a) $(\text{CrWV})_{90}(\text{TaTi})_{10}$ and (b) $(\text{CrWV})_{80}(\text{TaTi})_{20}$ initial powder without milling. After two hours of milling, Fig. 8 (a2) and (b2), the individual peaks of the elements disappeared, and a bcc type structure with a lattice parameter of $a = 0.316$ nm, displaying a lattice parameter very close to that of pure W ($a = 0.316$ nm [38]), formed. Additionally, the presence of pure tantalum and chromium with low intensity was also observed (identified by the black diamond and black triangle symbols), as shown in Figs. 8 (a2) and (b2), respectively. In addition, some weak peaks corresponding to WC are observed, indicating its presence in the material due to the use of WC grinding balls during mechanical alloying. Since pure Ta and Cr were detected after two hours of milling, the powders were milled for an additional hour at 350 rpm to promote a single solid solution. After a total of 3 hours of milling, as shown in Figs. 8 (a3) and (b3), the experimental diffractogram displayed a bcc type structure with a lattice parameter of $a = 0.315$ nm for both the $(\text{CrWV})_{90}(\text{TaTi})_{10}$ and $(\text{CrWV})_{80}(\text{TaTi})_{20}$ systems, respectively. The WC peaks are still observed, whereas those for pure tantalum and chromium have disappeared.

Fig. 9 shows the morphology for the milled (a) $(\text{CrWV})_{90}(\text{TaTi})_{10}$ and (b) $(\text{CrWV})_{80}(\text{TaTi})_{20}$ powders, as well as the respective EDS maps. These two compositions were milled by the mechanical alloying process for 3 hours. Fig. 9 (a1) and (b1) revealed that the milled powders for both compositions consist of small particles agglomerated with larger ones. Fig. 9 (a2) to (a6) and (b2) to (b6) exhibits the EDS maps for both systems, showing that all elements for both compositions are very well mixed and display a homogeneous distribution, in agreement with the experimental diffractograms bcc type-structures shown in Fig. 8 (a3) and (b3).

3.3. Consolidated samples characterization

The $(\text{CrWV})_{90}(\text{TaTi})_{10}$ diffractogram shown in Fig. 10 (a) exhibited a

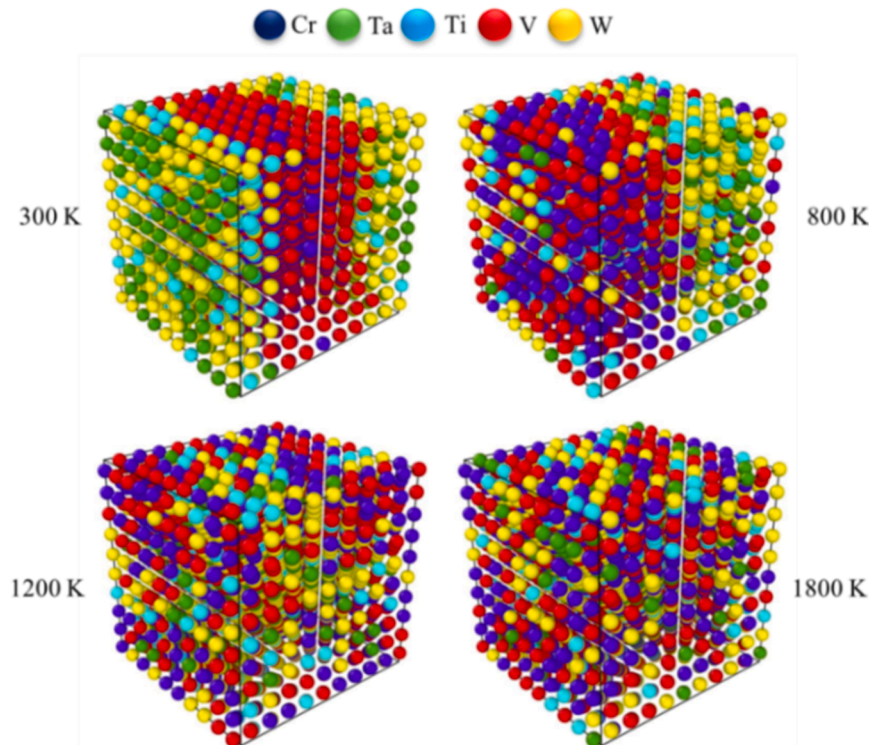


Fig. 6. - Atomic structures obtained from Monte Carlo simulations for a $10 \times 10 \times 10$ bcc-supercell at four different temperatures: 400 K, 800 K, 1200 K, and 1800 K for $(\text{CrWV})_{80}(\text{TaTi})_{20}$.

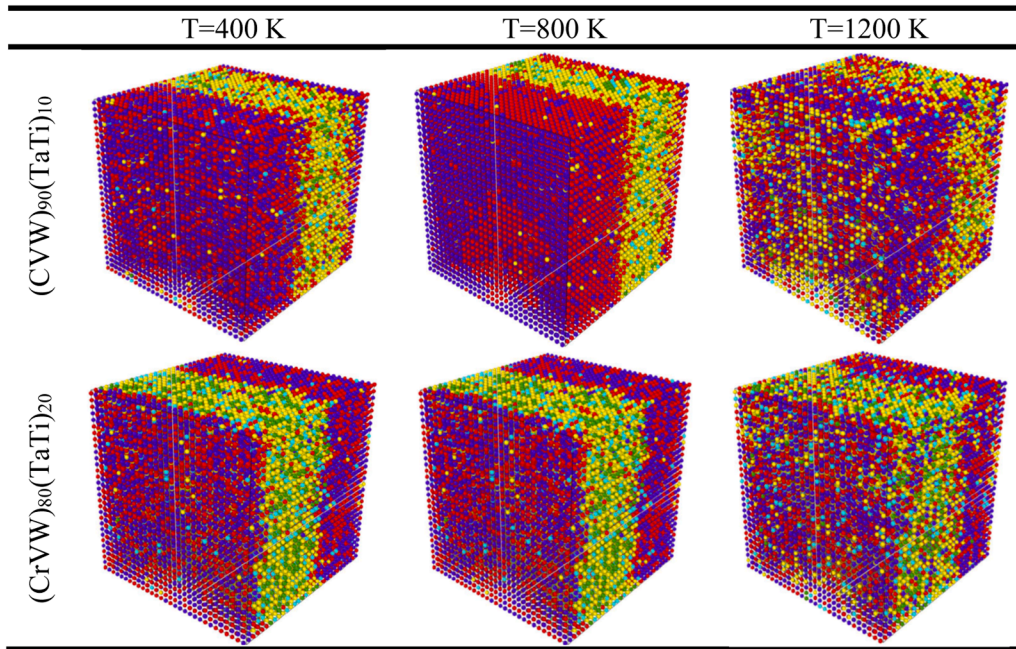


Fig. 7. - Larger scale ($30 \times 30 \times 30$ bcc supercell) Monte Carlo simulation results at three temperatures (400 K, 800 K, and 1200 K) for $(\text{CrVW})_{90}(\text{TaTi})_{10}$ (top) and $(\text{CrVW})_{80}(\text{TaTi})_{20}$ (down) HEAs.

