Senary Refractory High-Entropy Alloy $\text{Cr}_x\text{MoNbTaVW}$

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Abstract

This paper demonstrates that a senary refractory high-entropy alloy $\text{Cr}_x\text{MoNbTaVW}$ can be tailored over a certain range of Cr content with the BCC structure for different microstructures and physical properties, assisted by CALPHAD simulations. Microstructure characterizations are performed using X-ray diffraction and scanning electron microscopy. Chemical micro-segregation during solidification predicted using the Scheil model generally agrees with the experimental results. The lattice constant, density, and Vickers' micro-hardness of the high-entropy alloy samples in the as-cast state are measured and discussed. For $\text{Cr}_x\text{MoNbTaVW}$, $x=2.0$ case appears exceeding the upper limit of maintaining a single BCC phase HEA, determined by the XRD patterns. The elemental dependence of the mixing thermodynamic properties (entropy, enthalpy and Gibbs energy) in BCC phase in the senary system is analyzed. The calculated entropy of mixing and enthalpy of mixing for CrMoNbTaVW are 14.7 J/K/mol and -662.5 J/mol respectively.

Keywords

Alloy design; High entropy alloy; CALPHAD; Microstructure; Phase diagram;

1. Introduction

Refractory alloys are used in many industry sectors—chemical processing, aerospace, and microelectronics. To design a refractory alloy, the conventional design approach is to use single principal metal refractory elements, such as W, Mo, Nb, and Ta. Using single-element based alloy design imposes limitations, not only in terms of compositional availabilities, but also the range of achievable properties. Poor low-temperature ductility and low oxidation resistance are common shortfalls for conventional refractory alloys[1].

A new alloy development strategy, namely multi-principal-element alloys or high-entropy alloys (HEAs), has been proposed by Yeh et al. [2] and developed by many researchers in recent years. The HEA approach employs five or more principal metallic elements at near equal molar ratios in a solid solution, with atomic percentage of each element varying between 5% and 35%. The high configurational entropy of mixing can stabilize solid-solution phases than intermetallic phases. As reported in literature, HEAs can be tailored to possess excellent wear and oxidation resistance [3], high temperature strength [4] and low temperature ductility [5]. Recently, a new branch of refractory alloys—refractory HEAs—has been proposed and characterized by Senkov

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et al. [6-8] by extending the HEA design concept to refractory alloys. It has been shown that the high temperature strength of refractory HEAs MoNbTaW and MoNbTaVW with the body-centered cubic (BCC) structure at high temperatures are even higher than that of conventional super-alloys [6]. Other HEA compositions, such as MoNbTaTiVW [9], HfMoTaTiZr [8], HfNbTaTiVZr [10] and HfMoNbTaTiZr [11], were also experimentally studied. However, to date the progresses in the design and validation of refractory HEAs are slow, mainly due to the lack of effective design guidance. For a typical HEA composition of more than five principal elements, the combinatorial possibilities follow factorial growth. Recently an efficient strategy was proposed by Gao and Alman [12, 13] to accelerate single-phase HEA design by integrating experimental phase diagram inspection, CALPHAD (CALculation of PHase Diagrams) modeling and first-principle density functional theoretical calculations.

The goal of this paper is to demonstrate that senary refractory high-entropy alloys $\text{Cr}_x\text{MoNbTaVW}$ ($x = 0.5, 1, \text{ and } 2$ in molar ratio) can be tailored over a certain range of Cr contents to form BCC phase HEAs with different microstructures and physical properties. The phase stability of $\text{Cr}_x\text{MoNbTaVW}$ HEAs was first evaluated using the CALPHAD method. Then experimental effort was applied to validate the phase structures, the microstructures, and the influence of Cr content. Formation of single BCC phase MoNbTaVW HEA has been reported by Senkov et al. [6] who identified all peaks on the X-ray diffraction (XRD) patterns of MoNbTaVW in the as-cast condition to be a single BCC phase, despite the presence of elemental segregation associated with the dendritic microstructure. However, proper homogenization and subsequent annealing (or thermo-mechanical processing) are required to achieve chemical homogeneity and thus to further improve mechanical and other properties.

