

Article

A Strategic Design Route to Find a Depleted Uranium High-Entropy Alloy with Great Strength

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Abstract: The empirical parameters of mixing enthalpy (ΔH_{mix}), mixing entropy (ΔS_{mix}), atomic radius difference (δ), valence electron concentration (VEC), etc., are used in this study to design a depleted uranium high-entropy alloy (HEA). X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to assess the phase composition. Compression and hardness tests were conducted to select alloy constituents with outstanding mechanical properties. Based on the experimental results, the empirical criteria of HEAs are an effective means to develop depleted uranium high-entropy alloys (DUHEAs). Finally, we created UNb_{0.5}Zr_{0.5}Mo_{0.5} and UNb_{0.5}Zr_{0.5}Ti_{0.2}Mo_{0.2} HEAs with outstanding all-round characteristics. Both alloys were composed of a single BCC structure. The hardness and strength of UNb_{0.5}Zr_{0.5}Mo_{0.5} and UNb_{0.5}Zr_{0.5}Ti_{0.2}Mo_{0.2} were 305 HB and 1452 MPa, and 297 HB and 1157 MPa, respectively.

Keywords: depleted uranium high-entropy alloy; empirical parameters; BCC structure; phase composition; strengthen



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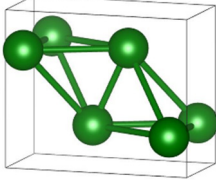
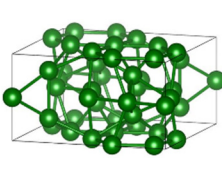
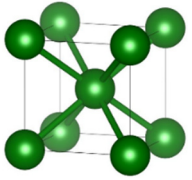
1. Introduction

The concept of high-entropy alloys (HEAs) offers a new approach to exploring materials, expanding the research scope and the compositional palette. Due to the high entropy effect, HEAs can form a simple solid solution structure with excellent properties under a high concentration of multiple components [1]. HEAs with high strength and toughness [2,3], stability at high temperatures [4,5], and corrosion resistance [4,6] have been investigated. The HEA system mainly focuses on the 3rd to 5th period, 3d electron layer elements, and other main group elements, which usually form face-centered cubic (FCC) and body-centered-cubic (BCC) structures. Meanwhile, the rare earth elements, such as Tb, Dy, Lu, Tm, and Ho, usually form a hexagonal-close-packed (HCP) structure [7,8].

Unlike uranium, depleted uranium (DU) has very little radioactivity and is often used in military applications because of its self-sharpening properties and high density [9–11]. There are three structures of U (Table 1), and the γ -U structure with a BCC structure has ideal symmetry and properties at high temperatures. Alloying elements Zr [12], Ti [11,13], Mo [14], Nb [15,16], amongst others, usually have a wide range of solubility in γ -U of the BCC structure. Zr and Nb can dissolve completely with U and form the γ -phase at high temperatures. Ti can dissolve in the U matrix and form the γ -phase at a temperature above 725 °C, and the maximum solubility of Mo in γ -U is 21.2 weight percent (wt.%). HEAs

have superior properties to traditional alloys. By applying the concept of high entropy to DU alloys and taking full advantage of γ -U, we can design DUHEAs with excellent performance and provide more options for high-performance structural materials.

Table 1. Uranium allotropes and their characteristics, data from [17,18].

Allotrope	α -U	β -U	γ -U
Temperature (°C)	<667.7	667.7~774.8	774.8~1132.3
Crystal structure			
Density (g/cm ³)	19.05	18.13	17.91

2. Design Idea and Experimental Route for DUHEAs

2.1. Design Idea

HEAs design commonly includes high-throughput preparation, CALPHAD (phase diagram calculation) [19,20], and DFT (density functional theory) [21–23]. Generally, the factors considered in the calculation and simulation are ideal and are insufficient to reflect the actual casting process. In this study, we combined the solid solution formation criteria of HEA with an experimental search for high-performance DUHEAs. The elements Nb, Mo, Ti, and Zr, which have significant solubility in U, were selected. The physical properties are listed in Table 2.

Table 2. Physical properties of each element, data from [24–26].

Element	U ₂₃₈	Nb	Zr	Ti	Mo
Atomic number	92	41	40	22	42
Atomic radius (pm)	139	143	159	146	141
Density (g/cm ³)	19.05	8.52	6.49	4.51	10.20
Melting point (K)	1405	2750	2128	1941	2896
Electronegativity	1.38	1.60	1.33	1.54	2.16
Lattice content (pm)	343.3	330.1	360.9	327.6	314.7
Valence electron concentration (VEC)	3	5	4	4	6

Yeh et al. [27] believe that the mixing entropy (ΔS_{mix}) is the main factor promoting the formation of solid solutions in HEAs. Zhang [28] extended the Hume-Rothery criterion to HEAs and proposed δ , ΔH_{mix} , and Ω as the factors affecting the formation of HEA solid solution phases.

The mixing entropy can be calculated by the following formula [1]:

$$\Delta S_{mix} = -R \sum_{i=1}^n (c_i \ln c_i) \quad (1)$$

where R is the ideal gas constant ($\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$); n is the number of components in the alloy; and c_i is the atomic fraction of the i th component in the alloy. From Formula (1), ΔS_{mix} reaches the maximum when the atomic ratio of the elements in the alloy is equal. In general, alloys are assigned to the class of HEAs when the mixing entropy is higher than $1.5 R$ [29].

The parameter, δ , for the difference in atomic radius can be expressed as follows [1]:

$$\delta = \sqrt{\sum_{i=1}^n c_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} \quad (2)$$

$$\bar{r} = \sum_{i=1}^n c_i r_i \quad (3)$$

where $\bar{r}$ is the average atomic radius of the alloy (Å), and r_i is the atomic radius of the i th element of the alloy (Å).

The mixing enthalpy of a multi-component alloy can be calculated by the following Formula [1]:

$$\Delta H_{mix} = \sum_{i=1, i \neq j}^n 4H_{AB}^{mix} c_i c_j \quad (4)$$

where H_{AB}^{mix} is the mixing enthalpy of the i th and j th elements ($\text{kJ} \cdot \text{mol}^{-1}$); c_i is the atomic percentage of the i th element in the alloy; and c_j is the atomic percentage of the j th elements in the alloy. The mixing enthalpy among U, Nb, Zr, Ti, and Mo are listed in Table 3.

Table 3. Mixing enthalpy between elements, data from [24–26] (H_{AB}^{mix} , kJ/mol).