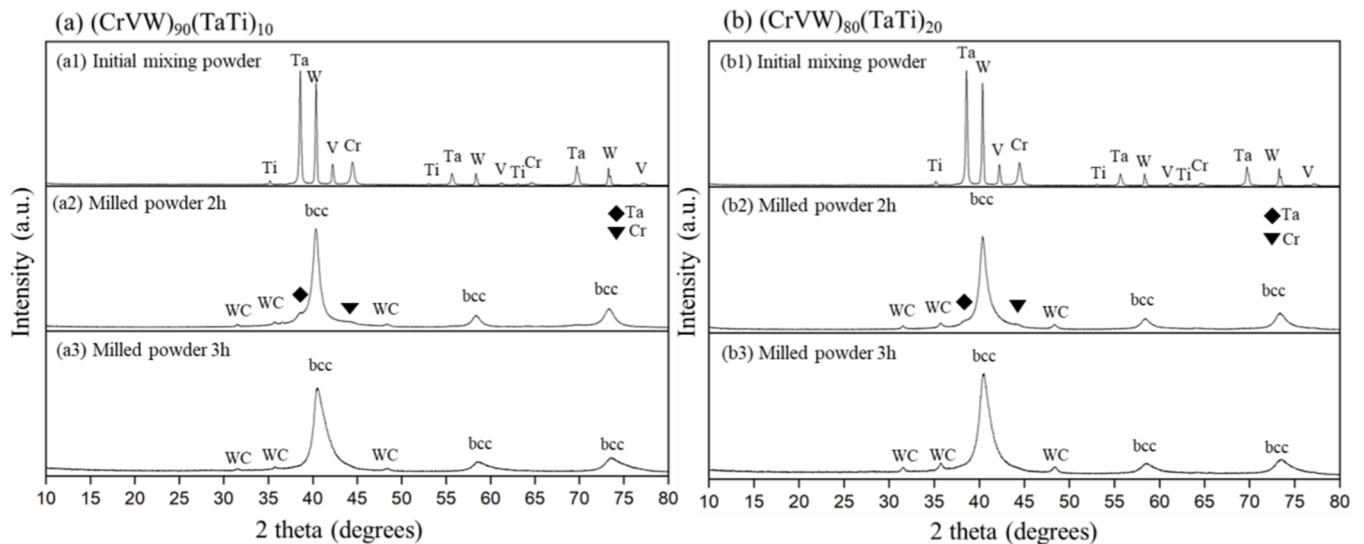


Fig. 8. - Experimental diffractograms for $(\text{CrVW})_{90}(\text{TaTi})_{10}$ and (d) $(\text{CrVW})_{80}(\text{TaTi})_{20}$ compositions. Experimental diffractograms for (a1) and (b1) the initial powder mixture, (a2) and (b2) the milled powders after 2 hours of mechanical alloying at 350 rpm, and (a3) and (b3) the milled powders after a total of 3 hours of mechanical alloying at 350 rpm.

bcc type-structure with a lattice parameter of $a = 0.305$ nm. Additionally, it displayed peaks with similar intensity associated with the intermetallic $\text{Ta}_{0.5}\text{V}_{0.5}$, which has a bcc type structure and exhibits a lattice parameter of $a = 0.317$ nm, as well as the CdI_2 - PbI_2 polytype carbide Ta_2C phase. The presence of such carbides was observed in similar high entropy alloys, WTaTiVCr [39], produced under the same conditions as the materials presented in this paper, with identical lattice parameters. This similarity may be attributed to the use of graphite dies during sintering. Fig. 10 (b) exhibits the experimental diffractogram for the $(\text{CrVW})_{80}(\text{TiTa})_{20}$ sample. A bcc type-structure was observed on the diffractogram exhibiting the highest intensity peak with a lattice parameter of $a = 0.307$ nm.

Additionally, another bcc type-structure (identified with a black star)

displaying a lattice parameter of $a = 0.317$ nm, which corresponds to an intermetallic $\text{Ta}_{0.5}\text{V}_{0.5}$ with a bcc type-structure. Moreover, peaks (identified with a black circle and black diamonds) corresponding to CdI_2 - PbI_2 polytype simulated carbide (Ta_2C) and an unidentified peak, respectively, were also identified. The system's thermodynamic behavior can explain the $\text{Ta}_{0.5}\text{V}_{0.5}$ phase observed in the XRD patterns. As shown in Figs. 3 and 4, the Ta-V SRO parameter approaches zero above 1500 K, indicating a neutral interaction at the sintering temperature, with neither strong attraction nor repulsion. This suggests that phase formation is primarily thermodynamically driven rather than dictated by chemical short range ordering. Additionally, below 1500 K, a positive Ta-V SRO (repulsion) is observed, indicating phase stability cannot be inferred from SRO alone. If the overall thermodynamic

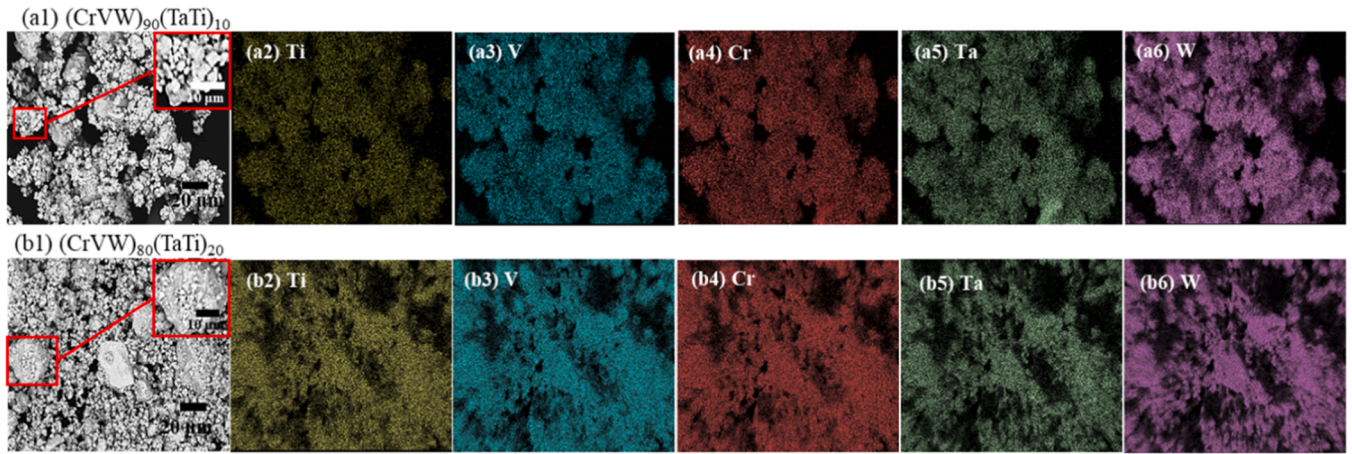


Fig. 9. - BSE images of the milled powders of (a) $(\text{CrVW})_{90}(\text{TaTi})_{10}$ and (b) $(\text{CrVW})_{80}(\text{TaTi})_{20}$ compositions, together with EDS maps for (a2) and (b2) Ti-K α , (a3) and (b3) V-K α , (a4) and (b4) Cr-K α , (a5) and (b5) Ta-L α , and (a6) and (b6) W-L α X-ray lines.

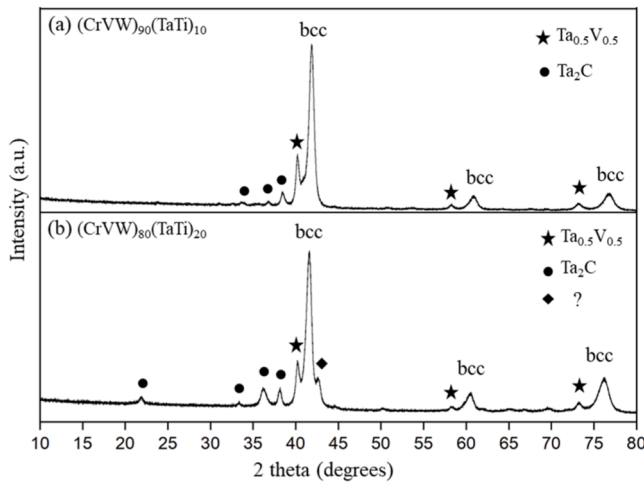


Fig. 10. - Experimental diffractograms for (a) $(\text{CrVW})_{90}(\text{TaTi})_{10}$ and (d) $(\text{CrVW})_{80}(\text{TaTi})_{20}$ compositions. A black star and circle indicate the presence of $\text{Ta}_{0.5}\text{V}_{0.5}$, and Ta_2C , respectively. Black diamonds indicate the presence of an unidentified peak.

balance favors the Ta-V configuration, the phase can remain stable despite locally positive SRO values at temperatures below 1500 K. This can provide valuable experimental information to incorporate into the simulation parameters to improve accuracy or to optimize the Ta or V concentration.

