

EFFECT OF Hf, V AND Mo ADDITION ON THE MICROSTRUCTURE AND HARDNESS OF EQUIATOMIC TiNbTaZr-BASED BIOLOGICAL HIGH ENTROPY ALLOYS (BIO-HEAS)

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Abstract

High entropy alloys (HEAs), unlike conventional alloy systems, have attracted growing attention due to their unique combination of structural and functional properties arising from their multi-principal element design. In recent years, Bio-HEAs, composed of elements with proven biocompatibility, have emerged as promising candidates for biomedical applications. In this study, four equiatomic HEAs (TiNbTaZr, TiNbTaZrMo, TiNbTaZrHf, and TiNbTaZrV) were produced using vacuum arc melting. The structural characteristics of the HEAs were analyzed by X-ray diffraction (XRD), while their microstructures were examined via scanning electron microscopy (SEM). Elemental distributions within the microstructures were investigated using energy dispersive X-ray spectroscopy (EDS). Mechanical behavior was assessed through Vickers hardness testing, which revealed a clear correlation between alloying elements, structure, and hardness. Among the HEAs, TiNbTaZrMo exhibited the highest hardness value of 516 ± 2.65 HV, whereas the base alloy, TiNbTaZr, showed a hardness of 323.6 ± 5.18 HV. The additions of V and Hf resulted in hardness values of 410.2 ± 4.27 HV and 316.2 ± 4.66 HV, respectively. XRD analysis indicated the presence of dual BCC phases in the Mo- and V-containing alloys, while a single BCC phase was observed in the base and Hf-containing HEAs. Microstructural analysis revealed two distinct phase regions: Ta-rich and Zr-rich domains. These findings highlight the significant influence of alloying element selection on phase evolution and mechanical performance, demonstrating the potential for tailoring bio-HEAs for specific biomedical applications.

Keywords: Biological high entropy alloys, hardness, microstructure

1. INTRODUCTION

High entropy alloys (HEAs) are alloys produced by combining five or more elements in equal or nearly equal proportions, representing an alternative approach to conventional alloy design [1,2]. HEAs possess four core effects: high entropy, sluggish diffusion, severe lattice distortion, and the cocktail effect, which lead to superior mechanical and chemical properties [3]. Therefore, HEAs are used not only in structural applications but also in functional fields, such as corrosion-resistant materials, biomedicine, and nuclear technologies [4–7]. Especially in biomedical applications, the use of HEAs has gained importance [7,8]. These HEAs are referred to as bio-HEAs [9] or biological high entropy alloys [7]. Bio-HEAs should be composed of non-cytotoxic and non-allergenic metals, which typically include Ti, Zr, Hf, Nb, Ta, V, Mo, and W [7,9].

Recent studies in the literature have demonstrated that HEAs composed of non-toxic elements hold significant promise for biomedical applications [10–14]. Lai et al. [10] investigated the structural, electrochemical, and biological properties of equimolar TiNbTaZrMoV and TiNbTaZrMo HEAs. Their results indicated that the homogenized TiNbTaZrMoV alloy exhibited superior biocompatibility compared to Ti6Al4V, as well as enhanced corrosion resistance in PBS solution [10]. Additionally, Yuan et al. [13] studied various compositional

configurations of TiZrHfNbTa HEA systems with different crystal structures and concluded that these alloys can offer low magnetic susceptibility, low elastic modulus, and good mechanical biocompatibility, which are critical properties for biomedical applications [13]. Similarly, Hua et al. [11] studied that corrosive and non-corrosive wear properties along with corrosion and mechanical properties, of $Ti_xZrNbTaMo$ ($x = 0.5, 1, 1.5$, and 2, molar). They found that decreasing the Ti content improved the wear resistance, hardness, and yield strength, with $Ti_{0.5}ZrNbTaMo$ exhibiting the highest resistance to corrosive wear among the studied compositions [11].