	U	Nb	Zr	Ti	Mo
U	-	4	−3	0	2
Nb	-	-	4	2	−6
Zr	-	-	-	0	−6
Ti	-	-	-	-	−4
Mo	-	-	-	-	-

To simplify the prediction standard of an HEA solid solution structure, Zhang [30] proposed the Ω parameter, the definition of which is expressed as follows [1]:

$$\Omega = \frac{T_m \Delta S_{mix}}{|\Delta H_{mix}|} \quad (5)$$

where T_m is the melting point of a multi-component alloy (K); ΔS_{mix} is the mixing entropy of a multi-component alloy ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$); and ΔH_{mix} is the mixing enthalpy of a multi-component alloy ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$).

To develop DUHEAs with excellent mechanical properties, Zr and Nb, which can dissolve indefinitely with γ -U at a high temperature to form a BCC solid solution structure, were added to the DU ternary alloy. Then, Ti and Mo were added to the DU ternary alloy to refine its properties. The study path is shown in Figure 1.

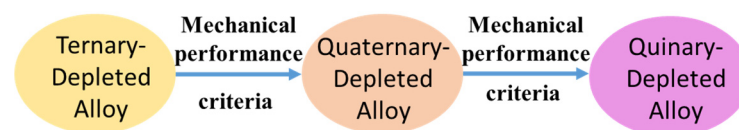


Figure 1. Alloy design path.

2.2. Test Method

Ingots with a mass of approximately 50 g were prepared using a Vacuum arc melting furnace and pure metals of U, Nb, Mo, Ti, and Zr (purity was higher than 99 wt.%). To ensure chemical homogeneity, the ingots were re-melted at least 4–5 times. An X-ray diffractometer (XRD, Bruker D8 Advance, Bruker AXS, Bruker AXS, Karlsruhe, Germany), with Cu K α radiation, was used to measure the phase composition of the alloys. The scanning range was from 15° to 90°, and the scanning speed was 5°/min. The micro-morphologies of the alloys were observed by scanning electron microscopy (SEM, EVO18, Carl Zeiss AG, Jena, Germany) operating at 20 keV. The chemical composition was observed by energy-dispersive spectroscopy (EDS) equipped in the SEM. The standard bright-field (BF), image, and selected area electron diffraction (SAED) patterns were obtained by transmission electron microscope (TEM, Tecnai F30, FEI, Hillsboro, OR, USA) operating at 300 kV, and the TEM data were processed using the Digital Micrograph software. Hardness

of the alloys was measured using the Wilson Brinell hardness meter BH3000 (Wilson, Norwood, MA, USA) under a load of 1840 N for 10 s. Room temperature compression tests were carried out by CMT5105 (Suns, Shenzhen, China). The specimen was a Φ 6 mm cylinder with a height-to-diameter ratio of between 1.5 and 2. The compression tests were performed at a compression rate of 10^{-3} s^{-1} .

3. Design Process and Experimental Results

3.1. Ternary U-Nb-Zr Medium-Entropy Alloy (MEA)

Firstly, the U-Nb-Zr alloy system was studied. The thermodynamic parameters of the alloy system are listed in Table 4, and the relationship between δ - ΔH and δ - Ω of the alloy is shown in Figure 2. Zr and Nb are infinitely soluble in U, indicating that the alloy system has a strong tendency to form solid solutions. From Figure 2a all alloys had a disordered solid solution phase. While in Figure 2b, UNbZr0.5 and UNb1.5Zr are in the solid solution and intermetallic compound zones, UNbZr is on the boundary of the solid solution and intermetallic compound zones, which does not tend to form a solid solution. The value of VEC for every alloy was lower than 6.87, forming a stable BCC solid solution structure [31]. The results show that the alloys have a disordered solution phase.

Table 4. Thermodynamic parameters of the U-Nb-Zr alloy system.

Alloys	δ (%)	ΔH_{mix} (KJ/mol)	ΔS_{mix} (KJ/mol)	Tm (K)	Ω	VEC
UNbZr	5.88	2.22	9.13	2094	8.6	4.00
UNb0.5Zr	6.26	0.64	8.77	1963	26.9	3.80
UNbZr0.5	5.13	2.88	8.77	2087	6.4	4.00
UNb0.5Zr0.5	5.69	1.50	8.64	1922	11.1	3.75
UNb1.5Zr	5.55	2.94	8.97	2188	6.7	4.14
UNbZr1.5	6.08	1.80	8.97	2099	10.5	4.00

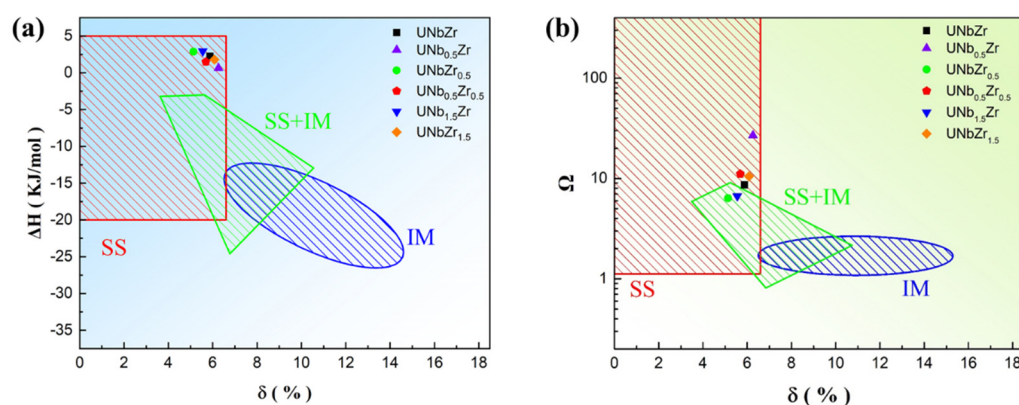


Figure 2. The distribution of the entropy alloy in the ternary U-Nb-Zr in the relationship diagram of (a) δ - ΔH and (b) δ - Ω (SS: solid solution; IM: intermetallic compound).

The XRD pattern of the medium entropy alloys are presented in Figure 3. Regardless of the uranium oxides, the phase compositions of the alloys were almost identical and were composed of a single BCC phase. In addition, the diffraction peaks appeared to shift with the change in Nb and Zr contents. Combining Bragg's Law with $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$ (d_{hkl} is the interplanar spacing), the diffraction peaks shifted suggesting lattice content changes [32]. Because U, Nb, and Zr have different lattice constants, the variation of the lattice constants of the alloys is complex. According to the electron diffraction of the UNbZr alloy in Figure 4a,b, the alloy exhibited a single-phase BCC structure, which is consistent with the prediction of the alloy formation.