The $(\text{CrVW})_{90}(\text{TaTi})_{10}$ microstructure is shown in Fig. 11, featuring a subnanometric microstructure with black spots and a major phase containing small particles. The sample densities were measured, with densification around 98%. No porosity was observed in the microstructure, corroborating the high densification values. Figs 11 (b) to (f) show the EDS maps for the $(\text{CrVW})_{90}(\text{TaTi})_{10}$ sample, indicating an almost homogeneous distribution of all elements as well as an extremely fine microstructure. The dark areas in Figs 11 (a) and (b) point to a titanium-rich phase. In contrast, the small light areas correspond to tungsten-rich regions in Figs 11(a) and 11 (f). Moreover, Fig. 12 displays the SEM images and EDS maps for the $(\text{CrVW})_{80}(\text{TaTi})_{20}$ sample, which shows a microstructure similar to that of $(\text{CrVW})_{90}(\text{TaTi})_{10}$. Due to the subnanometric microstructure, it is extremely difficult to characterize the phases present in both samples.

Fig. 13 exhibits the representative EDS spectra for the consolidated $(\text{CrVW})_{80}(\text{TaTi})_{20}$ and (b) $(\text{CrVW})_{90}(\text{TaTi})_{10}$ high entropy alloy. As

shown in Fig. 13, only a very weak carbon signal is detected in both samples, indicating that any potential carbon contamination introduced during the SPS process is negligible and does not significantly affect the overall chemical composition of the alloys. Furthermore, no evidence of oxide or nitride contamination is observed in either sample.

Due to the fine microstructures of the alloys, a heat treatment was performed on $(\text{CrVW})_{90}(\text{TaTi})_{10}$ and $(\text{CrVW})_{80}(\text{TaTi})_{20}$ in a tubular furnace under vacuum at 1523 K for 8 days. The experimental diffractogram of the annealed $(\text{CrVW})_{90}(\text{TaTi})_{10}$ alloy is shown in Fig. 14 (a), which demonstrates the appearance of a bcc-type structure with a lattice parameter of $a = 0.312$ nm (presented as bcc₁). It exhibits a minor bcc-type structure with a lattice parameter of $a = 0.296$ nm (presented as bcc₂). Also, it is possible to observe the presence of non-identified weak peaks indicated as a black diamond in Fig. 14 (a). The experimental diffractogram of the annealed $(\text{CrVW})_{80}(\text{TaTi})_{20}$, shown in Fig. 14 (b), exhibits the appearance of a bcc-type structure with a lattice parameter of $a = 0.311$ nm. Another phase identified after heat treatment was a C14 type Laves phase (indicated by a black square). The phase simulated from Pearson crystal data [29] to compare with the peaks of the experimental diffractograms was Cr_2Ta , which has an HCP (hexagonal close-packed) C14 Laves-type structure. However, the Cr_2Ta lattice parameter does not match the experimental diffraction pattern. A simulated AB₂ intermetallic $\text{Fe}_2\text{Ta}_{0.5}\text{W}_{0.5}$ appears to fit well with the X-ray pattern of $(\text{CrVW})_{80}(\text{TaTi})_{20}$, however, there is no iron in our HEA systems. Hence, the only possibility is to replace Fe with Cr, given their similar atomic radii and still displaying a C14 AB₂ stoichiometry. The Laves phase is common in alloys with elements that differ significantly in atomic size, especially during SPS and subsequent annealing at elevated temperatures. Zareipour, Farzaneh [40] shows HEA with intermetallic AB₂ (or B₂A) stoichiometry compounds, where the bigger atomic radius atoms (such as W, Ti, Mo, Zr, Ta) occupy the A sites while the smaller atoms (such as Cr, Fe, V) occupy the B sites [40]. A similar AB₂ Laves phase was clearly observed before [30], in which a bcc-type structure with a hexagonal C14 Laves phase was reported in chromium- and vanadium-based HEAs. Larry Kaufman [31] studied the thermodynamics of the Cr-Ta-W system by combining Ab Initio and CALPHAD methods, demonstrating the possibility of C14 Laves phases in the Cr-Ta-W system.

Fig. 15 (a) shows the SEM image of the heat treated $(\text{CrVW})_{90}(\text{TaTi})_{10}$ sample, revealing microstructural grain growth and multiple distinct phases. This growth is created by diffusion between the elements, which generated the present phases. Nevertheless, the microstructure still shows sub-nanometric features. Five phases were identified: a darker phase, three intermediate phases, and a lighter phase. The darker phases (indicated by the purple arrow in Fig. 15 (a))

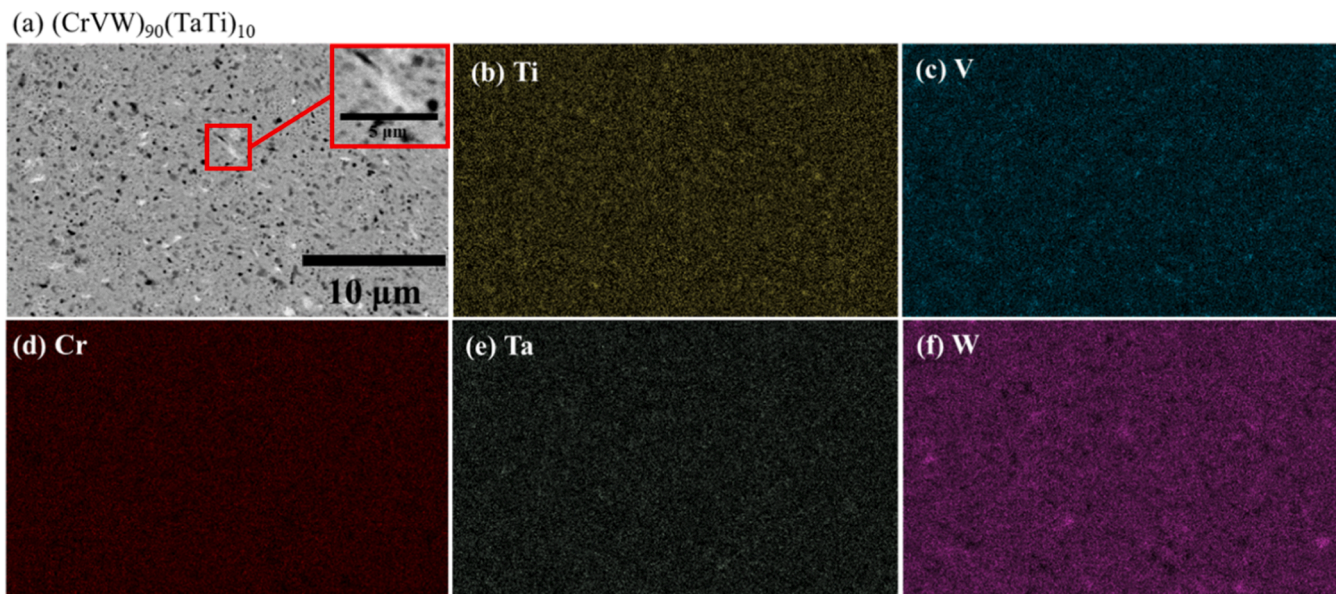


Fig. 11. - (a) SEM images of the samples (a) consolidated spark plasma sintering $(\text{CrVW})_{90}(\text{TaTi})_{10}$ sample. EDS maps for (b) Ti-K α , (c) Cr-K α , (d) Ta, L α , and (e) W-L α X-ray lines.