2. CALPHAD modeling

2.1 Phase diagrams

All the CALPHAD modeling were carried out using the TCNI7 thermodynamic database via ThermoCalcTM software [14]. Although TCNI7 database is primarily optimized for Ni-based super-alloys, it does cover all the edge binaries of the Cr-Mo-Nb-Ta-V-W system. To show the influence of Cr addition to the MoNbTaVW system, the pseudo-binary phase diagram of $\text{Cr}_x\text{MoNbTaVW}$ is shown in Fig. 1. For $x \leq 5$, the BCC phase is the primary crystallization phase. With increasing Cr molar ratio, both the liquidus and solidus temperatures decrease while the solvus temperature increases. As a result, the single BCC phase field shrinks with the increasing of Cr ratio, due to the formation of competing BCC#2 phase that is rich in Cr and V, μ phase, and C15 phase. Predicted equilibrium compositions of BCC#1 and BCC#2 are listed in Table 1. The pseudo-binary phase diagram with a wider Cr content can be found in supplementary [14].

Fig. 1. Predicted pseudo-binary section of $\text{Cr}_x\text{MoNbTaVW}$

Table 1. Predidcted equilibrium phase compositions at (at.%).

Condition	Phase	Cr	Mo	Nb	Ta	V	W
x=0.5	BCC#1	6.1	19.2	19.2	19.3	17.0	19.2
T=1000 °C	BCC#2	54.8	3.0	1.9	1.0	36.0	3.3
x=1	BCC#1	5.7	20.2	20.4	20.6	13.0	20.1
T=1000 °C	BCC#2	61.0	2.6	1.5	0.8	31.4	2.7
x=2	BCC#1	16.8	17.6	17.9	18.5	11.4	17.8
T=1300 °C	BCC#2	60.6	5.4	4.4	2.9	22.0	4.7

2.2 Solidification of Cr-Mo-Nb-Ta-V-W

Predicted equilibrium and non-equilibrium solidification (Figure 2b-2d, 2f, 2h) behaviors of $\text{Cr}_x\text{MoNbTaVW}$ are shown in Figure 2. The predicted equilibrium phase mole fraction plots (Figure 2a, 2e, 2g) show formation of a single BCC phase at higher temperatures. The BCC phase starts to form at 2540 °C in CrMoNbTaVW , 2616 °C for $x = 0.5$, and 2683 °C for $x = 2$. The BCC#2 phase starts to form at $T \leq 1276$ °C for CrMoNbTaVW , $T \leq 1100$ °C for $x = 0.5$, and at $T \leq 1421$ °C for $x = 2$.

The actual cooling rate of the HEA sample preparation process, in a lab arc melting furnace, is way higher than the equilibrium assumption, thus it is expected that the observed microstructures may deviate from the predicted equilibrium solidification. The non-equilibrium solidification was simulated using the Scheil-Gulliver models [15, 16], which assumed equilibrium in the liquid but no diffusions in the solid phase(s). Only disordered BCC phase (BCC#1) was observed at $T \geq 1607$ °C for CrMoNbTaVW (Fig. 2(b)), $T \geq 1705$ °C for $x = 0.5$ (Fig. 2(e)), and $T \geq 1604$ °C for $x = 2$ (Fig. 2(g)). The BCC phase is found to be the disordered

type [14]. The elemental composition evolutions in the liquid and BCC phases during the Scheil solidification are shown in Fig. 2(c) and (d) respectively to evaluate the possible micro-segregation in CrMoNbTaVW. At the beginning of solidification, it is predicted that W, Ta and Mo are depleted in the liquid while Cr and V are enriched. The solid BCC phase in the form of dendrites observed in the experiments is predicted to be enriched in W, Ta and Mo but depleted in Cr and V. At the later stages of the solidification where the inter-dendrites form, it predicts that inter-dendrites will be enriched in Cr and V but depleted in W and Ta. The Scheil-Gulliver solidification for Cr₂MoNbTaVW predicates the formation of C14 laves phase and C15 laves phase at the last stage of the solidification. However, the predicted contents of C14 and C15 phases are extremely low (0.23% and 0.81%), and they were not detected by the XRD measurements. In short, the non-equilibrium solidification simulations suggest that micro-segregation is very likely to occur in alloy CrMoNbTaVW.