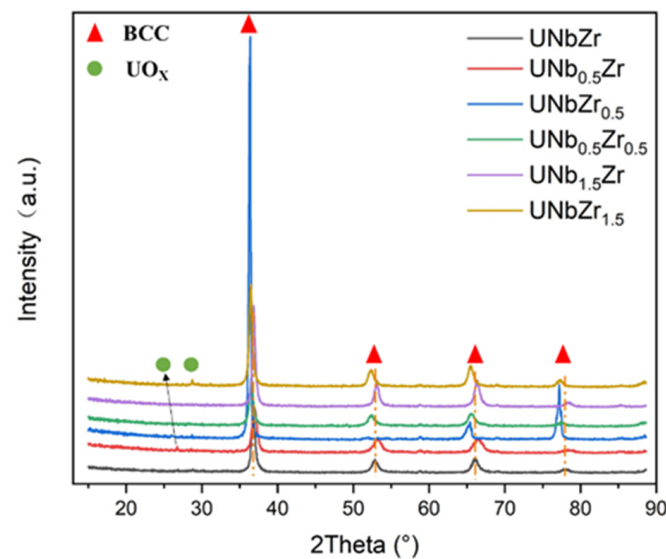


Figure 3. XRD diffraction patterns of the medium entropy alloy in U-Nb-Zr.

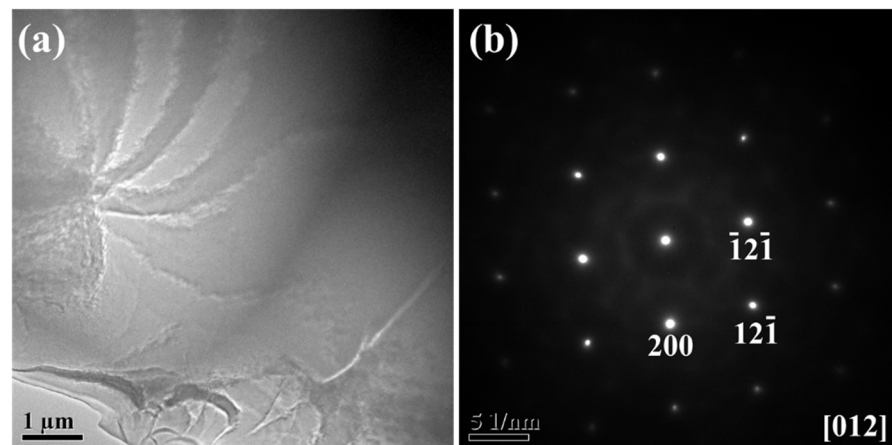


Figure 4. (a) TEM bright-field image; (b) selected area-electron-diffraction image of the UNbZr alloy.

The microstructures of the medium-entropy alloys in the U-Nb-Zr system are shown in Figure 5. The microstructure of UNbZr is presented in Figure 5a. The light-colored region was a U-enriched interdendritic structure, while Zr and Nb formed the BCC dendritic structure of the primary phase due to their higher melting points. When the Nb content decreased, as shown in Figure 5b, the segregation of UNb_{0.5}Zr was more pronounced than that of UNbZr. When the Zr content decreased, the segregation of UNbZr_{0.5} decreased, as shown in Figure 5c, and the dendrite structure become finer. In Figure 5d,e, the alloy compositions of UNb_{0.5}Zr_{0.5} and UNb_{1.5}Zr are uniform. The structure of the UNbZr_{1.5} alloy is shown in Figure 5e, which was similar to UNbZr and displayed a typical as-cast dendrite structure (uniform region) with segregation of the components (U-enriched region).

The hardness and yield strength of the alloys of the U-Nb-Zr system are given in Table 5. The hardness and strength of UNbZr_{0.5} and UNbZr_{1.5} were lower than those of other alloys. It seems that the mechanical properties of UNb_{0.5}Zr, UNbZr, and UNb_{1.5}Zr were higher than those of UNb_{0.5}Zr_{0.5}. In particular, the organization of UNb_{0.5}Zr was more homogeneous than that of UNb_{0.5}Zr_{0.5} (see Figure 5). However, this study aimed to utilize waste DU and improve its potential availability; therefore, UNb_{0.5}Zr_{0.5} was selected as the base alloy for the subsequent work.

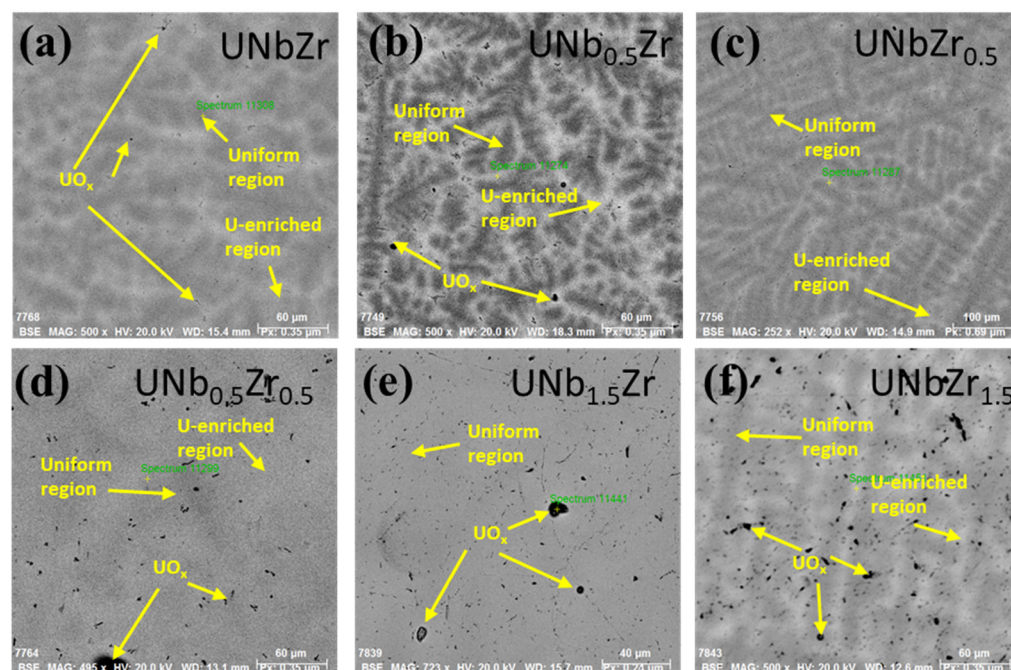


Figure 5. SEM images of the U-Nb-Zr system alloys. (a) UNbZr, (b) UNb_{0.5}Zr, (c) UNbZr_{0.5}, (d) UNb_{0.5}Zr_{0.5}, (e) UNb_{1.5}Zr, (f) UNbZr_{1.5}.

Table 5. Hardness and strength of the U-Nb-Zr alloy system.