In this study, equiatomic TiNbTaZr-based Bio-HEAs alloyed with Hf, V, and Mo were produced using a vacuum arc melting technique and characterized regarding their microstructural (XRD, SEM) and mechanical (Vickers hardness) properties.

2. MATERIALS AND METHODS

High purity Ti (99.9%), Ta (99.65%), Zr (99.2%), Mo (99.6%), Hf (99.7%), and V (99.7%) granules and chunks (Thermo Fisher Scientific), and Nb (>99.96%, Alfa Aesar) were used for the production of HEAs. Each metal was precisely weighed to achieve a total mass of 1 g for the HEA, and then melted using a vacuum arc melter with a current of 180 A under an argon atmosphere to minimize oxygen contamination. Each HEA was remelted seven times with flipping to achieve a homogeneous alloy. The final HEA was allowed to cool gradually on a water-cooled copper hearth. The nominal compositions of the produced bio-HEAs were given in **Table 1**.

Table 1 The nominal compositions of the produced bio-HEAs (at%)

Bio-HEAs	Ti	Nb	Ta	Zr	Hf	V	Mo
TiNbTaZr	25	25	25	25	-	-	-
TiNbTaZrHf	20	20	20	20	20	-	-
TiNbTaZrV	20	20	20	20	-	20	-
TiNbTaZrMo	20	20	20	20	-	-	20

As-cast bio-HEA ingots were polished with conventional metallographic methods following cold mounting in polyester resin. X-ray diffraction (XRD) analyses of as-cast HEAs were performed using a PANalytical EMPYREAN diffractometer. Cu-K α radiation ($\lambda = 0.15406$ nm) was used as the X-ray source, and the diffraction patterns were collected in the 2θ range of 10° – 140° with a step size of 0.01° . HighScore Plus software was used for peak analysis and fitting processes. The microstructures of as-polished bio-HEAs were observed using a scanning electron microscope (HITACHI SU1510) equipped with a tungsten filament at an accelerating voltage of 20 kV and a probe current of 60 pA, utilizing backscattered electrons (BSE). Additionally, elemental compositions were analyzed using an energy dispersive spectrometer (Oxford X-act). The hardness measurements of the bio-HEAs embedded in the mount were conducted using a Vickers hardness tester (EMCO-TEST DuraScan) under a load of 0.5 kgf. The hardness measurements were taken from at least five different regions, and the average values were used for evaluation.

3. RESULTS AND DISCUSSION

3.1 Microstructural characterization

The X-ray diffraction (XRD) patterns of the produced Bio-HEAs are presented in **Figure 1**. As observed, the TiNbTaZr and TiNbTaZrHf alloys exhibit a single BCC structure, whereas the TiNbTaZrV and TiNbTaZrMo alloys display a dual-phase BCC structure. The equiatomic addition of Hf to the TiNbTaZr alloy results in an increase in lattice parameter from 0.33643 nm to 0.34091 nm, attributed to the larger atomic radius of Hf compared to the other constituent elements. However, two BCC phases (BCC1, BCC2) were observed in the TiNbTaZrV HEA, exhibiting closely related lattice parameters of 0.3294 nm and 0.32754 nm, respectively.

Similarly, the relatively lower lattice parameters compared to the base alloy can be attributed to the smaller atomic radius of V. On the other hand, in the TiNbTaZrMo alloy, the BCC1 and BCC2 phases are more distinctly observed in **Figure 1**. The lattice parameters corresponding to these phases were determined to be 0.33027 nm and 0.32771 nm, respectively. Thermo-physical properties such as mixing enthalpy, mixing entropy, and valence electron concentration (VEC) are widely used to assess the structural properties of HEAs. In this study, the thermophysical properties of the designed HEAs were calculated using the HEAPs [15]. The VEC values for the TiNbTaZr, TiNbTaZrHf, TiNbTaZrV, and TiNbTaZrMo alloys were found to be 4.5, 4.4, 4.6, and 4.8, respectively. According to Guo et al. [16], alloys with a VEC below 6.87 are likely to form a BCC structure. The obtained results are consistent with [16] and explain the formation of BCC phases observed in the XRD patterns. Moreover, the XRD patterns of the produced Bio-HEAs are consistent with the literature, confirming single BCC phase formation for TiNbTaZr [13,17], TiNbTaZrHf [13,18], and dual-phase BCC structures for TiNbTaZrV [19] and TiNbTaZrMo [10,11,20].