Fig. 2. Predicted equilibrium phase mole fraction: (a) Cr₁MoNbTaVW, (e) Cr_{0.5}MoNbTaVW and (g) Cr_{2.0}MoNbTaVW; Scheil solidification: solid phase mole fraction (b) Cr₁MoNbTaVW, (f) Cr_{0.5}MoNbTaVW (h) Cr_{2.0}MoNbTaVW; the composition of (c) the liquid phase and (d) BCC phase in Cr₁MoNbTaVW.

3. Experimental results and discussions

3.1 Material synthesis and characterization methods

The refractory HEA Cr_xMoNbTaVW system with different chromium contents ($x = 0.5, 1$, and 2) was prepared by arc melting (model Edmund Bühler /MAM-1) the constituent elements in a water-cooled copper hearth to validate the CALPHAD modeling. Around 2 gram of commercial chromium, molybdenum, niobium, tantalum, vanadium and tungsten powders in total, with purity higher than 99.5%, were mixed inside a polystyrene ball mill jar before melting. During the melting process, the ingots were inverted and re-melted for 4 times to ensure homogeneity. The cooled ingots were then mounted into epoxy resin (SamplKwick fast cure acrylic resin, produced by Buehler) for easy handing and retention. The mounted specimens

were cut through the ingot using a low-speed saw in order to expose a flat surface of the sample cross-section. The exposed surface was subsequently ground by # 240, #400, #600, and #800 SiC sandpapers in sequence, before wet-polished with 1, 0.3 and 0.05 μm Al_2O_3 suspensions. An X-ray diffractometer (Empyrean, PANalytical) equipped with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) was used for the identification of the structure, with the 2θ scan ranging from 5 to 145 degrees at a rate of 10 degree per min at 45 kV and 40 mA. Field-emission scanning electron microscope FE-SEM (FEI, Quanta 3DFEG) equipped with backscatter electron (BSE) and energy dispersive spectroscopy (EDS) detectors was used to characterize the microstructure and the chemical compositions of the samples along the cross-sections.

The bulk compositions of the alloys were estimated by EDS area scan, as listed in Table 2. The different evaporation losses during the arc-melting process caused a small deviation from the design point. The elemental proportions of Table 2 are used as the bulk concentrations to estimate the theoretical average properties of density, hardness and lattice constant. The measured compositions were also used to rerun the CALPHAD simulations for $\text{Cr}_x\text{MoNbTaVW}$ ($x \approx 0.5, 1, 2$) and the results/features were found to be very similar to the results presented in Fig. 2 [14].

Table 2. EDS bulk composition analysis results for $\text{Cr}_x\text{MoNbTaVW}$ HEA, (at.%).

	Cr	Mo	Nb	Ta	V	W
$x \approx 0.5$	8.43	16.95	19.65	15.91	23.10	15.95
$x \approx 1.0$	17.89	16.31	18.15	13.94	19.59	14.12
$x \approx 2.0$	27.05	13.68	13.63	13.64	15.18	16.81

The density of the specimen was determined by measuring the samples' weight and volume. An analytical digital balance (Scientech, SA210) with a precision of 0.1 mg was used to measure the weight. Archimedes' principle was used to determine the sample volume. The hardness of the specimen was measured using a Vickers micro hardness tester under a load of 1 kgf for 15 seconds.

