

Medium Entropy Alloys for Biomedical Applications

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Abstract

High entropy alloys (HEAs) is a rapidly emerging class of metallic materials consisting of four or more elements in equimolar or quasi-equimolar compositions. These alloys often have simple crystal structures and tailorable properties attracting significant interest for different applications. Common metallic materials for orthopaedic and dental implants include stainless steel, Co-Cr and Ti- alloys. Although these materials are widely in use, issues relevant to biocompatibility and suspected toxicity and the elastic modulus mismatch compared to that of hard tissue have been raised in recent years. High entropy alloys specifically designed for bio-medical applications can offer solutions to overcome these limitations. Bio-HEAs have emerged in the last couple of years and currently receive increasing scientific attention. In this work, we discuss on the design of new entropic alloys using only non-toxic elements such as Ti, Zr, Nb, Ta and Mo. We use a systematic approach to investigate the effect of additional elements on the microstructure and properties of the alloys starting from the binary Ti-Nb and extending to the ternary Ti-Zr-Nb, the quaternary Ti-Zr-Nb-Ta and the Ti-Zr-Nb-Ta-Mo alloy. The alloy design is building on previous work on beta Ti- alloys which has shown promising trends for reducing the elastic modulus of implant materials. The alloys were produced by arc-melting and suction casting under Ar inert atmosphere. X-ray diffraction, and scanning electron microscopy were employed to reveal their crystal structure and microstructure. respectively. The developed alloys exhibit BCC crystal structure and a dendritic microstructure in their as-cast condition. The addition of Zr and Mo was found to increase the hardness of the alloys.

Keywords: Biomedical materials; High / medium entropy alloys; multi principal element alloys; β -phase Ti alloy, Ti-based alloys.

1. Introduction

The aging society is in constant need of novel materials to address health problems caused by long-used organs and tissues. Some requirements of metallic materials for biomedical application such as dental and orthopaedic implants, including biocompatibility, reasonable corrosion resistance, and proper mechanical properties. Novel alloys such as bulk metallic glasses (BMGs) and high entropy alloys (HEAs) hold the potential to overcome limitations of commercial or conventional metallic biomaterials attracting researchers' attention.

1.1. Materials for Biomedical applications

'Biomedical materials' can be used in medical devices either applied with or without intimate contact with living tissue, including dental and orthopaedic implants. Biocompatibility is essential because the material must not be harmful to the host tissues. This can be investigated in two ways: physical impact which is governed by mechanical properties, and chemical impact which is controlled by elements involved [1,2]. In the last 2 decades,

some metallic biomedical materials such as Ti-6Al-4V [3-5], 316/316L stainless steel (316/316L SS), Co-Cr based alloys [6] and commercially pure titanium (cp-Ti) are used for replacement material for human bones and joints.

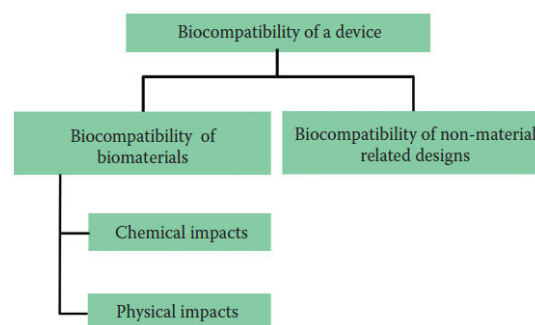


Fig. 1. Contributors to the biocompatibility of a medical device [1].

Although these materials show reasonable corrosion resistance, they still possess high elastic modulus and toxic elements which is harmful to host tissues. Compared with the other materials commercial Ti-6Al-4V has an elastic modulus of about 110 GPa but still much higher than of human

cortical bone (~30 GPa) [7]. A big mismatch of elastic modulus can lead to reduction in bone density and finally cause osteoporosis and poor osseointegration [8]. Some elements like V and Ni are to be avoided in biomedical materials due to their cytotoxicity [9,10]. This means new biomedical materials with non-toxic elements and lower elastic modulus as human bones' need to be investigated.