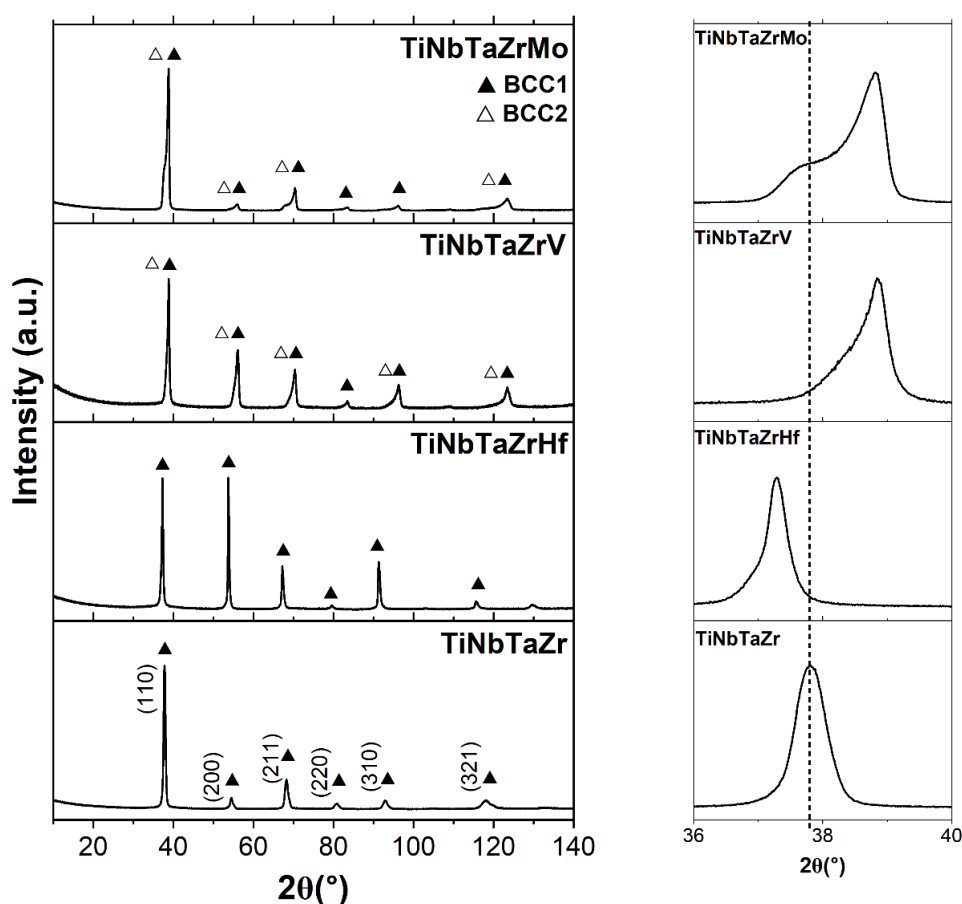


Figure 1 XRD Patterns of TiNbTaZr, TiNbTaZrHf, TiNbTaZrV, TiNbTaZrMo HEAs

Figure 2 presents the backscattered electron images and EDS maps of the HEAs. All HEAs exhibited dendritic microstructures and consisted of compositionally distinct regions. According to the EDS analysis (**Figure 2a**, **2b**, and **2d**), the TiNbTaZr, TiNbTaZrV, and TiNbTaZrMo HEAs showed Ta-rich (light gray in BSE images, dendritic) and Zr-rich regions (dark gray in BSE images, interdendritic). In the Hf-containing HEA (**Figure 2c**), such segregated regions were not observed, although Ta-rich areas were still detected. In the base HEA (TiNbTaZr), Ti and Nb were enriched in the Zr-rich regions. A similar distribution was also observed in the Mo- and V-containing HEAs. Furthermore, V segregated in the Zr-rich regions, while Mo was detected in both Ta-rich and Zr-rich regions. Other studies focusing on TiNbTaZr-based HEAs have also reported that Ti- and Zr-rich phases tend to segregate in the interdendritic regions, while Ta-rich regions are primarily located within the dendritic areas [11,17,20].