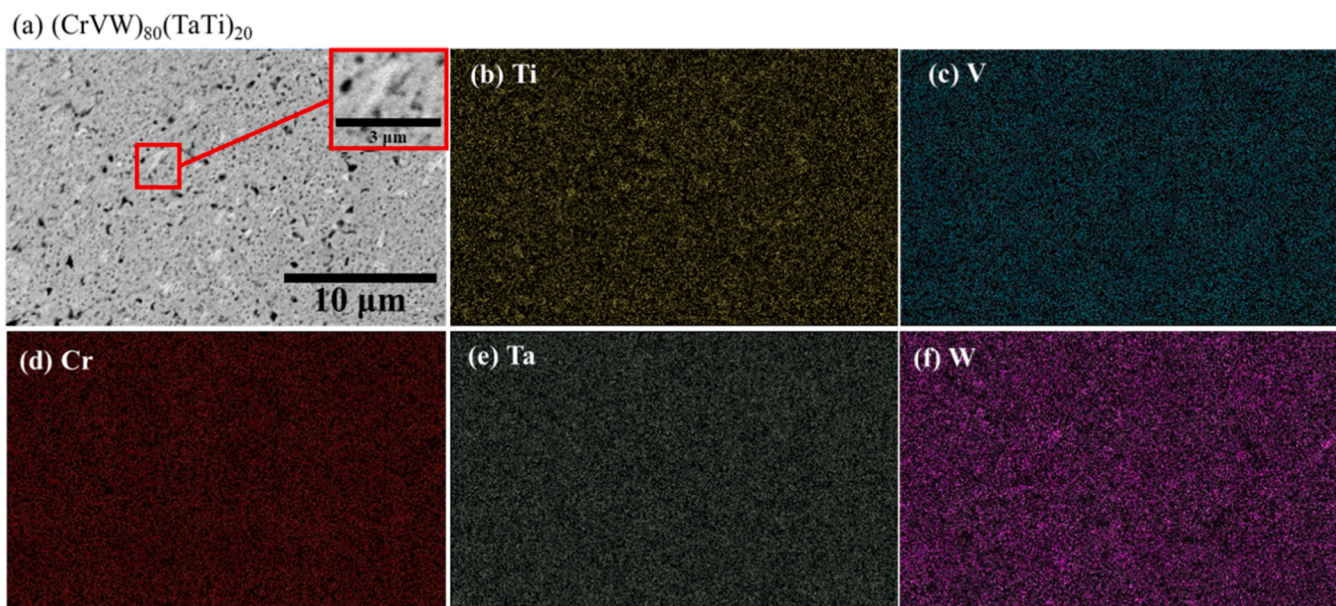


Fig. 12. - (a) SEM images of the samples (a) consolidated spark plasma sintering $(\text{CrVW})_{80}(\text{TaTi})_{20}$ sample. EDS maps (b) Ti-K α , (c) Cr-K α , (d) Ta, L α , and (e) W-L α X-ray lines.

and (b)) correspond to a Ti-rich phase. The intermediate phases correspond to V, Ta, and Cr-rich phases (indicated by the green, blue, and orange arrows in Fig. 15 (c), (d), and (e)), and the light phase corresponds to the W-rich areas (indicated by the yellow arrow in Fig. 15 (a) and (f)). A similar microstructure was observed in the $(\text{CrVW})_{80}(\text{TaTi})_{20}$ composition shown in Fig. 16. However, upon examining the microstructure, Ta, Cr, and V appear to be more evenly distributed.

It is worth noting that most diffusion studies on high-entropy alloys focus on fcc-type structures due to their relatively well-characterized and straightforward nature, leading to low lattice distortion and strain [41–43]. In contrast, body centered cubic structures can exhibit significant distortions and higher lattice strain, which strongly influence diffusion behavior [44,45]. Before heat treatment, both alloys exhibited subnanometric microstructures that were difficult to characterize.

However, post heat treatment analysis revealed apparent differences in phase evolution. The $(\text{CrVW})_{90}(\text{TaTi})_{10}$ alloy developed five distinct phases (Fig. 15), while the $(\text{CrVW})_{80}(\text{TaTi})_{20}$ alloy, shown in Fig. 16, displayed four phases. However, small Cr- and V-rich areas form an intermediate, darker phase (identified with the orange arrow in Figs. 16 (a), (c), and (d)). Since both samples were heat treated under the same conditions, this disparity suggests that the $(\text{TaTi})_{10}$ composition promoted the formation of a new phase when compared with the $(\text{TaTi})_{20}$ one. Tantalum and titanium have atomic radii of 0.143 nm and 0.146 nm [46], respectively, which are significantly larger than those of Cr, V, and W. As a result, increasing the (TaTi) content and decreasing (CrVW) concentrations led to a higher atomic size difference (δ) within the crystal structure, a key parameter in high entropy alloy thermodynamic calculation, that powers the solid solution crystal structure development

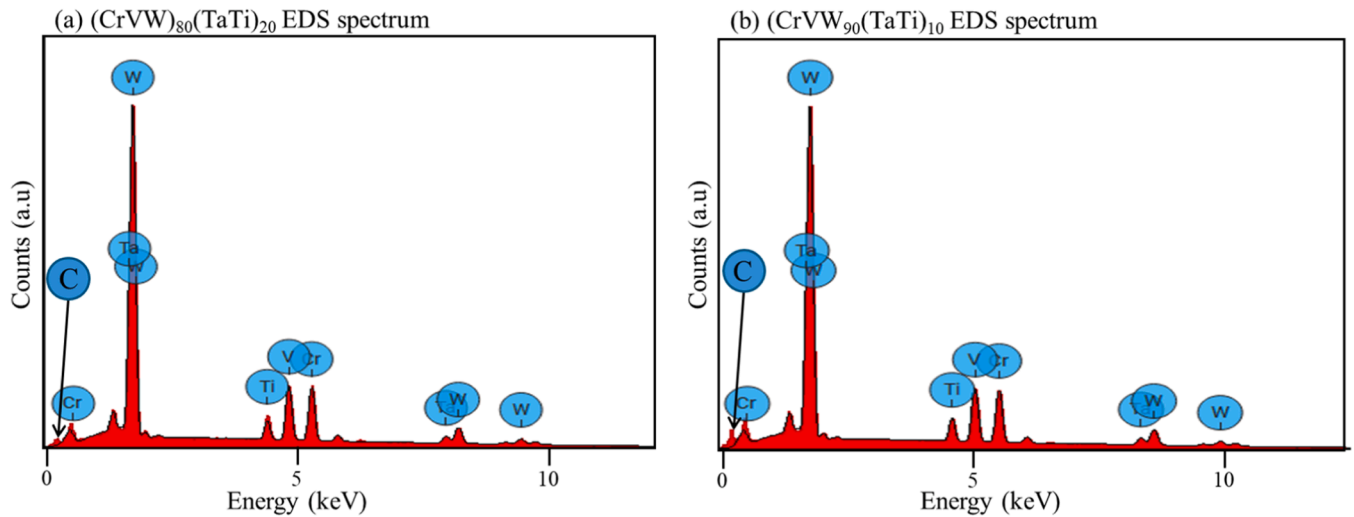


Fig. 13. – EDS spectra for as-sintered (CrVW)₈₀(TaTi)₂₀ and (b) (CrVW)₉₀(TaTi)₁₀ high entropy alloy.