Properties	UNb _{0.5} Zr _{0.5}	UNb _{0.5} Zr	UNbZr _{0.5}	UNbZr	UNb _{1.5} Zr	UNbZr _{1.5}
Hardness (HB)	246	263	211	235	243	238
Strength (MPa)	793	883	748	863	858	755

3.2. Quaternary U-Nb-Zr-X HEA

From the microstructural study of the U-Nb-Zr ternary alloys, the elemental distribution of the UNb_{0.5}Zr_{0.5} alloy is the most uniform, the segregation phenomenon was not obvious, and its comprehensive mechanical properties were excellent. Table 6 shows the thermodynamic parameters of UNb_{0.5}Zr_{0.5}-X (Ti/Mo) HEAs. From the relationship diagram of δ - ΔH and δ - Ω in Figure 6, the studied UNb_{0.5}Zr_{0.5}-X (Ti/Mo) HEAs were solid solution phases. Based on their VEC, it was discovered that these alloys were BCC phases.

Table 6. Thermodynamic parameters of UNb_{0.5}Zr_{0.5}-X HEAs.

Alloys	δ (%)	ΔH_{mix} (KJ/mol)	ΔS_{mix} (KJ/mol)	T _m (K)	Ω	VEC
UNb _{0.5} Zr _{0.5} Ti _{0.2}	5.42	1.40	10.39	1924	14.3	3.77
UNb _{0.5} Zr _{0.5} Ti _{0.5}	5.09	1.28	11.07	1926	16.7	3.80
UNb _{0.5} Zr _{0.5} Ti	4.64	1.11	11.05	1928	19.2	3.83
UNb _{0.5} Zr _{0.5} Mo _{0.2}	5.49	0.58	10.39	2011	36.1	3.95
UNb _{0.5} Zr _{0.5} Mo _{0.5}	5.23	−0.32	11.07	2117	73.3	4.20
UNb _{0.5} Zr _{0.5} Mo	4.87	−1.11	11.05	2247	22.4	4.50

The XRD results of UNb_{0.5}Zr_{0.5}-X (Ti/Mo) HEAs presenting BCC structures are represented in Figure 7. Ignoring the uranium oxides, most of the alloys consisted of a single BCC structure, UNb_{0.5}Zr_{0.5}Ti and UNb_{0.5}Zr_{0.5}Mo HEAs forming two BCC structures. The diffraction peak changed to a higher angle as the concentrations of Ti and Mo grew, showing that the lattice constant dropped [32]. As presented in Table 2, the lattice contents of U, Mo, and Ti at room temperature are 343.3 pm, 314.7 pm, and 327.6 pm [17,26], respectively. With the addition of Ti and Mo, the lattice constant of the matrix decreased, indicating the

occurrence of solid solution and the generation of lattice distortion. When the content of Mo reached the maximum, $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}$ was composed of two BCC structures, which was because Mo has the highest melting point of the elements.

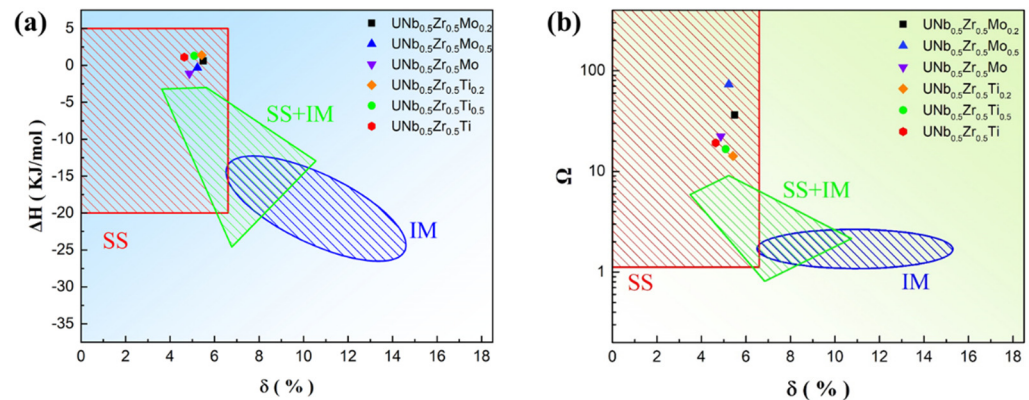


Figure 6. (a) δ - ΔH and (b) δ - Ω distribution diagram of $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{-X}$ HEAs.

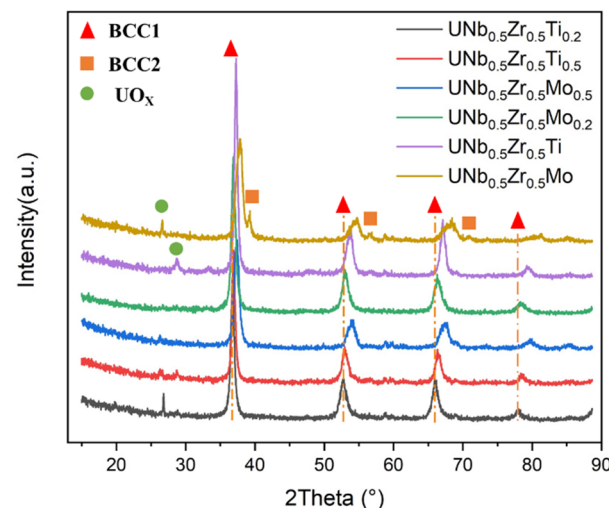


Figure 7. XRD pattern of the $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{-X}$ (Ti/Mo) HEAs.

The as-cast microstructures of $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{-X}$ (Ti/Mo) HEAs are shown in Figure 8, and the alloys all have a typical as-cast dendritic structure similar to the U-Nb-Zr system alloys. Composition segregation was obvious as the concentration of Ti and Mo increased. $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}$, $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}$, $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}$, $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}_{0.2}$, and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}_{0.5}$ consisted of a uniform region, a U-enriched region and a UO_x region. Compared with $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}$, the segregation of the U-enriched region in $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}$ was high obviously. $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}$ was composed of a U-enriched region, Mo-enriched region, and UO_x , which was different from $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}_{0.2}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}_{0.5}$. As Figure 8f shows, the Mo-enriched region formed the BCC2 phase that is in line with the XRD patterns of Figure 7.

Table 7 shows the Brinell hardness and yield strength of the $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{-X}$ HEAs. The addition of Ti significantly reduced the hardness of the alloy. When the molar ratio of Ti was 0.5, the yield strength of the alloy reached 881 MPa. While the hardness of the alloy improved dramatically as the Mo percentage increased, the yield strength decreased. This was because the hardness of Mo was higher than that of other elements. In addition, the melting point of Mo was the highest of the five elements, which will improve segregation during the solidification process. As a result, the hardness increased dramatically, and segregation of the alloy increased along with the Mo content, dramatically influencing the mechanical characteristics of the alloy.