1.2. High Entropy Alloys (HEAs)

A new category of metallic materials, high entropy alloys (HEAs), attracts the attentions of researchers over the last 15 years. The concept behind was first mentioned by the groups of Brian Cantor and Jien-Wei Yeh in 2004 [11,12]. Different from traditional alloys, HEAs increase elemental complexity to modify the properties which conventional alloys lacked while forming simple single or dual phase crystal structures only. The cocktail effect of HEAs offers the possibility of property customisation, which can be used to develop new biomaterials alleviating the issues mentioned above.

There are mainly two kinds of definitions for HEAs: entropy-based and composition-based. The entropy-based definition demands an entropy of mixing of the alloy being larger than 1.5 R (R = 8.314 J/K·mol is the ideal gas constant). Yeh et al. also suggested that alloys with entropy of mixing less than 1 R are called low-entropy while medium-entropy if $1 R < \Delta S_{\text{mix}} \leq 1.5 R$ [13]. The composition-based definition claims that the alloy should contain at least 5 elements and each element should at least have a content of 5~35 at.%. Although actual alloys may not strictly follow these definitions, they may be still considered HEAs. Due to elemental complexity, phase stability of HEAs will be different from that of pure elements and conventional alloys. Thus, the parameters will promote alloy design which meets the corresponding criteria.

According to entropy-based definition, entropy of mixing (ΔS_{mix}) is the parameter which identifies whether the alloy is high entropy or not. An exact calculation of the mixing entropy is much more complex as it includes at least four parts (configurational entropy, vibrational entropy, magnetic dipole entropy, electronic randomness entropy). Since the configurational entropy is the dominant contribution, entropy of mixing can be estimated by the value of configurational entropy. The ideal configurational entropy for a random n-component solid solution alloy can be written as

$$\Delta S_{\text{mix}} \approx \Delta S_{\text{mix}}^{\text{conf}} = -R \sum_{i=1}^n x_i \cdot \ln(x_i) \quad (\text{eq.1})$$

where x_i is the molar fraction of the i-th element. Equation 1 can be simplified to

$$\Delta S_{\text{mix}} \approx \Delta S_{\text{mix}}^{\text{conf}} = R \ln(n) \quad (\text{eq.2})$$

if the alloy is equiatomic.

Enthalpy of mixing (ΔH_{mix}) expresses the bonding between each (binary) pair of elements and is used to predict the phase formation in HEAs. The of enthalpy of mixing of an alloy can be expressed by

$$\Delta H_{\text{mix}} = \sum_{i=1, i \neq j}^n 4 \cdot \Delta H_{\text{AB}}^{\text{mix}} \cdot x_i x_j \quad (\text{eq.3})$$

where $\Delta H_{\text{AB}}^{\text{mix}}$ is the mixing enthalpy of a binary equiatomic AB alloy of components i and j with their molar fractions x_i and x_j . The values for $\Delta H_{\text{AB}}^{\text{mix}}$ are taken from the literature [14]. For HEAs to form solid solutions rather than intermetallic compounds the criterion $-15 \text{ kJ/mol} < \Delta H_{\text{mix}} < 5 \text{ kJ/mol}$ was proposed [15].

The dimensionless parameter

$$\Omega = \frac{T_m \cdot \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|} \quad (\text{eq.4})$$

proposed by Yang and Zhang [16], combines the effect of ΔS_{mix} and ΔH_{mix} on the stability of a multicomponent solid solution, where

$$T_m = \sum_{i=1}^n x_i \cdot (T_m)_i \quad (\text{eq.5})$$

is the estimated melting point of the n-component alloy and $(T_m)_i$ the melting point of the i-th element of the alloy. The Ω parameter is useful to predict the probability to form a single-phase random solid solution in HEAs. Voiculescu et al. reported that solid solutions only form when $\Omega > 10$ [17].