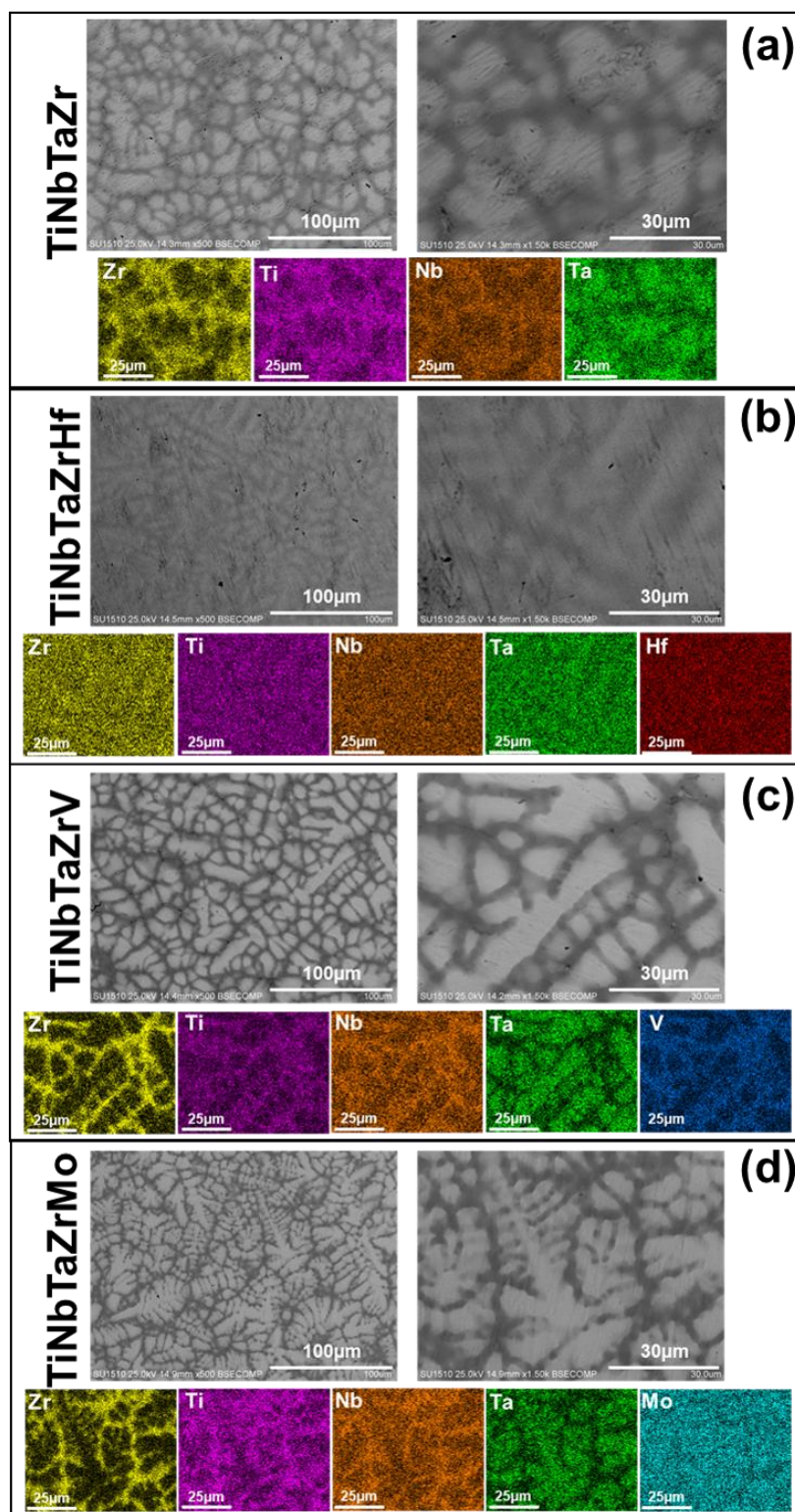


Figure 2 Microstructures and EDS analysis of HEAs a)TiNbTaZr b)TiNbTaZrHf c)TiNbTaZrV d)TiNbTaZrMo

3.2 Mechanical properties

The Vickers hardness test was performed to correlate the mechanical properties of the HEAs with their microstructural characteristics. The hardness test results are presented in **Figure 3**. According to **Figure 3**, the TiNbTaZr and TiNbTaZrHf HEAs exhibited relatively lower hardness values, measured as 323.6 ± 5.18 HV

and 316.2 ± 4.66 HV, respectively. On the other hand, the hardness values of TiNbTaZrV and TiNbTaZrMo HEAs were obtained as 410.2 ± 4.27 and 516 ± 2.65 HV, respectively. Similar results were also reported by [11,19]. Accordingly, it can be deduced that the significant increase in hardness with the addition of V and Mo into TiNbTaZr HEAs can be attributed to the formation of dual BCC phase structures, as shown in **Figure 1**. It can also be stated that the inherently higher hardness of pure elements such as Mo contributed to the overall hardness of the HEAs.