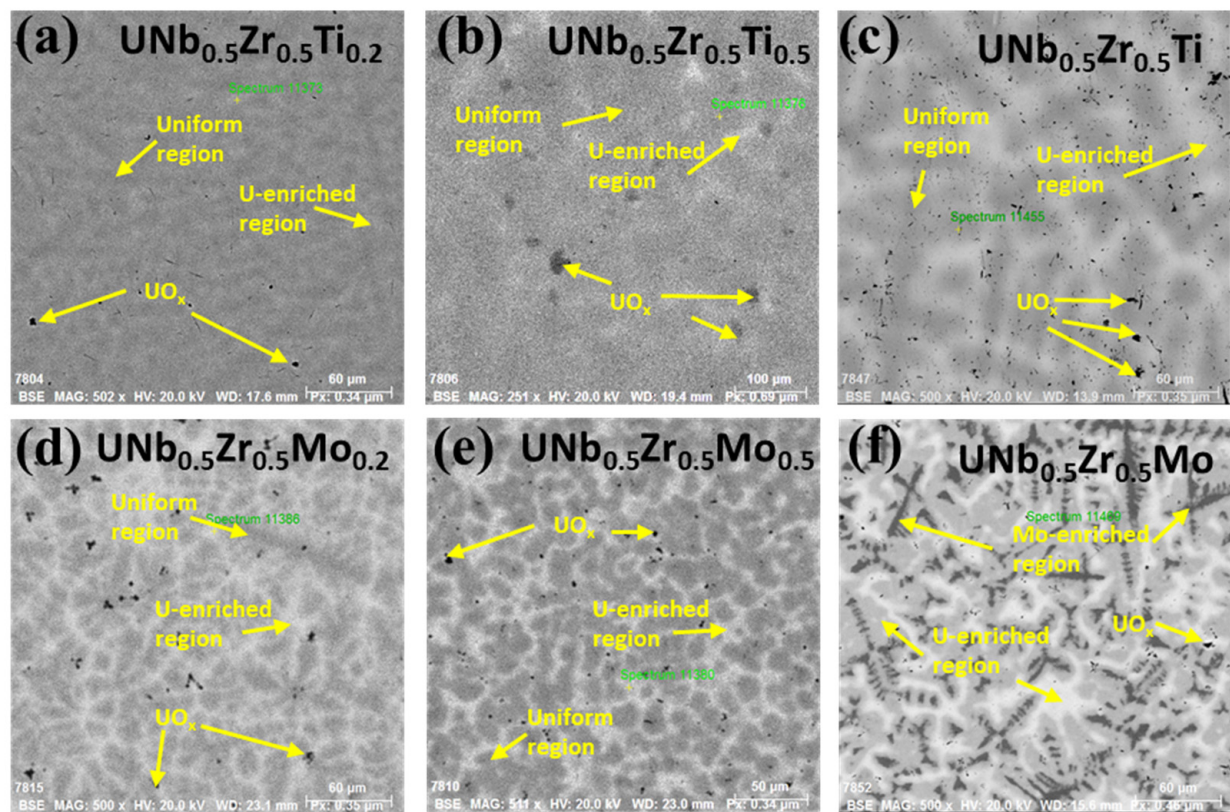


Figure 8. Microstructures of the UNb_{0.5}Zr_{0.5}-X (Ti/Mo) HEAs. (a) UNb_{0.5}Zr_{0.5}Ti_{0.2}, (b) UNb_{0.5}Zr_{0.5}Ti_{0.5}, (c) UNb_{0.5}Zr_{0.5}Ti, (d) UNb_{0.5}Zr_{0.5}Mo_{0.2}, (e) UNb_{0.5}Zr_{0.5}Mo_{0.5}, (f) UNb_{0.5}Zr_{0.5}Mo.

Table 7. Hardness and strength of the UNb_{0.5}Zr_{0.5}-X HEAs.

Properties	UNb _{0.5} Zr _{0.5} Ti _{0.2}	UNb _{0.5} Zr _{0.5} Ti _{0.5}	UNb _{0.5} Zr _{0.5} Ti	UNb _{0.5} Zr _{0.5} Mo _{0.2}	UNb _{0.5} Zr _{0.5} Mo _{0.5}	UNb _{0.5} Zr _{0.5} Mo
Hardness (HB)	233	220	214	289	305	367
Strength (MPa)	760	881	754	/	1452	1668.9 (Crashed)

3.3. Quinary U-Nb-Zr-Ti-Mo HEAs

We can observe from the previous section on the quaternary HEAs that the proposed alloys could form a stable solid solution phase of a BCC structure. The UNb_{0.5}Zr_{0.5}Ti_{0.2}, UNb_{0.5}Zr_{0.5}Ti_{0.5}, UNb_{0.5}Zr_{0.5}Mo_{0.2}, and UNb_{0.5}Zr_{0.5}Mo_{0.5} alloys had the most uniform elemental distributions, and the segregation phenomenon was not observed. A five-element DUHEA was prepared by varying the ratio of Ti and Mo and choosing UNb_{0.5}Zr_{0.5}Ti_xMo_x.

The thermodynamic properties of Nb-Zr-U-Ti-Mo HEAs are shown in Table 8. The planned UNb_{0.5}Zr_{0.5}Ti_xMo_x HEAs were all solid solution phases, as evidenced by the relationship between δ - ΔH and δ - Ω in Figure 9. Based on its VEC, we can predict that the developed alloy will be a BCC phase.

Table 8. Thermodynamic parameters of U-Nb-Zr-Ti-Mo HEAs.

Alloys	δ (%)	ΔH_{mix} (KJ/mol)	ΔS_{mix} (KJ/mol)	T _m (K)	Ω	VEC
UNb _{0.5} Zr _{0.5} Ti _{0.2} Mo _{0.2}	5.26	0.51	11.91	2005	46.46	3.96
UNb _{0.5} Zr _{0.5} Ti _{0.5} Mo _{0.5}	4.79	−0.44	12.98	2088	60.94	4.17

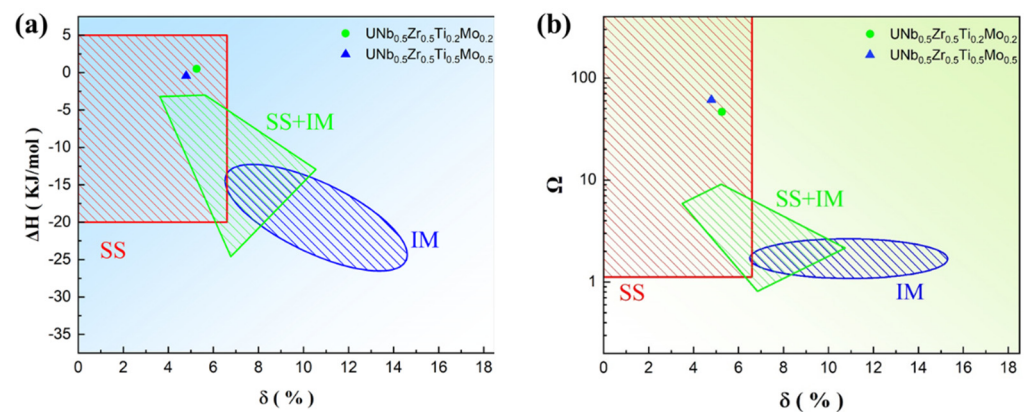


Figure 9. (a) δ - ΔH and (b) δ - Ω distribution map of U-Nb-Zr-Ti-Mo HEAs.