3.2 X-ray diffraction of $\text{Cr}_x\text{MoNbTaVW}$

XRD patterns of the premixed metal powders and the as-solidified $\text{Cr}_x\text{MoNbTaVW}$ HEA samples are shown in Fig. 3. The XRD peaks of Cr, Mo, Nb, Ta, V and W can be traced in the ball-mixed powders. However, after the arc-melting process, all the crystalline structures of the alloys are confirmed to be BCC phases, with a minor difference of the lattice constants. With increasing the Cr content from $x = 0.5, 1$, to 2, lattice constant of the BCC phase decreases from 0.31899 ± 0.00013 nm, 0.31826 ± 0.00049 nm to 0.31583 ± 0.00035 nm respectively. Despite the presence of elemental micro-segregation in these samples presented in section 3.3, these values agree well with the ones estimated from the mixture rule, as shown in Table 3. As expected, the increase of Cr content leads to the decrease of the lattice constant, which agrees with the experimental results.

Table 3. The experimental lattice constant a , Vickers hardness HV , density ρ of the HEA alloy and the estimated average (experimental/ estimated [17]).

	Vickers hardness, HV	ρ^* , g/cm ³	a , nm
TiMoNbTaVW[9]	505.1 (4954 MPa)	11.7/11.19	0.3216/0.3174
MoNbTaVW [6]	535.3±28.6 (5250 MPa)	12.36/12.36	0.31832/0.31827
Cr_{0.5}MoNbTaVW	675.5±27.5 (6624.7±269.2 MPa)	11.5/11.4	0.31899/0.31586
Cr_{1.0}MoNbTaVW	704.6±17.4 (6910.3±170.5MPa)	11.4/11.1	0.31826/0.31290
Cr_{2.0}MoNbTaVW	754.9± 43.1 (7403.4±422.5MPa)	11.2/11.4	0.31583/0.31103

* Estimated data were calculated using equation (1).

In the XRD pattern of $x=2.0$, apparent secondary BCC peaks appear beside the main BCC peaks with a smaller lattice constant. This observation is supported by phase diagram calculations, Figs. 1 and 2g. With x increasing from 0.5 to 2, the formation temperature for the secondary BCC increases. Thus it's more likely for the secondary BCC structure to form during the arc melting process.

Fig. 3. XRD patterns of (a) mixed metal powders and (b) as-solidified Cr_xMoNbTaVW alloys

3.3 Microstructures for Cr_xMoNbTaVW

SEM backscatter electron images were taken separately on the finely polished surfaces of Cr_xMoNbTaVW ($x = 0.5, 1, 2$) HEA alloys. Typical solidification microstructures were observed in all samples. Fig. 4 shows the transition from a cellular structure to a dendritic structure as the Cr content increases. It is well known that the constitutional undercooling leads to the formation of dendritic structures [18]. The increase of the Cr concentration will lead to the increase of the undercooling effects. So as shown in Fig. 4 (a), when $x=0.5$, the undercooling is relatively weak, thus the cellular structure forms. With the x increases to 1.0, Fig. 4 (b), the stronger undercooling facilitates the growth of the primary dendrite arms to around 10 μm . As x goes even larger in Fig. 4 (c), the dendrite arms grow to around 30 μm long and the branch arms start to form.

Fig. 4. SEM backscatter electron image of the HEA $\text{Cr}_x\text{MoNbTaVW}$: (a) $x=0.5$, (b) $x=1.0$, (c) $x=2.0$

In dendritic growth, mass of low melting temperature solute is ejected between the dendrite arms and causes micro-segregation. In backscatter images (Fig.4), the heavier metal elements (higher atomic number Z) have a brighter color. In this case, the order of brightness is W and Ta first, followed by Mo and Nb, and Cr and V last. The micro-segregation was measured by EDS mapping, as shown in Figs. 5, 6 and 7. The Mo, Ta and W elements are clearly seen inside the dendritic structures, while most of other elements can be clearly seen with enrichments in the inter-dendritic regions.