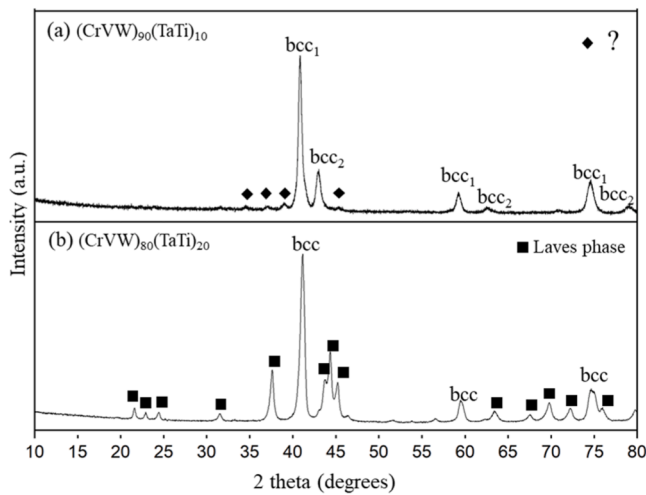


Fig. 14. - Experimental diffractograms for annealed (a) (CrVW)₉₀(TaTi)₁₀ samples and (d) annealed (CrVW)₈₀(TaTi)₂₀ samples. Black diamond indicates the presence of unknown phases, and the black square indicates the presence of the Laves phase.

[34], raising it from $\delta = 4.6$ in (CrVW)₉₀(TaTi)₁₀ to $\delta = 5.6$ for (CrVW)₈₀(TaTi)₂₀. This increase in δ likely contributes to the so-called sluggish diffusion effect, a characteristic often attributed to HEAs. This phenomenon is driven by complex, disordered local bonding environments that elevate the activation energy for atomic migration, thereby slowing diffusion. Consequently, the higher Ta and Ti content are expected to suppress phase growth by hindering atomic mobility. Our results support this: the alloy with greater δ exhibited fewer phases after heat treatment, indicating a higher degree of sluggish diffusion, which aligns with the experimental results. This could stem from a combination of mass disorder, increased lattice strain, and/or altered local structural dynamics. Razumovsky [35] noted that different diffusion mechanisms vary among elements. While Ta, Nb, Mo, and Hf primarily diffuse via the vacancy mechanism, Zr and Ti diffuse through the much faster interstitial mechanism.

Furthermore, simulation results indicate that W-Ta and W-Ti exhibit a strong negative CSRO below 1500 K, suggesting a higher probability of segregation. Considering that the ODTT is around 1300 K, the consolidated temperature at 1673 K might not be sufficient to promote complete diffusion of the elements into the microstructure. This incomplete

diffusion process may also contribute to the formation of phases and/or intermetallic compounds. In addition, simulation results show that increasing Ta and Ti concentrations and decreasing Cr, W, and V concentrations lead to a significant change in CSRO between (CrVW)₉₀(TaTi)₁₀ and (CrVW)₈₀(TaTi)₂₀. A weaker CSRO simulated between Ta and Ti observed in (CrVW)₈₀(TaTi)₂₀, together with a stronger Cr and V bonding pair, could lead to the formation of the four phases microstructure on this system, while the (CrVW)₉₀(TaTi)₁₀ HEA exhibits a stronger Ta and Ti CSRO and a weaker Cr and V bonding pair, which could lead to the formation of a microstructure with five phases. Although these phenomena are interesting, they require further characterization to be conclusive.

3.4. Thermal diffusivity

Fig. 17 illustrates the thermal diffusivity of the (CrVW)₈₀(TaTi)₂₀ and (CrVW)₉₀(TaTi)₁₀ high-entropy alloys over the range of 300 to 1000 K. Both samples exhibited a similar thermal diffusivity behavior as a function of temperature, with diffusivity values increasing as the temperature rises, reaching values between 7 mm²/s and 9 mm²/s. The (CrVW)₉₀(TaTi)₁₀ exhibited slightly higher thermal diffusivity values than (CrVW)₈₀(TaTi)₂₀. Compared to pure tungsten [47] and CuCrZr [48,49], both (CrVW)₈₀(TaTi)₂₀ and (CrVW)₉₀(TaTi)₁₀ high entropy alloys demonstrate significantly lower diffusivity values. As proposed by the author in [50], the enhanced thermal diffusivity observed at higher temperatures in HEAs is attributed to lattice dilation, which lengthens the phonon mean free path as temperature rises. In high entropy alloys, the phonon mean free path is short due to atomic-level disorder, resulting in high phonon scattering rates. Tantalum and titanium have atomic radii of 0.143 nm and 0.146 nm [46], respectively, which are significantly larger than those of Cr, V, and W. As a result, increasing the (TaTi) content and decreasing the (CrVW) concentrations led to a larger atomic size difference (δ), which can account for the small changes in thermal diffusivity observed. HEA works like VFeTiTaW [22], (CrFe-TaTi)₇₀W₃₀ [21], and W₅₇Ta₂₁V₁₁Ti₈Cr₃ alloys [44], which report similar thermal diffusivity values at elevated temperatures, in the range of 3 to 10 mm²/s.

4. Conclusions

This study investigated the structural evolution of the high entropy alloys (CrVW)₉₀(TaTi)₁₀ and (CrVW)₈₀(TaTi)₂₀ systems as potential thermal barriers to reduce the mismatch between tungsten plasma facing components and CuCrZr heat sinks in nuclear fusion divertors.

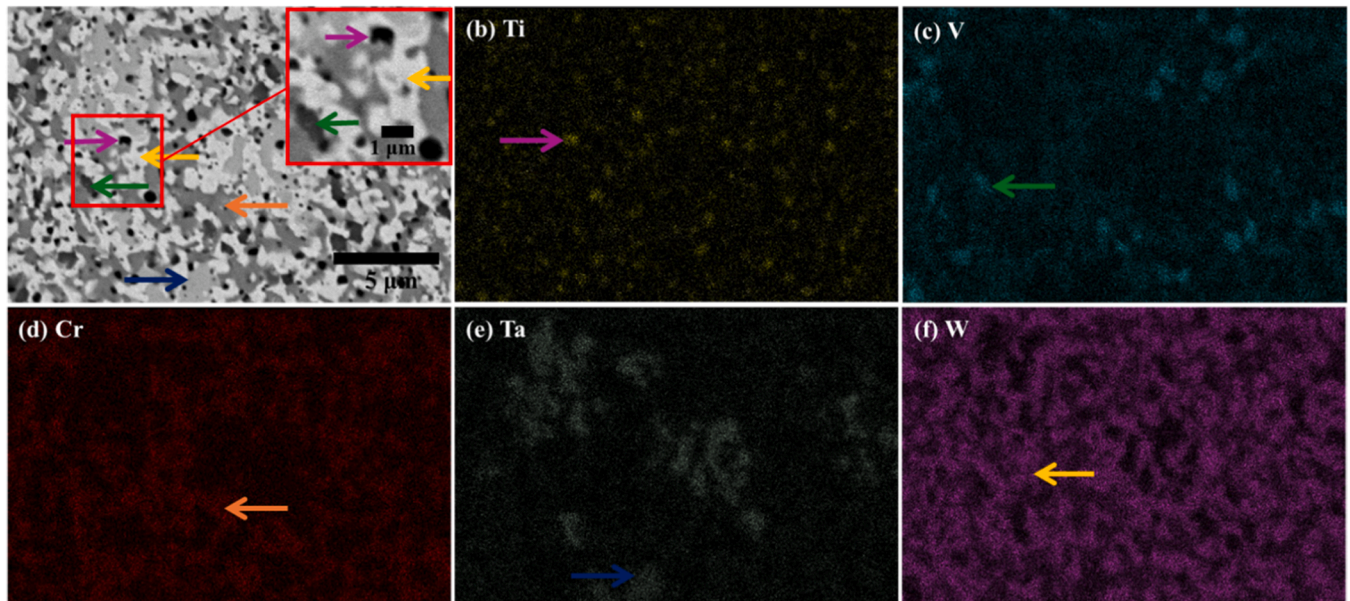
(a) $(\text{CrVW})_{90}(\text{TaTi})_{10}$ HT

Fig. 15. - (a) SEM images of the samples (a) consolidated annealed spark plasma sintering $(\text{CrVW})_{90}(\text{TaTi})_{10}$ sample. EDS maps for Ti-K α , (c) Cr-K α , (d) Ta-L α , and (e) W-L α X-ray lines.