Another dimensionless parameter

$$\delta = \sqrt{\sum_{i=1}^n x_i \cdot \left(1 - \frac{r_i}{\sum_{j=1}^n x_j r_j}\right)^2} \quad (\text{eq.6})$$

quantifies the atomic size difference was proposed by Zhang et al [15] and is also used to predict the probability to form solid solutions in HEAs, where r_i (r_j) is the atomic radius of the i-th (j-th) component. Yang and Zhang concluded that solid solutions occur when $\Omega \geq 1.1$ and $\delta \leq 6.6\%$ [16]. Comparably, recently Voiculescu et al., concluded that solid solutions only form if $\Omega \geq 1.1$ and $\delta \leq 3.6\%$. They also reported that solid solutions and

intermetallic compounds will occur if $1.1 < \Omega < 10$ and $3.6\% < \delta < 6.6\%$ [17]. Thus, to elucidate the relevance of Ω and δ further research is required.

Valence electron concentration (VEC) is a parameter suggested by Guo et al [18], which is used to predict the phase stability of BCC and FCC structure. VEC can be calculated by

$$VEC = \sum_{i=1}^n c_i \cdot (VEC)_i \quad (\text{eq.7})$$

where $(VEC)_i$ is the VEC of the i -th component. As suggested by Guo et al. only BCC phase will form when $VEC \leq 6.87$, a mixture of BCC and FCC when $6.87 < VEC \leq 8$, and only FCC phase when $VEC > 8$ [18].

1.3. Biomedical HEAs (BioHEAs)

In the last few years, an increasing number of studies focused on HEAs for biomedical applications [19,20,32-34]. Compared to conventional biomedical alloys, non-toxic elements are selected in novel HEAs/MEAs. A review by Wong et al. found that the three elements Ti, Zr and Nb constitute nearly 50% of the selected elements, i.e., Ti-Zr-Nb is a promising starting point for the development BioHEAs [21].

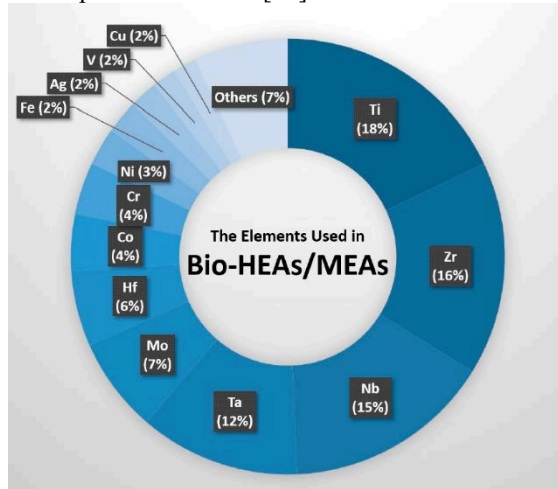


Fig. 2. Proportion of elements used in BioHEAs/MEAs [16].

The alloy design trends follow those suggested for beta Ti-alloys and metallic glasses [22, 23]. Ti alloys exhibit hexagonal α phase, body-centered β phase, and hexagonal ω phase. Alloys with β -phase can obtain lower elastic modulus than the other phases [22]. Nb is one of the β -stabiliser elements commonly used in Ti-alloys which generate Ti-Nb binaries as initial β -phase alloys [22, 24, 25]. Zr, also treated as β -stabiliser in the Ti-Nb system, can form stable oxides which is inert to host cells resulting in Ti-Zr-Nb alloys with a higher strength and relatively

lower elastic modulus [26,27]. A large group of Ti-Zr-Nb-Ta alloys are called ‘Gum metal’ or TNZT, was first mentioned by Nishino’s research team in 2005 [28]. Based on that, Ti-35Nb-7Zr-5Ta (wt.%) widely studied by several research groups, could be shown to have large potential to reach lower elastic modulus close to that of human bones via proper heat treatment [29-32]. The addition of Mo, as another β -stabiliser, generates the Ti-Zr-Nb-Ta-Mo alloy system, which is genuinely ‘high-entropy’, and makes the alloy stronger ($\sigma_{YS} > 1000$ MPa) and increases biocompatibility compared to commercial metallic biomaterials [33-35].

In the present work, a series of Ti-based alloys has been studied according to increasing of elemental complexity, to elucidate the relationship between composition, mechanical properties and crystalline/micro-structures.

2. Material and methods

2.1. Alloy design

Based on a Ti-Nb binary body-centered β -phase alloy, further alloys with gradually increasing elemental complexity towards ‘high entropy’ have been prepared. Table 1 lists the compositions investigated.