The phase composition and microstructure of the five-element DUHEA were investigated. Figure 10 shows the XRD data on the $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_x\text{Mo}_x$ ($x = 0.2, 0.5$) HEA. $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ was composed of a single BCC structure and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$ formed two BCC structures. The addition of Ti and Mo contributed to the formation of BCC2. In addition, when the concentration of Ti and Mo increased, the diffraction peaks were shifted to higher angles, indicating a decrease in the lattice constants. Moreover, the diffraction peaks became broader with the increase in the Ti and Mo contents, indicating grain refinement [33].

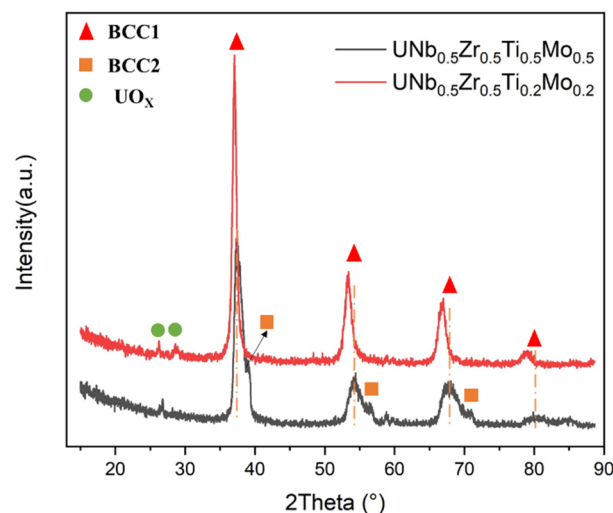


Figure 10. XRDs pattern of the $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$ HEAs.

The as-cast structures of the $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$ alloys are shown in Figure 11. These alloys had a typical cast dendritic structure of a uniform composition region and U-enriched region between the dendritic structures. It can be observed that the structure segregation phenomenon of the alloys improved as Ti and Mo concentrations increased. This was due to the fact that Mo had a high melting point (higher than U's melting point) and element redistribution during solidification. The alloy components are equally distributed without noticeable segregation, as seen in the surface scan findings of $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ in Figure 12.

The Brinell hardness and yield strength of the $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_x\text{Mo}_x$ HEAs are listed in Table 9. The addition of Ti and Mo promoted the hardness and yield strength of the alloys, and plasticity reduced dramatically. The mixing enthalpy of Mo with Nb, Zr, and Ti was negative, and Mo had a higher melting point, resulting in component segregation. It can be demonstrated by examining $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$, which has a higher hardness of 350 HB than that of $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$.

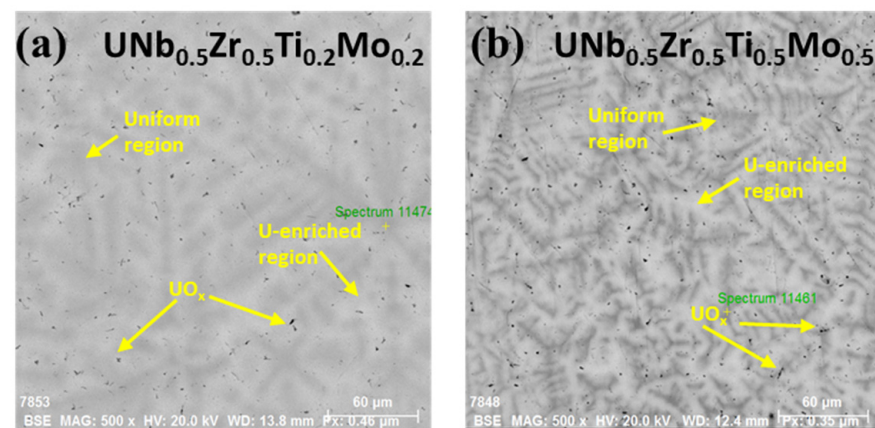


Figure 11. Microstructures of the (a) $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ and (b) $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$ alloys.

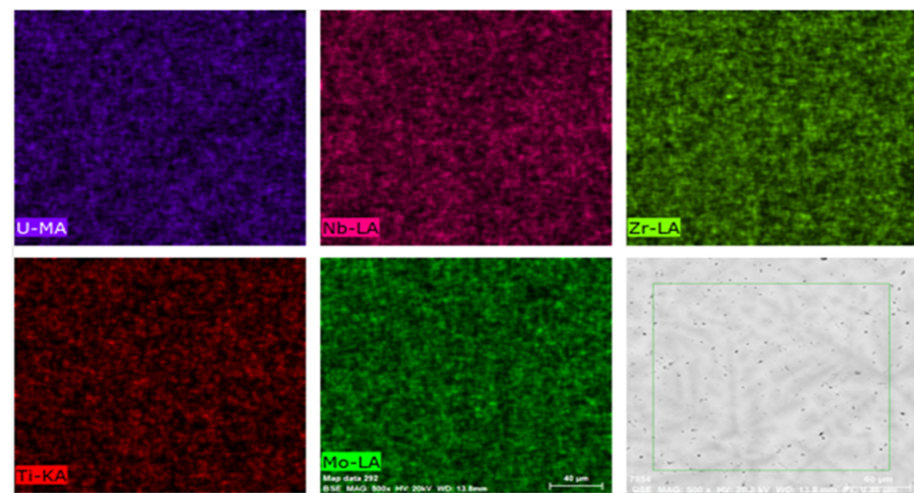


Figure 12. EDS map of the $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ alloy.

Table 9. Hardness and strength of the $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_x\text{Mo}_x$ HEAs.

