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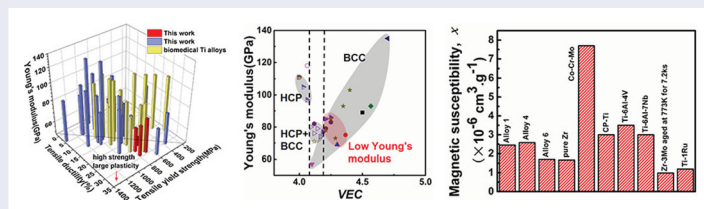
Formation, structure and properties of biocompatible TiZrHfNbTa high-entropy alloys

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ABSTRACT

Biocompatibility of HEAs in the TiZrHfNbTa system in which all the constituents are non-toxic and allergy-free was scrutinized systematically, and novel biomechanical materials with a unique combination of low modulus (57 GPa, almost half that of conventional biomedical titanium alloys), good mechanical biocompatibility and low magnetic susceptibility ($1.71 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$, similar to that of pure Zr) were successfully developed. Moreover, the underlying mechanisms responsible for phase formation and promising properties were explored. This work not only offers a series of novel bio-metallic materials with prominent properties for practical applications, but also shed light on understanding of phase formation and strengthening of HEAs in general.



IMPACT STATEMENT

Several biocompatible TiZrHfNbTa HEAs with prominent properties for practical applications were developed and the relevant alloy design principles were revealed.

ARTICLE HISTORY

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KEYWORDS

High-entropy alloys; Young's modulus; mechanical biocompatibility; magnetic susceptibility

1. Introduction

Metals and alloys are widely used as biomedical materials and therapeutic devices, especially as the replacement of hard tissues [1]. The most commonly used metallic biomaterials in the past decades include stainless steels (e.g. 316L SS and 304 SS), cobalt (Co)-chromium (Cr) alloys, and titanium (Ti) and its alloys [2]. However, Co-Cr alloys are too brittle and the famous Ti-6Al-4V alloy still suffers from a large degree of biomechanical incompatibility due to their relatively high elastic modulus (about 90 GPa higher than that of human bones) and release of toxic ions (i.e. V and Al) into the body. When used as an implant, the titanium alloy overtakes a considerable part of the body loading because of the elastic modulus

mismatch, which shields the bone from the necessary 'stressing' required to maintain its strength, density, and healthy structure. Such an effect, usually termed as 'stress shielding', eventually causes bone loss, implant loosening, and premature failure of prostheses [3]. Additionally, magnetic resonance imaging (MRI) diagnosis is greatly inhibited when conventional metallic biomaterials are implanted in the body due to their high magnetic susceptibility [4,5]. Exploring novel metallic materials concurrently possessing good biomechanical compatibility (e.g. a low Young's modulus and good strength/ductility balance) and low magnetic susceptibility through innovative routes is urgently required for enabling their practical applications as biomedical components.

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In recent years, a new alloy design concept, termed as high-entropy alloys (HEAs) which contain multiple principal elements with an atomic ratio ranging from 5 to 35 at.%, was proposed [6,7]. The basic idea is to utilize high mixing entropy and lattice disorder to enhance formation of solid solution phases [7,8]. The Young's modulus of HEAs can be more easily adjusted than conventional alloys due to the large compositional variation [7], providing great possibility to design biomedical metallic materials with a low modulus. In a previous study, colony-forming units were proven to be considerably inhibited on HEA coatings, and the antibacterial rates for four different bacteria exceed 99.999%, indicating that HEAs have efficient antibacterial ability [9]. Ti, Zr, Hf, Nb and Ta elements are known to be fully non-toxic and allergy-free [3]. Moreover, the combination of these elements is favorable for the formation of a single solid solution phase [10]. Therefore, it is interesting and imperative, both scientifically and technologically, to fabricate HEAs composed of these five elements and explore their biocompatibility. In this paper, we report our successful development of promising biocompatible TiZrHfNbTa HEAs with a unique combination of low modulus, good mechanical biocompatibility and low magnetic susceptibility.