Table 1. The 5 compositions studied.

Compositions (at.%)	number	Comments
Ti _{66.6} Nb _{33.3}	A1	base β -phase Ti-Nb alloy
Ti _{33.3} Zr _{33.3} Nb _{33.3}	A2	Zr addition to A1
(TiZr) ₆₇ Nb ₂₅ Ta ₈	A3	Ta addition to A2
(TiZr) ₇₅ Nb ₁₉ Ta ₆	A4	modified from A3.
(TiZrNb) ₈₈ (TaMo) ₁₂	A5	based on ref. [34]

Thermodynamic parameters for these alloy compositions will be discussed in section 3.1.

2.2. Alloy preparation

Pure elements Ti, Zr, Nb, Ta and Mo (purity $\geq 99.93\%$) were weighed according to alloy compositions. Arc melting under argon atmosphere was used to alloy the elements. Each alloy was flipped and re-melted 5 times to ensure homogeneity. The alloy ingots were subsequently re-melted and suction-cast into a copper mould with cylindrical cavity to obtain rods 5 mm in diameter, which were further processed to specimens for mechanical tests and structural characterisation.

2.3. Structural characterisation

The crystal structure of the alloys was investigated by X-ray diffraction (XRD, SIEMENS D5005 X-ray diffractometer) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the range of 2θ $10^\circ \sim 90^\circ$ at step width 0.02° . Microstructural characterisation was done by scanning electron microscopy (SEM, TESCAN VEGA 3) equipped with energy dispersive spectroscopy (EDS) for chemical analysis. Optical microscopy (OM, Leica DM2700) was done for observing the etched surface of samples to investigate microstructures.

2.4. Mechanical behaviour

Mechanical behaviour here mainly focuses on Vickers microhardness. Vickers microhardness test was performed with 200 g load (Zwick Roell Indentec ZHV) with 9 indentations along the cross-section of the samples.

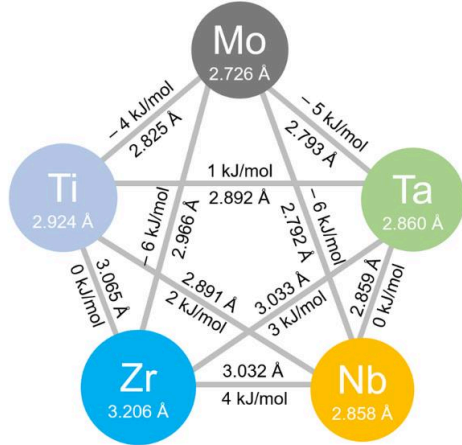


Fig. 3. Atomic diameters (labelled under chemical symbol, unit in Å) for the elements, enthalpies of mixing (ΔH_{mix} , unit in kJ/mol) and interatomic distances (unit in Å) for all pairs of elements [14, 36].

3. Results and discussion

3.1. Parameter-based phase prediction

Table 2 lists thermodynamic parameters for the 5 compositions in this study.

Table 2. Thermodynamic parameters for the 5 compositions.

Compositions (at. %)	ΔS_{mix}	ΔH_{mix} (kJ/mol)	Ω	δ (%)	VEC
$\text{Ti}_{66.6}\text{Nb}_{33.3}$	0.64R	1.78	6.58	1.06	4.33
$\text{Ti}_{33.3}\text{Zr}_{33.3}\text{Nb}_{33.3}$	1.10R	2.67	7.79	5.03	4.33
$(\text{TiZr})_{67}\text{Nb}_{25}\text{Ta}_8$	1.28R	2.44	10.11	5.02	4.33
$(\text{TiZr})_{75}\text{Nb}_{19}\text{Ta}_6$	1.22R	2.07	11.00	5.02	4.25
$(\text{TiZrNb})_{88}(\text{TaMo})_{12}$	1.42R	1.15	24.33	5.31	4.47

According to the entropy of mixing (ΔS_{mix}), table 2, $\text{Ti}_{66.6}\text{Nb}_{33.3}$ is a low-entropy alloy, whereas, the

other alloy studied here are medium-entropy alloys. Increasing the elements contained in the alloys result in a higher entropy of mixing. From the criteria mentioned in Section 1.2, the condition of parameters to achieve a single BCC β -phase: $-15 \text{ kJ/mol} < \Delta H_{\text{mix}} < 5 \text{ kJ/mol}$, $\Omega \geq 1.1$ and $\delta \leq 6.6\%$, $\text{VEC} \leq 6.87$. All of these compositions meet the criteria and β -stabiliser elements (Zr, Nb, Mo) promote the alloy system to form only BCC β -phase as a prediction [18, 22-25, 33-35].