Fig. 5. EDS mapping of the HEA $\text{Cr}_{0.5}\text{MoNbTaVW}$

Fig. 6. EDS mapping of the HEA $\text{Cr}_{1.0}\text{MoNbTaVW}$

Fig. 7. EDS mapping of the HEA $\text{Cr}_{2.0}\text{MoNbTaVW}$

The micro-segregation between the dendrite and inter-dendrite regions can be quantitatively identified through the EDS point scans. The elemental percentages of each element were taken on both dendrite areas (C_d) and inter-dendrite areas (C_{id}). Following Leo *et al.* [19], the partition coefficient $K = C_d/C_{id}$, was used to evaluate the micro-segregation quantitatively. It can be shown that in dendrite region of all three samples, the enriched elements are W first, followed by Mo, and then Ta, while the inter-dendrite region was enriched in Cr followed by V and then Nb. The sequence of the segregated elements qualitatively agrees with the prediction from Scheil model as shown in Fig. 2 (c and d). For $\text{Cr}_x\text{MoNbTaVW}$ ($x \approx 0.5, 1, 2$) partition coefficients, the lower end is Cr at $x \approx 0.5$, with a value near 1:9, and the higher end is W at $x \approx 2.0$, with a value close to 12:1, Table 4.

Table 4. Partition coefficient K of $\text{Cr}_x\text{MoNbTaVW}$ HEA

	Cr	Mo	Nb	Ta	V	W
$x \approx 0.5$	0.11(1:9)	1.60	0.50	1.14	0.17	5.50
$x \approx 1.0$	0.17	1.40	0.55	1.28	0.28	3.61
$x \approx 2.0$	0.34	4.18	0.83	1.46	0.55	11.66 (12:1)

The EDS line scan was used to quantify the level of element segregation between the dendrite arms and inter-dendritic regions. As shown in Fig. 8, the elemental compositions were collected at points along a straight line across the dendrites and inter-dendrites with an interval separation of 0.1 μm .

Fig. 8. SEM image with EDS line measurement locations marked of (a) $x=0.5$, (c) $x=1.0$, (e) $x=2.0$, and atom percentages of (b) $x=0.5$, (d) $x=1$, (f) $x=2$

3.4 Density and hardness for $\text{Cr}_x\text{MoNbTaVW}$

The density, hardness, and lattice constant of quinary MoNbTaVW alloy, senary HEAs $\text{Cr}_x\text{MoNbTaVW}$, and TiMoNbTaVW were listed in Table 3 to demonstrate the effect of introducing Cr or Ti into the base alloy MoNbTaVW. The densities of the $\text{Cr}_x\text{MoNbTaVW}$ alloys were determined to be 11.5 g/cm^3 for $x=0.5$, 11.4 g/cm^3 for $x=1.0$, and 11.2 g/cm^3 for $x=2.0$ (see Table 3). To compare with the experimental results, the density of a disordered solid solution can be estimated from the rule of mixture:

$$\rho_{est} = \frac{\sum c_i A_i}{\sum \frac{c_i A_i}{\rho_i}} \quad (1)$$

where c_i is the atomic percentage of an element; A_i is the atomic weight; and ρ_i is the density of the pure element. The calculated theoretical densities are also listed in Table. 3. The measured densities of the HEAs are very close to the corresponding calculated ones.

Table 5. The atomic radius r of the metal feedstock [20].

Metal	Ti	Cr	Mo	Nb	Ta	V	W
$r, \text{\AA}$	1.46	1.28	1.40	1.47	1.47	1.35	1.41

The values of Vickers micro-hardness were measured across the polished surface of HEA samples. Five random sites were tested on each sample and the averaged values were summarized in Table 3. The hardness of $\text{Cr}_x\text{MoNbTaVW}$ were calculated to be 675.5 ± 27.5 , 704.6 ± 17.4 , and 754.9 ± 43.1 for $x = 0.5$, $x = 1.0$ and $x = 2.0$, respectively. The experimental micro-hardness values are dramatically higher than the hardest component W in the system. Since the Cr is the smallest element in the $\text{Cr}_x\text{MoNbTaV}$ system, Table 5, adding more Cr into the system is expected to increase the atomic size misfit influence which will increase the hardness. Clearly, solid solution hardening mechanism plays an important role in this HEA system. Moreover, early study on the Ti addition into base alloy MoNbTaVW shows no hardening effect [9], since the radius of Ti is similar to rest of elements in the system. The small hardness difference between TiMoNbTaVW and MoNbTaVW is due to the grain size differences.