2. Experimental

Ingots of six Ti-Zr-Nb-Ta alloys, (i.e. alloy 1: Ti₂₅Zr₂₅Nb₂₅Ta₂₅; alloy 2: Ti_{31.67}Zr_{31.67}Nb_{31.66}Ta₅; alloy 3: Ti₃₅Zr₃₅Nb₂₅Ta₅; alloy 4: Ti₄₅Zr₄₅Nb₅Ta₅; alloy 5: Ti_{21.67}Zr_{21.67}Nb_{21.66}Ta₃₅; alloy 6: Ti₁₅Zr₁₅Nb₃₅Ta₃₅, and the numbers are in atomic percentage), ten Ta_xHfZrTi ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 1, and the numbers are in atomic ratio), five Nb_xHfZrTi ($x = 0, 0.2, 0.4, 0.8$ and 1) and seven Ta_xNb_xHfZrTi ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8$ and 1) alloys were synthesized by arc-melting a mixture of pure metals (purity > 99.9%) in a Ti-gettered high-purity argon atmosphere. The ingots were re-melted at least six times to ensure chemical homogeneity and eventually drop-cast into a mold with a dimension of $\phi 10$ mm $\times$ 60 mm. Phase identification was conducted using X-ray diffraction (XRD) with Cu K α radiation and neutron diffraction at the VULCAN instrument, Oak Ridge National Laboratory Spallation Neutron Source (ORNL, SNS), USA. Microstructures were characterized by scanning electron microscopy (SEM) using a Zeiss Supra55 microscope operated at 15 kV with an energy dispersive spectrometer (EDS). Standard bright-field and diffraction patterns were obtained using a transmission electron microscope (TEM, Tecnai F30) operated at 300 kV. Both tension and compression tests were carried out on a CMT4105 universal electronic tensile

testing machine with a strain rate of $1 \times 10^{-3} \text{ s}^{-1}$ at room temperature. The static Young's modulus of all the specimens was determined by linearly fitting the elastic stage of tension stress-strain curves. The magnetization (M) as a function of applied magnetic field (H) was measured and recorded using a SQUID (Superconducting Quantum Interference Device, Quantum Design, USA) at room temperature, and its magnetic susceptibility, $\chi = M/H$, was obtained from the slope by linear fitting of the data.

3. Results and discussion

Phase identification was conducted by both XRD and neutron diffraction, and as an example, representative XRD traces and neutron diffraction patterns of six as-cast Ti-Zr-Nb-Ta alloys (i.e. alloy 1–6) are shown in Figure 1(a). As can be seen, all the reflection peaks on the curves obtained by both kinds of techniques can be indexed as the BCC lattice, indicating that those six alloys have a single BCC solid solution structure with no formation of any second phase. Figure 1(b–d) shows the corresponding SEM and TEM images of three typical HEAs, i.e. alloys 1, 4 and 6. Typical dendritic morphology is observed in the alloys enriched in Nb and Ta, i.e. alloys 1 and 6, whilst equiaxed grains are seen in alloy 4 with much less Ta (i.e. 5%). EDS results reveal that the dendritic phase is enriched in Ta and Nb while the inter-dendrite contains a high concentration of Ti and Zr, manifesting occurrence of elemental segregation during solidification of alloys 1 and 6. TEM bright field images and the corresponding selected area electron diffraction (SAED) patterns of these three alloys evidence no other crystalline phases and/or precipitates in the BCC matrix, which is consistent with the XRD and neutron diffraction results. Detailed structure characterization and analysis of the other alloys investigated in this study are not shown, but summary of their microstructure characteristics are listed in Table 1.

Figures 2(a,b) show room-temperature tensile and compressive true stress-strain curves of the aforementioned six Ti-Zr-Nb-Ta alloys. The present alloys exhibit high strength ranging from 690 to 1050 MPa, together with significant tensile ductility (> 10%). The static Young's modulus deduced from the tensile stress-strain curves is estimated to be 89, 75, 69, 57, 93 and 135 GPa for alloys 1–6, respectively. The tensile properties including yield strength (YS), ductility (%) and Young's modulus (E) of all the fabricated HEAs are also compiled in Table 1. Mechanical properties of the currently developed HEAs actually changed drastically when the alloy composition is altered, indicating that mechanical properties can be remarkably tailored even in the same HEA