3.2. Phase identification and microstructure

Fig. 4a shows XRD spectra for the 5 alloys showing predominantly BCC structure, consistent with VEC predictions. A shift of the $(110)_\beta$ reflections to lower 2 -theta angles can be observed from $\text{Ti}_{66.6}\text{Nb}_{33.3}$ (A1) to $(\text{TiZr})_{75}\text{Nb}_{19}\text{Ta}_6$ (A4) indicating an increase in the lattice parameter with the increase in the Zr content, Fig 4b. Zr possesses the largest atomic diameter (3.206 Å) comparing to the other elements, Fig. 3. For the $(\text{TiZrNb})_{88}(\text{TaMo})_{12}$ (A5) a small shift of the $(110)_\beta$ reflections towards higher 2 -theta angles compared to A4 can be observed. This is attributed to the addition of Mo which is the smallest atom (2.726 Å) here, leading to a reduction of the lattice parameter, Fig. 3.

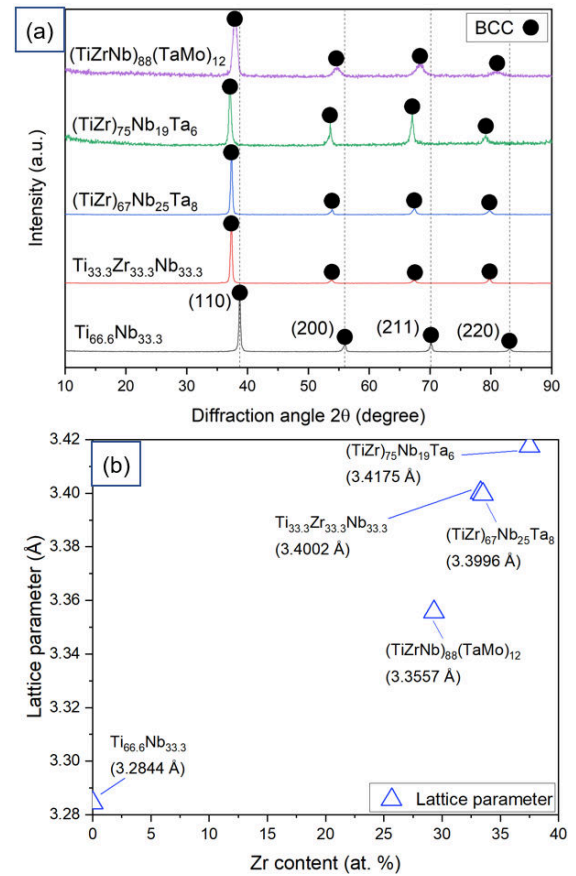


Fig. 4. a) XRD spectra acquired from the 5 alloys and b) their lattice parameter as a function of Zr content.