4 Further discussions on CALPHAD thermodynamic analysis

It is known that the Laves phases form in Cr-Nb [21], Cr-Ta [21], Nb-V [22], and Ta-V [21] binary systems, but the solubility of the Laves phases into the ternary systems of refractory metals is not huge [21]. Because both CALPHAD modeling (section 2) and experimental testing (section 3) state that disordered BCC solid solutions form in the CrMoNbTaVW alloys, more thermodynamic calculations were carried out on the BCC and C15 phases as a function of temperature and compositions. Fig. 9 compares the entropy, enthalpy and Gibbs energy of BCC and Laves phases in the senary CrMoNbTaVW alloy as a function of temperature using the default reference states (namely the stable structure at 25.15 °C and 1 atm). The BCC phase has significantly larger entropy than the C15 phase while the enthalpy is lower for the BCC phase by a small amount. The temperature dependence of entropy is presumed due to the lattice phonon vibration that strongly depends upon temperature. For quantitative evaluation of entropy sources of high-entropy alloys, please refer to recent publications [21, 22]. Note that direct comparison in the Gibbs energy between phases such as in Fig. 9c, 10c and 11c is most meaningful for single-phase region; for regions of co-existing phases, the tie-line is out of plane and thus the plots cannot be used for global phase equilibrium determination. Nonetheless, these plots show the trend of the Gibbs energy of each phase with respect to temperature and composition.

Fig. 9: calculated (a) entropy, (b) enthalpy and (c) Gibbs energy of the BCC and C15 Laves phases in CrMoNbTaVW as a function of temperature using the default reference states (namely the stable structure at 25.15 °C and 1 atm)

The entropy of mixing (ΔS_{mix}^{bcc}) and enthalpy of mixing (ΔH_{mix}^{bcc}) for the BCC phase in CrMoNbTaVW can be calculated using the BCC phase as the reference. Below 2400 °C, they are a constant of 14.7 J/K/mol and -662.5 J/mol respectively. That the short-range order is not considered in the BCC phase in the database is partly responsible for the constant values [21]. Future thermochemical measurements on entropy, enthalpy, and Gibbs energy for the senary CrMoNbTaVW alloy are desirable to compare with the predicted results.

Comparison in the thermodynamic mixing properties between the BCC and Laves phases in $\text{Cr}_x\text{MoNbTaVW}$ at 1000 °C is shown in Fig. 10, which is obtained by excluding the mechanical mixing from the pure components. It is predicted that ΔS_{mix}^{bcc} reaches its maximum of +15.3 J/K/mol at 31.3 at. % Cr, which deviates substantially from the equi-molar composition. ΔS_{mix}^{C15} evolves from negative to positive values with increasing Cr contents but the absolute value is very small compared to ΔS_{mix}^{bcc} . ΔH_{mix}^{bcc} reaches its maximum of +7.3 kJ/mol at 62.3 at. % Cr while ΔH_{mix}^{C15} reaches its minimum of -8.9 kJ/mol at 42.3 at. % Cr.

Fig. 10: calculated (a) entropy of mixing, (b) enthalpy of mixing and (c) Gibbs energy of mixing of the BCC and C15 Laves phases in $\text{Cr}_x\text{MoNbTaVW}$ at 1000 °C as a function of Cr contents. The reference states for all components are the BCC phase at 1000 °C and 1 atm.