Properties	$\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$	$\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$
Hardness (HB)	297	350
Strength (MPa)	1157	1215 (Crashed)

4. Discussion

The researched alloys in the present article are all BCC solid solution structures, per the solid-solution formation criteria and microstructure characterization. Figure 13 shows the concept of the DUHEA design process, which begins with the ternary U-Nb-Zr system, adds Ti and Mo elements to create the quaternary alloys and, ultimately, finishes with the quinary $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_x\text{Mo}_y$ alloy. The mixing enthalpy of U with Nb, Ti, Zr, and Mo had a significant impact on the structure and mechanical properties of the studied alloys. The relationship between the mixing enthalpy and the mechanical characteristics of the alloys are presented in Figure 14. The compressive yield strength and hardness exhibited a rising trend as the mixing enthalpy fell. Though $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}$ had higher strength, severe component segregation microstructures resulted in poor plasticity. This was due to the melting point of Mo being higher than those of other elements, resulting in component segregation and poor performance. Finally, based on our combined theoretical and experimental results, $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}_{0.5}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ had a homogeneous structure and outstanding mechanical characteristics.

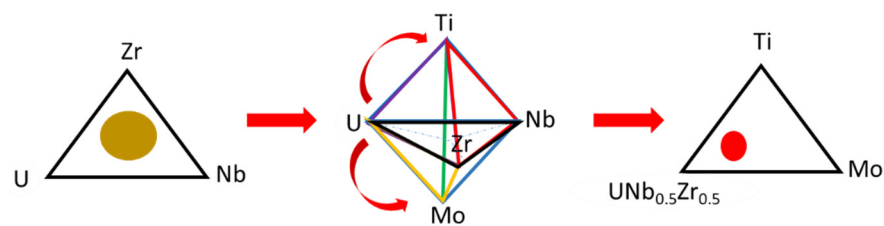


Figure 13. Design process of a DUHEA.

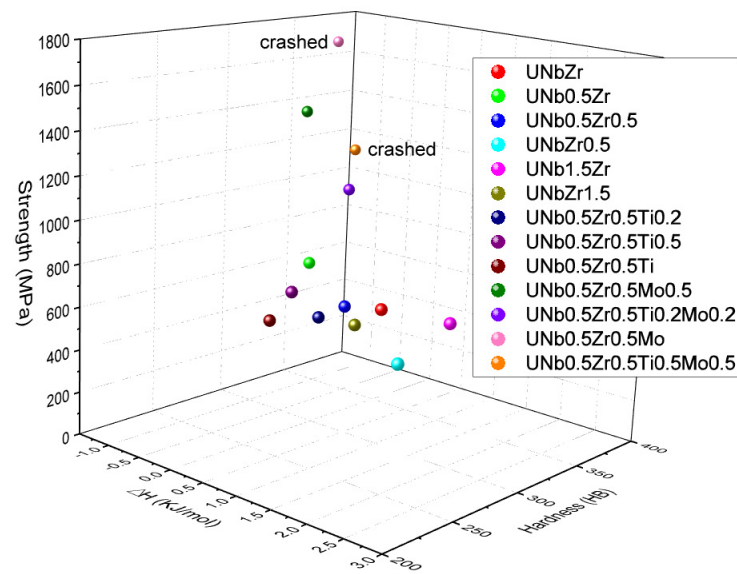


Figure 14. Trend graph of the relationship between the mixed enthalpy and mechanical properties of the U-Nb-Zr-Ti-Mo HEAs.

5. Conclusions

In this paper, we examined the composition of $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}_{0.5}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$, finding both to possess a homogeneous structure, low segregation, and outstanding mechanical properties. The alloys examined were screened during the design process from the DU ternary alloy to DUHEA according to the formation law of HEAs and based on experimental results. $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}_{0.5}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ were composed of a single BCC structure, which was in line with our theoretical calculations. The hardness and strength of $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Mo}_{0.5}$ and $\text{UNb}_{0.5}\text{Zr}_{0.5}\text{Ti}_{0.2}\text{Mo}_{0.2}$ were 305 HB and 1452 MPa, and 297 HB and 1157 MPa, respectively. This suggests that the HEA phase-formation criteria could have a wide range of applications in the design of DUHEAs, providing promising theoretical direction for the future development of specific BCC-structured HEAs.