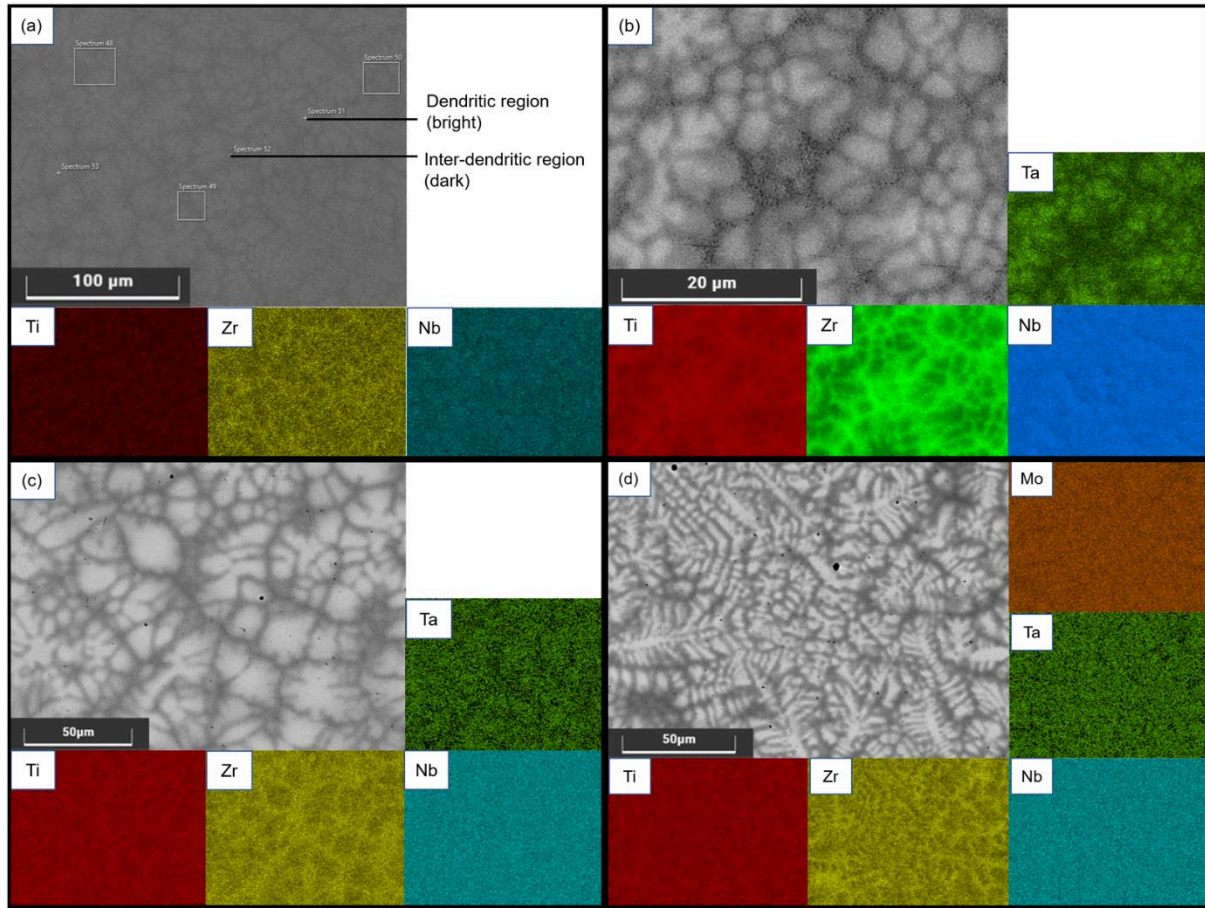


Fig. 5. BSE-SEM images for as-cast samples and corresponding elemental mapping: (a) $\text{Ti}_{33.3}\text{Zr}_{33.3}\text{Nb}_{33.3}$, (b) $(\text{TiZr})_{67}\text{Nb}_{25}\text{Ta}_8$, (c) $(\text{TiZr})_{75}\text{Nb}_{19}\text{Ta}_6$ and (d) $(\text{TiZrNb})_{88}(\text{TaMo})_{12}$.

Table 3. Chemical analysis for the 5 compositions.