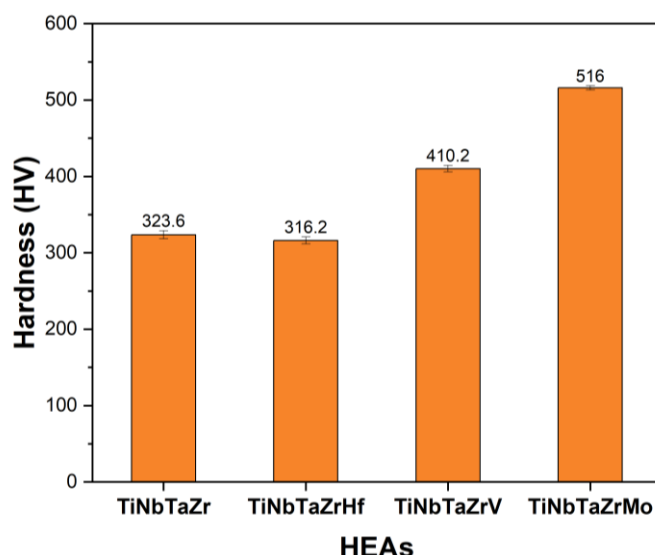


Figure 3 The Vickers hardness values of Bio-HEAs

4. CONCLUSION

In this study, TiNbTaZr-based Bio-HEAs containing Hf, V, and Mo were microstructurally and mechanically characterized to evaluate the effects of the constituent elements. Based on the microstructural observations and hardness evolution, the following conclusions were drawn:

- TiNbTaZr and TiNbTaZrHf HEAs exhibited a single BCC structure, whereas the Mo- and V-containing HEAs displayed dual BCC structures, as confirmed by the XRD results.
- The Bio-HEAs with dual BCC structures (TiNbTaZrV and TiNbTaZrMo) have higher hardness. The highest hardness value was obtained from TiNbTaZrMo HEA as 516.0 ± 2.65 HV.
- Except for the Hf-containing HEA, Zr-rich and Ta-rich regions were observed in the microstructures of the base, Mo-, and V-containing HEAs.
- Vanadium was enriched in the Zr-rich regions, whereas Mo and Hf were observed to be relatively uniformly distributed across all phases.

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