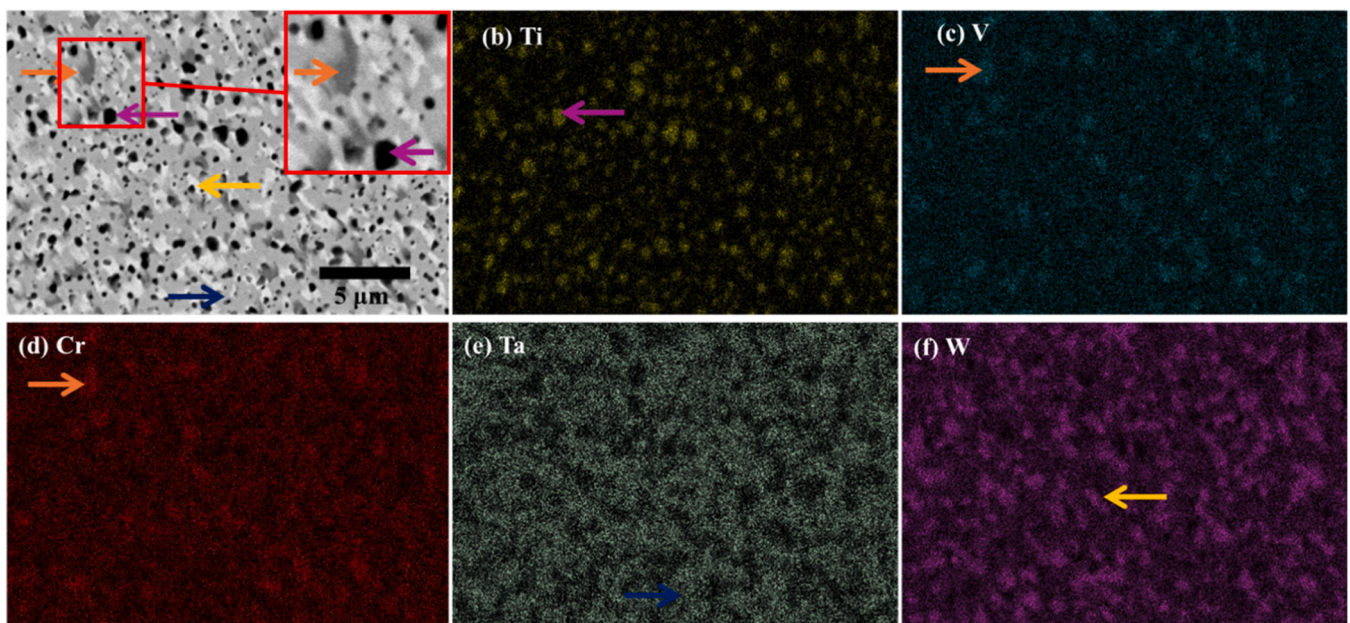
(a) $(\text{CrVW})_{80}(\text{TaTi})_{20}$ HT

Fig. 16. - (a) SEM images of the samples (a) consolidated annealed spark plasma sintering $(\text{CrVW})_{80}(\text{TaTi})_{20}$ sample. EDS maps for (b) Ti-K α , (c) Cr-K α , (d) Ta-L α , L α , and (e) W-L α X-ray lines.

Atomistic simulations showed temperature-dependent bonding and segregation trends up to 1500 K, with preferential bonding between W-Ta and W-Ti chemical pairs. The chemical short-range order (CSRO) and order-disorder transition temperature (ODTT) provide important insights into the bonding strength between all elements, leading to the conclusion that increasing the concentrations of Ta and Ti will result in a comparable microstructure at lower temperatures. This is supported by the thermodynamic ODTT limit, which shows that alloys with higher Ta and Ti concentrations exhibit greater segregation, reflecting the driving force between W and Cr at higher temperatures.

It is important to emphasize that the presence study of phase stability in HEAs only includes configuration entropy configuration within the CE formalism. The vibrational contribution to free energy calculations using the same DFT training data base can be considered within machine learned interatomic potentials (MLIPs) approach where the hydride MC and molecular dynamic simulations are performed [52]. Using MLIPs approach, it is also possible to predict the melting temperature in the subsystem system of the present HEAs as it has been shown in [53]. Last but not least the phase stability of HEAs can be characterized not only by the CSRO as it has been analyzed in this work but also by long-range

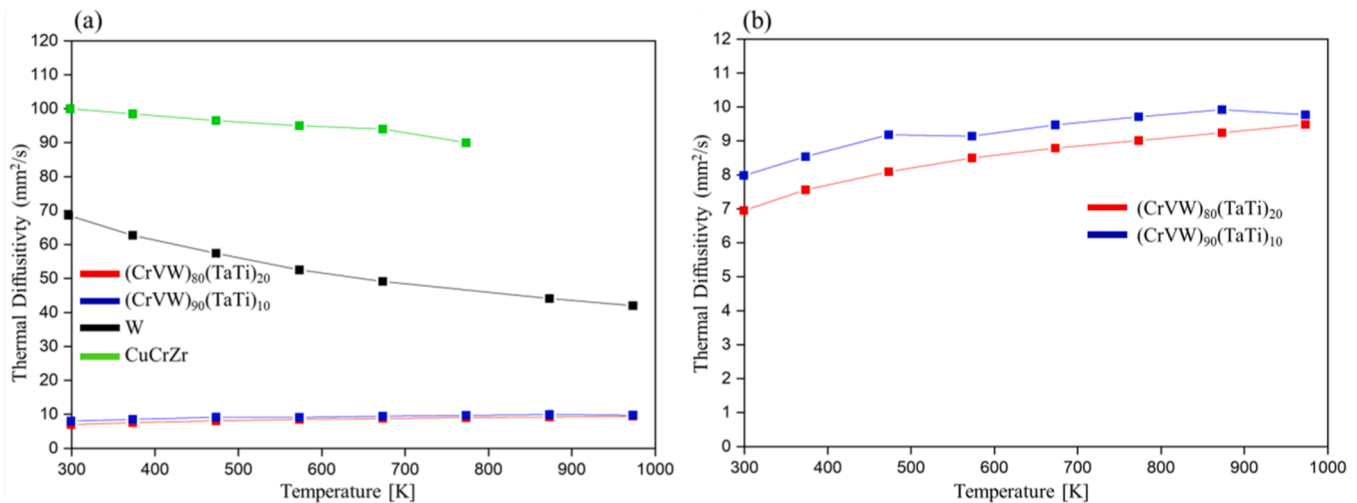


Fig. 17. - Thermal diffusivity of (CrVW)₉₀(TaTi)₁₀ and (CrVW)₉₀(TaTi)₁₀ consolidated sample together with pure W [51], and CuCrZr [48,49].

order as it has been investigated by using multi-cell Monte Carlo method as it is outlined in [54,55]. SEM images of both systems revealed a subnanometric microstructure after sintering. Due to grain growth following annealing, the microstructure evolved into a (CrVW)₈₀(TaTi)₂₀ with four phases and a (CrVW)₉₀(TaTi)₁₀ with five phases. After annealing treatment, it is evident that (CrVW)₉₀(TaTi)₁₀ exhibits a lower sluggish diffusion effect compared to (CrVW)₈₀(TaTi)₂₀. This is an occurrence reinforced due to the difference in atomic size (δ), rising from 4.6 in (CrVW)₉₀(TaTi)₁₀ to 5.6 for (CrVW)₈₀(TaTi)₂₀, and a significant change in CSRO values between (Ta and Ti) and (Cr and V) exhibited amongst (CrVW)₉₀(TaTi)₁₀ and (CrVW)₈₀(TaTi)₂₀. The thermal diffusivity values increase as the temperature rises, reaching values between 7 mm²/s and 9 mm²/s for both (CrVW)₉₀(TaTi)₁₀ and (CrVW)₈₀(TaTi)₂₀. These values are well within the range of other known HEA values. Overall, the simulations underscore the crucial role of computational modeling in elucidating phase stability and atomic interactions of each element in HEAs. Further characterization, particularly through transmission electron microscopy (TEM) or atomic probe tomography (APT), should be performed to provide additional information and lay the groundwork for future investigations into their functional and mechanical properties.