The chemical dependence of the thermodynamic mixing properties of the BCC phase is shown in Fig. 11 for six pseudo-binaries at 1000 °C. It can be seen that variation of Cr has greater impact to the thermodynamic properties than any other elements in the Cr-Mo-Nb-Ta-V-W senary alloy system. For ΔS_{mix}^{bcc} , $\text{CrMoNb}_x\text{TaVW}$ behaves the closest to the ideal mixing followed by $\text{CrMo}_x\text{NbTaVW}$ while $\text{Cr}_x\text{MoNbTaVW}$ deviates from it the most. In terms of ΔH_{mix}^{bcc} , increasing Cr contents in $\text{Cr}_x\text{MoNbTaVW}$ increases it as reflected in a steep concave shape while for the rest systems it shows a shallow convex trend. The Cr-absent alloy (namely MoNbTaVW) has the lowest and dominating ΔH_{mix}^{bcc} and thus the lowest ΔG_{mix}^{bcc} . As a result, it is expected that addition of Cr to MoNbTaVW will result in narrower phase field in composition and temperature for the BCC phase, despite the senary CrMoNbTaVW has higher configurational entropy than the quinary MoNbTaVW, agreeing with a prior study [21].

Fig. 11: calculated (a) entropy of mixing, (b) enthalpy of mixing and (c) Gibbs energy of mixing of the BCC phase at 1000 °C in $\text{Cr}_x\text{MoNbTaVW}$, $\text{CrMo}_x\text{NbTaVW}$, $\text{CrMoNb}_x\text{TaVW}$, $\text{CrMoNbTa}_x\text{VW}$, $\text{CrMoNbTaV}_x\text{W}$, and CrMoNbTaVW_x , which is labeled as Cr, Mo, Nb, Ta, V and W respectively in the plots. The reference states for all components are the BCC phase at 1000 °C and 1 atm.

5. Conclusions

To demonstrate the design envelope of BCC phase HEAs, a senary refractory high-entropy alloy system, $\text{Cr}_x\text{MoNbTaVW}$ ($x=0.5, 1.0, 2.0$), was examined using CALPHAD simulations and validated experimentally using XRD and SEM. The lattice constant, density, and Vickers' micro-hardness of this HEA alloy in the as-cast state were also measured accordingly.

For three Cr contents ($x=0.5, 1.0, 2.0$) in the $\text{Cr}_x\text{MoNbTaVW}$ system, all the EDS results show that the dendrite was enriched most in W and weakly by Mo and Ta while the interdendritic region was enriched most by Cr and V and weakly by Nb. With the increase of the Cr content, the microstructure is gradually changed from the cellular to dendritic structure. In addition, the lattice constant decreases and the Vickers' hardness increases with the Cr content grows. CALPHAD modeling predicts phase decomposition of the BCC phase for all three alloys studied at lower temperatures, and the tendency of phase decomposition increases with the increase of Cr contents. This has been confirmed by the experimental testing results, where a secondary BCC phase became detectable by XRD for $\text{Cr}_{2.0}\text{MoNbTaVW}$.

The thermodynamic analysis on the elemental dependence of the mixing thermodynamic properties (entropy, enthalpy and Gibbs energy) in BCC phase in this senary system shows that $\text{Cr}_x\text{MoNbTaVW}$ deviates from the ideal mixing the most compared to $\text{CrMo}_x\text{NbTaVW}$, $\text{CrMoNb}_x\text{TaVW}$, $\text{CrMoNbTa}_x\text{VW}$, $\text{CrMoNbTaV}_x\text{W}$ and CrMoNbTaVW_x . Increasing Cr contents sharply increases the enthalpy of mixing and accordingly the Gibbs energy of mixing of the BCC phase, and as a result, destabilizes the BCC phase significantly. The calculated entropy of mixing and enthalpy of mixing for CrMoNbTaVW are 14.7 J/K/mol and -662.5 J/mol respectively. The CALPHAD calculation is a valuable tool for predicting phase stability in the $\text{Cr}_x\text{MoNbTaVW}$ system and provided instructive insights to the three studied HEAs. However, due to the general lacking of coverage for ternary and higher-order systems in the database TCNi7, experimental work should be performed to validate CALPHAD predictions on other HEA systems.

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