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References

1. Zhang, Y.; Zuo, T.T.; Tang, Z.; Gao, M.C.; Dahmen, K.A.; Liaw, P.K.; Lu, Z.P. Microstructures and properties of high-entropy alloys. *Prog. Mater. Sci.* **2014**, *61*, 1–93. [\[CrossRef\]](#)
2. Li, D.Y.; Li, C.X.; Feng, T.; Zhang, Y.D.; Sha, G.; Lewandowski, J.J.; Liaw, P.K. High-entropy $\text{Al}_{0.3}\text{CoCrFeNi}$ alloy fibers with high tensile strength and ductility at ambient and cryogenic temperatures. *Acta Mater.* **2017**, *123*, 285–294. [\[CrossRef\]](#)
3. Moravcikova-Gouvea, L.; Moravcik, I.; Omasta, M.; Vesely, J.; Cizek, J.; Minarik, P.; Cupera, J.; Zadera, A.; Jan, V.; Dlouhy, I. High-strength $\text{Al}_{0.2}\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}$ high-entropy alloy produced by powder metallurgy and casting: A comparison of microstructures, mechanical and tribological properties. *Mater. Charact.* **2020**, *159*, 110046. [\[CrossRef\]](#)
4. Zhang, W.; Liaw, K.P.; Zhang, Y. A Novel Low-Activation VCrFeTaW_x ($x = 0.1, 0.2, 0.3, 0.4$, and 1) High-Entropy Alloys with Excellent Heat-Softening Resistance. *Entropy* **2018**, *20*, 951. [\[CrossRef\]](#) [\[PubMed\]](#)
5. King, D.J.M.; Cheung, S.T.Y.; Humphry-Baker, S.A.; Parkin, C.; Couet, A.; Cortie, M.B.; Lumpkin, G.R.; Middleburgh, S.C.; Knowles, A.J. High temperature, low neutron cross-section high-entropy alloys in the Nb-Ti-V-Zr system. *Acta Mater.* **2019**, *166*, 435–446. [\[CrossRef\]](#)
6. Zhou, Q.; Sheikh, S.; Ou, P.; Chen, D.; Hu, Q.; Guo, S. Corrosion behavior of $\text{Hf}_{0.5}\text{Nb}_{0.5}\text{Ta}_{0.5}\text{Ti}_{1.5}\text{Zr}$ refractory high-entropy in aqueous chloride solutions. *Electrochem. Commun.* **2019**, *98*, 63–68. [\[CrossRef\]](#)
7. Miracle, D.B.; Senkov, O.N. A critical review of high entropy alloys and related concepts. *Acta Mater.* **2017**, *122*, 448–511. [\[CrossRef\]](#)
8. Zhang, W.; Liaw, P.K.; Zhang, Y. Science and technology in high-entropy alloys. *Sci. China Mater.* **2018**, *61*, 1–21. [\[CrossRef\]](#)
9. Wakeford, R. Depleted uranium. *J. Radiol. Prot. Off. J. Soc. Radiol. Prot.* **2001**, *21*, 76. [\[CrossRef\]](#)
10. Jiang, G.C.; Aschner, M. *Depleted Uranium. Handbook of Toxicology of Chemical Warfare Agents*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 447–460.
11. Wang, B.; Dong, Y.; Huang, G. An investigation on the adiabatic shear bands in depleted U-0.75 wt% Ti alloy under dynamic loading. *Metals* **2018**, *8*, 145. [\[CrossRef\]](#)
12. Sheldon, R.I.; Peterson, D.E. The U-Zr (Uranium-Zirconium) system. *Bull. Alloy. Phase Diagr.* **1989**, *10*, 165–171. [\[CrossRef\]](#)
13. Bian, B.; Zhou, P.; Wen, S.; Du, Y. Atomic mobilities and diffusivities in U-X ($X = \text{Nb, Zr, Ti}$) bcc alloys. *Calphad* **2018**, *61*, 85–91. [\[CrossRef\]](#)
14. Sinha, V.; Hegde, P.; Prasad, G.; Dey, G.; Kamath, H. Phase transformation of metastable cubic γ -phase in U-Mo alloys. *J. Alloys Compd.* **2010**, *506*, 253–262. [\[CrossRef\]](#)
15. Liu, X.J.; Li, Z.S.; Wang, J.; Wang, C.P. Thermodynamic modeling of the U-Mn and U-Nb systems. *J. Nucl. Mater.* **2008**, *380*, 99–104. [\[CrossRef\]](#)
16. Morais, N.W.S.; Lopes, D.A.; Schön, C.G. Effect of thermo-mechanical processing on microstructure and mechanical properties of U-Nb-Zr alloys: Part 1—U-6 wt. % Nb-6 wt. % Zr. *J. Nucl. Mater.* **2017**, *488*, 173–180. [\[CrossRef\]](#)
17. Shi, J.; Zhao, Y.W.; Jiang, C.L.; Wang, X.; Zhang, Y.Z.; Zou, D.L.; Xu, H.Y.; Huang, H.; Luo, C. Development of single-phase bcc UHfNbTi high-entropy alloy with excellent mechanical properties. *Mater. Lett.* **2022**, *307*, 130822. [\[CrossRef\]](#)
18. Koike, J.; Kassner, M.E.; Tate, R.E.; Rosen, R.S. The Nb-U (Niobium-Uranium) System. *J. Phase Equilib.* **1998**, *19*, 253–260. [\[CrossRef\]](#)
19. Gao, M.C.; Zhang, B.; Yang, S.; Guo, S.M. Senary Refractory High-Entropy Alloy HfNbTaTiVZr . *Metall Mater. Trans. A* **2016**, *47*, 3333–3345. [\[CrossRef\]](#)
20. Chen, H.L.; Mao, H.H.; Chen, Q. Database development and Calphad calculations for high entropy alloys: Challenges, strategies, and tips. *Mater. Chem. Phys.* **2017**, *210*, 279–290. [\[CrossRef\]](#)
21. Jiang, C.; Uberuaga, B.P. Efficient ab initio modeling of random multicomponent alloys. *Phys. Rev. Lett.* **2016**, *116*, 105501. [\[CrossRef\]](#)
22. Mu, S.; Wimmer, S.; Mankovsky, S.; Ebert, H.; Stocks, G.M. Influence of local lattice distortions on electrical transport of refractory high entropy alloys. *Scr. Mater.* **2019**, *170*, 189–194. [\[CrossRef\]](#)
23. Gao, M.C.; Gao, P.; Hawk, J.A.; Ouyang, L.; Alman, D.E.; Widom, M. Computational modeling of high-entropy alloys: Structures, thermodynamics and elasticity. *J. Mater. Res.* **2017**, *32*, 3627–3641. [\[CrossRef\]](#)
24. Yan, X.; Zhang, Y. A body-centered cubic $\text{Zr}_{50}\text{Ti}_{35}\text{Nb}_{15}$ medium-entropy alloy with unique properties. *Scr. Mater.* **2020**, *178*, 329–333. [\[CrossRef\]](#)
25. Mathiou, C.; Pouliou, A.; Georgatis, E.; Karantzalis, A.E. Microstructural features and dry—Sliding wear response of MoTaNbZrTi high entropy alloy. *Mater. Chem. Phys.* **2018**, *210*, 126–135. [\[CrossRef\]](#)
26. Shi, J.; Huang, H.; Hu, G.; Zhang, P.; Jiang, C.; Xu, H.; Luo, C. Microstructure and mechanical properties of two uranium-containing high-entropy alloys. *J. Alloys Compd.* **2020**, *860*, 158295. [\[CrossRef\]](#)
27. Yeh, J.W.; Chen, S.K.; Lin, S.J.; Gan, J.Y.; Chin, T.S.; Shun, T.T.; Tsau, C.-H.; Chang, S.-Y. Nanostructured high-entropy alloys with multiple principal elements: Novel alloy design concepts and outcomes. *Adv. Eng. Mater.* **2004**, *6*, 299–303. [\[CrossRef\]](#)

28. Zhang, Y.; Zhou, Y.J.; Lin, J.P.; Chen, G.L.; Liaw, P.K. Solid-solution phase formation rules for multi-component alloys. *Adv. Eng. Mater.* **2008**, *10*, 534–538. [[CrossRef](#)]
29. Gao, M.C.; Yeh, J.W.; Liaw, P.K.; Zhang, Y. *High-Entropy Alloys: Fundamentals and Applications*; Springer: Berlin/Heidelberg, Germany, 2016.
30. Yang, X.; Zhang, Y. Prediction of high-entropy stabilized solid-solution in multi-component alloys. *Mater. Chem. Phys.* **2012**, *132*, 233–238. [[CrossRef](#)]
31. Guo, S.; Ng, C.; Lu, J.; Liu, C. Effect of valence electron concentration on stability of fcc or bcc phase in high entropy alloys. *J. Appl. Phys.* **2011**, *109*, 103505. [[CrossRef](#)]
32. Yan, X.-H.; Ma, J.; Zhang, Y. High-throughput screening for biomedical applications in a Ti-Zr-Nb alloy system through masking co-sputtering. *Sci. China Phys. Mech. Astron.* **2019**, *62*, 996111. [[CrossRef](#)]
33. Tan, X.-R.; Zhang, G.-P.; Zhi, Q.; Liu, Z.-X. Effects of milling on the microstructure and hardness of Al₂NbTi₃V₂Zr high-entropy alloy. *Mater. Design* **2016**, *109*, 27–36. [[CrossRef](#)]