CRediT authorship contribution statement

R. Martins: Validation, Methodology, Formal analysis, Data curation. **S. de Lara:** Validation, Formal analysis. **F. Neves:** Methodology. **A. Sá:** Methodology. **P. Luz:** Methodology. **A.P. Gonçalves:** Methodology. **A. Galatanu:** Methodology, Investigation. **D. Sobieraj:** Methodology, Formal analysis, Data curation. **D. Nguyen-Manh:** Methodology, Formal analysis, Data curation. **M. Dias:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Marta Dias reports financial support was provided by Instituto Superior Técnico, Universidade de Lisboa. Marta Dias reports a relationship with Instituto Superior Técnico that includes: employment. No conflict of interests.

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Data availability

Data will be made available on request.

References

- [1] C.-J. Tong, et al., Mechanical performance of the Al x CoCrCuFeNi high-entropy alloy system with multiprincipal elements, *Metall. Mater. Trans. A* 36 (5) (2005) 1263–1271, <https://doi.org/10.1007/s11661-005-0218-9>. May.
- [2] ITER, <https://www.iter.org/proj/inafewlines#4>, 2022.
- [3] J.N. Brooks, et al., Plasma-surface interaction issues of an all-metal ITER, *Nucl. Fusion* 49 (3) (2009), <https://doi.org/10.1088/0029-5515/49/3/035007>.
- [4] P.M. Raole, S.P. Deshpande, Structural materials for fusion reactors, *Trans. Indian Inst. Met.* 62 (2) (2009) 105–111, <https://doi.org/10.1007/s12666-009-0014-0>.
- [5] V. Barabash, et al., Materials challenges for ITER - current status and future activities, *J. Nucl. Mater.* 367–370 A (SPEC. ISS) (2007) 21–32, <https://doi.org/10.1016/j.jnucmat.2007.03.017>.
- [6] V. Barabash, et al., Materials challenges for ITER - current status and future activities, *J. Nucl. Mater.* 367–370 A (SPEC. ISS) (2007) 21–32, <https://doi.org/10.1016/j.jnucmat.2007.03.017>.
- [7] A.J. Cackett, H.T. Vo, J.J.H. Lim, A.J. Bushby, P. Hosemann, C.D. Hardie, Effects of radiation damage and precipitate distribution on micro-pillar compression testing of irradiated CuCrZr, *J. Nucl. Mater.* 553 (2021), <https://doi.org/10.1016/j.jnucmat.2021.153028>.
- [8] T.R. Barrett, et al., Enhancing the DEMO divertor target by interlayer engineering, *Fusion Eng. Des.* 98–99 (2015) 1216–1220, <https://doi.org/10.1016/j.fusengdes.2015.03.031>.
- [9] J.H. You, et al., European DEMO divertor target: operational requirements and material-design interface, *Nucl. Mater. Energy* 9 (2016) 171–176, <https://doi.org/10.1016/j.nme.2016.02.005>.
- [10] P.-K. Huang, J.-W. Yeh, T.-T. Shun, S.-K. Chen, Multi-principal-element alloys with improved oxidation and wear resistance for thermal spray coating, *Adv. Eng. Mater.* 6 (12) (2004) 74–78, <https://doi.org/10.1002/adem.200300507>.
- [11] M. Fursdon, et al., The development and testing of the thermal break divertor monoblock target delivering 20MWm⁻² heat load capability, *Phys. Scr.* 2017 (T170) (2017), <https://doi.org/10.1088/1402-4896/aa8c8e>.