Compositions (at. %)	Ti	Zr	Nb	Ta	Mo
$\text{Ti}_{66.6}\text{Nb}_{33.3}$ Nominal	66.6	---	33.3	---	---
Dendritic region	64.6	---	35.4	---	---
Inter-dendritic region	70.1	---	29.9	---	---
$\text{Ti}_{33.3}\text{Zr}_{33.3}\text{Nb}_{33.3}$ Nominal	33.3	33.3	33.3	---	---
Dendritic region	31.0	27.6	41.4	---	---
Inter-dendritic region	34.4	39.1	26.5	---	---
$(\text{TiZr})_{67}\text{Nb}_{25}\text{Ta}_8$ Nominal	33.5	33.5	25.0	8.0	---
Dendritic region	33.2	29.3	28.5	9.1	---
Inter-dendritic region	37.8	41.7	17.4	3.2	---
$(\text{TiZr})_{75}\text{Nb}_{19}\text{Ta}_6$ Nominal	37.5	37.5	19.0	6.0	---
Dendritic region	35.8	35.4	23.2	5.7	---
Inter-dendritic region	39.3	43.9	14.4	2.4	---
$(\text{TiZrNb})_{88}(\text{TaMo})_{12}$ Nominal	29.3	29.3	29.3	6.0	6.0
Dendritic region	27.9	23.3	35.2	8.0	5.7
Inter-dendritic region	32.0	42.4	19.1	2.5	4.0

SEM micrographs obtained using backscattered electrons (BSE) from the cross-section of A2~A5 as-cast alloys are shown in Fig. 5. The alloys show dendritic microstructure, with the darker grey

contrast area corresponding to the inter-dendritic region and the light grey contrast areas to the dendrites, Fig. 5(a). The EDS elemental maps in Fig 5 reveal that the dendritic areas are richer in Nb, Ta and Mo, whereas inter-dendritic areas are richer in Zr and Ti, table 3.

The dendritic structure forms due to the redistribution of the constituent elements during solidification. The distribution of the constituent elements can be qualitatively described in terms of heat of mixing between the constituent elements. During solidification, the main dendritic phase which is richer in the elements with higher melting temperature Nb, Ta (and Mo) forms primarily. On the other hand, Ti and Zr were ejected from the dendrite phase because of the positive heat of mixing between of Ta, Nb, with Ti, and Zr, fig 3, resulting in the enrichment of the inter-dendritic region with lower-melting-point elements Ti and Zr.

Table 3 further indicates that Zr and Ta show higher segregation in dendritic and inter-dendritic regions compared to the other elements, which may be attributed to the higher positive enthalpy of mixing (ΔH_{mix}) between Zr and Ta [37, 38].

3.3. Mechanical properties

Vickers microhardness measurements are presented in Fig. 6. A5 (TiZrNb)₈₈(TaMo)₁₂ possess the highest hardness value 317 ± 8 HV, whereas the lowest value 164 ± 7 HV achieved by A1 Ti_{66.6}Nb_{33.3}. The addition of Zr to the binary Ti-Nb alloy resulted in an increase in hardness, whereas with the further addition of Ta substituting Nb caused a slight decrease in hardness. Comparing A3 (TiZr)₆₇Nb₂₅Ta₈ and A4 (TiZr)₇₅Nb₁₉Ta₆ the content Ta is slightly lower resulting in a decrease in hardness from 253 ± 9 HV to 221 ± 11 HV.

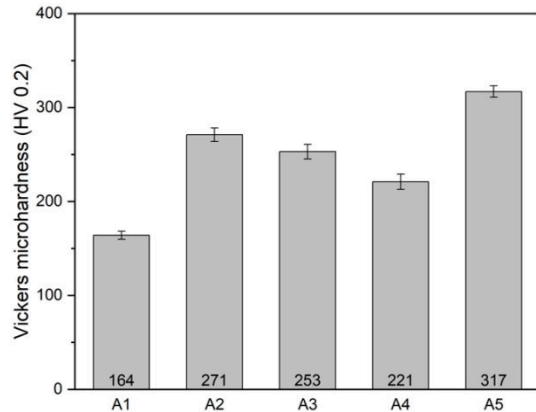


Fig. 6. Vickers microhardness for the 5 compositions.

4. Conclusions

This work addresses the alloy design and characterization of a series of alloys starting from the binary TiNb. Key findings are as follows:

- The 5 alloy compositions are designed with increasing elemental complexity from the binary, to the ternary, quaternary and quinary in the system TiZrNbTaMo.
- The developed alloys possess BCC structure.
- Chemical analysis reveals that dendritic structure is rich in Nb, Ta and Mo. Ti, Zr are enriched in inter-dendritic areas due to different element melting points.
- Hardness has a trend to increase with increasing elemental complexity, but the detailed correlation between hardness value and compositions needs to be further investigated.

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