- [12] D.J.M. King, et al., High temperature zirconium alloys for fusion energy, *J. Nucl. Mater.* 559 (2022) 153431, <https://doi.org/10.1016/j.jnucmat.2021.153431>.
- [13] A. Rodríguez-López, B. Savoini, M.A. Monge, A. Galatanu, M. Galatanu, Evaluation of the V (Ti, Ta, W, Mo) for nuclear fusion applications, *Nucl. Mater. Energy* 41 (April) (2024) 101767, <https://doi.org/10.1016/j.nme.2024.101767>.
- [14] C.-Y. Hsu, J.-W. Yeh, S.-K. Chen, T.-T. Shun, Wear resistance and high-temperature compression strength of fcc CuCoNiCrAl_{0.5}Fe alloy with boron addition, *Metall. Mater. Trans. A* 35 (5) (2004) 1465–1469, <https://doi.org/10.1007/s11661-004-0254-x>.
- [15] Y.Y. Chen, U.T. Hong, H.C. Shih, J.W. Yeh, T. Duval, Electrochemical kinetics of the high entropy alloys in aqueous environments - A comparison with type 304 stainless steel, *Corros. Sci.* 47 (11) (2005) 2679–2699, <https://doi.org/10.1016/j.corsci.2004.09.026>.
- [16] M. Dias, et al., CuxCrFeMoTi (x = 0.21, 0.44, 1) high entropy alloys as novel materials for fusion applications, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.* 238–239 (October) (2018) 18–25, <https://doi.org/10.1016/j.mseb.2018.11.026>.
- [17] M.-H. Tsai, et al., Thermal stability and performance of NbSiTaTiZr high-entropy alloy barrier for copper metallization, *J. Electrochem. Soc.* 158 (11) (2011) H1161, <https://doi.org/10.1149/2.056111jes>.
- [18] H.P. Chou, Y.S. Chang, S.K. Chen, J.W. Yeh, Microstructure, thermophysical and electrical properties in AlxCoCrFeNi (0 ≤ x ≤ 2) high-entropy alloys, *Mater. Sci. Eng. B* 163 (3) (2009) 184–189, <https://doi.org/10.1016/j.mseb.2009.05.024>.
- [19] I. Toda-Caraballo, P.E.J. Rivera-Díaz-Del-Castillo, A criterion for the formation of high entropy alloys based on lattice distortion, *Intermetallics* 71 (2016) 76–87, <https://doi.org/10.1016/j.intermet.2015.12.011>.
- [20] J.-W. Yeh, Recent progress in high-entropy alloys, *Eur. J. Control - EUR J Control* 31 (2006) 633–648, <https://doi.org/10.3166/acsm.31.633-648>, Dec.
- [21] R. Martins, et al., Influence of Cr on the quaternary FeTaTiW medium entropy alloy, *J. Mater. Sci. Mater. Eng.* 20 (1) (2025) 1–13, <https://doi.org/10.1186/s40712-025-00256-1>.
- [22] R. Martins, et al., Simulation, structural, thermal and mechanical properties of the FeTiTaVW high entropy alloy, *Metals* 14 (436) (2024), <https://doi.org/10.3390/met14040436>.
- [23] Y. Chen, et al., Effect of Ti content on the microstructure and properties of CoCrFeNiMnTi_x high entropy alloy, *Entropy* 24 (2) (2022) 1–11, <https://doi.org/10.3390/entropy24020241>.
- [24] B. Sun, et al., Thermodynamic assessment of the quaternary WTaCrV refractory high entropy alloy as a means to guide experimental approaches, *Acta Mater.* 299 (August) (2025) 121435, <https://doi.org/10.1016/j.actamat.2025.121435>.
- [25] A. Fernández-Caballero, J.S. Wróbel, P.M. Mummery, D. Nguyen-Manh, Short-range order in high entropy alloys: theoretical formulation and application to Mo-Nb-Ta-V-W system, *J. Phase Equilibria Diffus.* 38 (4) (2017) 391–403, <https://doi.org/10.1007/s11669-017-0582-3>.
- [26] F.R.A.N.C.O.I. Ducastelle, Order and phase stability in alloys. Interatomic Potential and Structural Stability, Springer, Berlin Heidelberg, 1993, https://doi.org/10.1007/978-3-642-84968-8_14.
- [27] Q. Wu, B. He, T. Song, J. Gao, S. Shi, Cluster expansion method and its application in computational materials science, *Comput. Mater. Sci.* 125 (2016) 243–254, <https://doi.org/10.1016/j.commatsci.2016.08.034>.
- [28] R. Chinnappan, B.K. Panigrahi, A. van de Walle, First-principles study of phase equilibrium in Ti–V, Ti–Nb, and Ti–Ta alloys, *Calphad Comput. Coupling Phase Diagr. Thermochem.* 54 (2016) 125–133, <https://doi.org/10.1016/j.calphad.2016.07.001>.
- [29] J.M. Sanchez, Foundations and practical implementations of the cluster expansion, *J. Phase Equilibria Diffus.* 38 (3) (2017) 238–251, <https://doi.org/10.1007/s11669-017-0521-3>.
- [30] J.M. Sanchez, F. Ducastelle, D. Gratias, Generalized cluster description of multicomponent systems, *Phys. A Stat. Mech. Appl.* 128 (1–2) (1984) 334–350, [https://doi.org/10.1016/0378-4371\(84\)90096-7](https://doi.org/10.1016/0378-4371(84)90096-7).
- [31] A.M.F. Fernández-Caballero, J.S. Wróbel, P.M. Mummery, D. Nguyen-Manh, Configurational entropy in multicomponent alloys : matrix formulation from ab initio based hamiltonian and application to the FCC Cr-Fe-Mn-Ni system, *Entropy* 21 (1) (2019) 68, <https://doi.org/10.3390/entropy21010068>.
- [32] D. Sobieraj, et al., Chemical short-range order in derivative Cr–Ta–Ti–V–W high entropy alloys from the first-principles thermodynamic study, *Phys. Chem. Chem. Phys.* 22 (41) (2020) 23929–23951, <https://doi.org/10.1039/d0cp03764h>.
- [33] D. Sobieraj, “Phase stability and short-range ordering of W-based SMART materials and high-entropy alloys predicted from first-principles modelling,” Warsaw University of Technology, 2025.
- [34] S. Guo, C.T. Liu, Phase stability in high entropy alloys: formation of solid-solution phase or amorphous phase, *Prog. Nat. Sci. Mater. Int.* 21 (6) (2011) 433–446, [https://doi.org/10.1016/S1002-0071\(12\)60080-X](https://doi.org/10.1016/S1002-0071(12)60080-X).
- [35] Y. Zhang, Y.J. Zhou, J.P. Lin, G.L. Chen, P.K. Liaw, Solid-solution phase formation rules for multi-component alloys, *Adv. Eng. Mater.* 10 (6) (2008) 534–538, <https://doi.org/10.1002/adem.200700240>.
- [36] B.E. Warren, X-ray diffraction, Dover Publications, 1990.
- [37] J.M. Cowley, An approximate theory of order in alloys, *Phys. Rev.* 77 (5) (1950) 669–675, <https://doi.org/10.1103/PhysRev.77.669>.
- [38] X. Qi, N. Cai, T. Chen, S. Wang, B. Li, Experimental and theoretical studies on the elasticity of tungsten to 13 GPa, *J. Appl. Phys.* 124 (7) (2018), <https://doi.org/10.1063/1.5044519>.
- [39] S. Alvi, O.A. Waseem, F. Akhtar, High temperature performance of spark plasma sintered w_{0.5}(tativcr)_{0.5} alloy, *Metals* 10 (11) (2020) 1–12, <https://doi.org/10.3390/met10111512>.
- [40] F. Zareipour, H. Shahmir, Y. Huang, Formation and significance of topologically close-packed laves phases in refractory high-entropy alloys, *J. Alloys. Compd.* 986 (2024) 174148, <https://doi.org/10.1016/j.jallcom.2024.174148>, September 2023.
- [41] J. Dąbrowa, W. Kucza, G. Cieślak, T. Kulik, M. Danielewski, J.W. Yeh, Interdiffusion in the FCC-structured Al-Co-Cr-Fe-Ni high entropy alloys: experimental studies and numerical simulations, *J. Alloys. Compd.* 674 (2016) 455–462, <https://doi.org/10.1016/j.jallcom.2016.03.046>.
- [42] J. Dąbrowa, M. Danielewski, State-of-the-art diffusion studies in the high entropy alloys, *Metals* 10 (3) (2020), <https://doi.org/10.3390/met10030347>.
- [43] M.S. Daw, M. Chandross, Sluggish diffusion in random equimolar FCC alloys, *Phys. Rev. Mater.* 5 (4) (2021) 43603, <https://doi.org/10.1103/PhysRevMaterials.5.043603>.
- [44] S.V. Divinski, A.V. Pokoev, N. Esakirajra, A. Paul, A mystery of ‘sluggish diffusion’ in high-entropy alloys: the truth or a myth? *Diffus. Found.* 17 (2018) 69–104, <https://doi.org/10.4028/www.scientific.net/df.17.69>.
- [45] M.I. Razumovsky, B.S. Bokstein, A.O. Rodin, A.V. Khvan, Interdiffusion in refractory metal system with a BCC lattice: Ti/TiZrHfNbTaMo, *Entropy* 25 (3) (2023) 1–22, <https://doi.org/10.3390/entropy25030490>.
- [46] O.N. Senkov, D.B. Miracle, Effect of the atomic size distribution on glass forming ability of amorphous metallic alloys, *Mater. Res. Bull.* 36 (12) (2001) 2183–2198, [https://doi.org/10.1016/S0025-5408\(01\)00715-2](https://doi.org/10.1016/S0025-5408(01)00715-2).
- [47] C. Pradère, J.M. Goyhenèche, J.C. Batsale, S. Dilhaire, R. Pailler, Thermal diffusivity measurements on a single fiber with microscale diameter at very high temperature, *Int. J. Therm. Sci.* 45 (5) (2006) 443–451, <https://doi.org/10.1016/j.ijthermalsci.2005.05.010>.
- [48] M. Rohde, et al., Intercomparison of thermal diffusivity measurements on CuCrZr and PMMA, in: *High Temp., 42, High Press.*, 2014, pp. 469–474.
- [49] F.M. Copper, CuCr1Zr. <http://www.fcx.com/>, 2024.
- [50] C.L. Lu, S.Y. Lu, J.W. Yeh, W.K. Hsu, Thermal expansion and enhanced heat transfer in high-entropy alloys, *J. Appl. Crystallogr.* 46 (3) (2013) 736–739, <https://doi.org/10.1107/S0021889813005785>.
- [51] B. Hay, et al., Uncertainty assessment for very high temperature thermal diffusivity measurements on molybdenum, tungsten and isotropic graphite, *Int. J. Thermophys.* 43 (1) (2022), <https://doi.org/10.1007/s10765-021-02926-6>.
- [52] J. Byggmästar, et al., Segregation, ordering, and precipitation in WTaV-based concentrated refractory alloys, *Acta Mater.* 296 (June) (2025) 121276, <https://doi.org/10.1016/j.actamat.2025.121276>.
- [53] J.S. Wr, et al., Data-driven prediction of thermoelastic and defect properties of Ti-V-Ta-W high-entropy alloys up to the melting point, *Phys. Rev. B* 112 (22) (2025) 224110, <https://doi.org/10.1103/6xkw-m6s3>.
- [54] C. Niu, Y. Rao, W. Windl, Multi-cell Monte Carlo method for phase prediction, *NPJ. Comput. Mater. (Mc)* (2019) 1–5, <https://doi.org/10.1038/s41524-019-0259-z>.
- [55] T.D. Doležal, A.J. Samin, Adsorption of oxygen to high entropy alloy surfaces for up to 2 ML coverage using density functional theory and Monte Carlo calculations, *Langmuir* 38 (10) (2022) 3158–3169, <https://doi.org/10.1021/acs.langmuir.1c03191>.