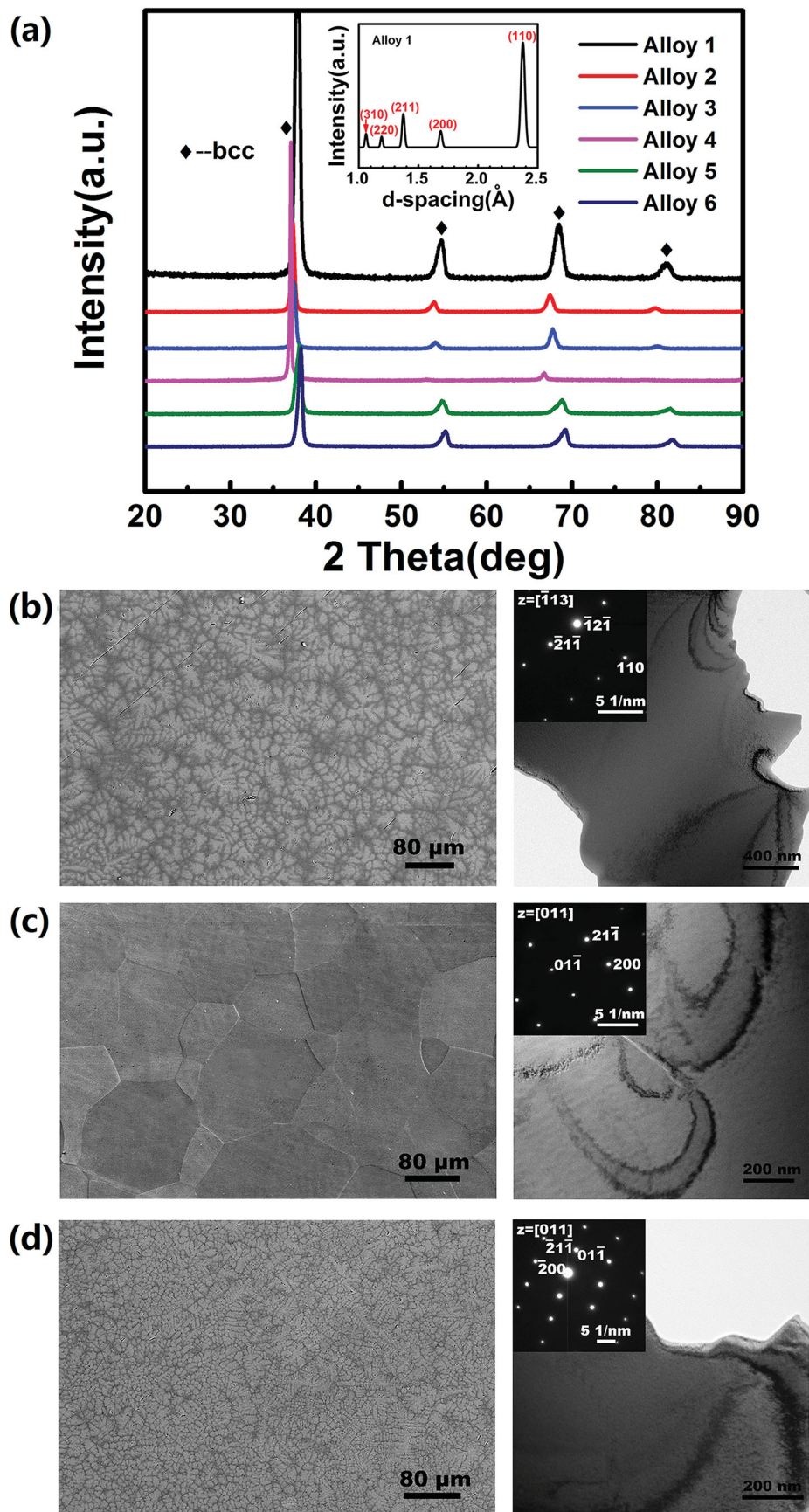


Figure 1. (a) XRD patterns of alloys 1–6. The inset shows neutron diffraction pattern of alloy 1 as an example. (b–d) SEM images and TEM bright-field photos of typical alloys 1, 4 and 6, respectively. The insets show the corresponding selected area electron diffraction (SAED) patterns.

Table 1. Phase constitution and mechanical properties for all the fabricated HEAs. 'E' denotes Young's modulus while 'YS' represents yield strength.

Alloys		Structure	E (GPa)	YS (MPa)	Elongation (%)
Ti-Zr-Nb-Ta	Alloy 1	BCC	89	970	23
	Alloy 2	BCC	75	790	29
	Alloy 3	BCC	69	780	26
	Alloy 4	BCC	57	690	24
	Alloy 5	BCC	93	1050	12.7
	Alloy 6	BCC	135	970	12.5
TaxHfZrTi	x = 0	HCP	111	822	13.6
	x = 0.1	HCP	105	890	5.3
	x = 0.2	HCP	97	1020	5.08
	x = 0.3	HCP + BCC	80	225	13.96
	x = 0.4	HCP + BCC	76	365	30.26
	x = 0.5	HCP + BCC	79	683	29
	x = 0.6	HCP + BCC	74	738	21.73
	x = 0.7	BCC	77	1046	14.31
	x = 0.8	BCC	85	1120	4.63
	x = 1	BCC	86	1367	4.07
Nb _x HfZrTi	x = 0	HCP	111	822	13.6
	x = 0.2	HCP + BCC	118	906	0.73
	x = 0.4	BCC	82	744	11.9
	x = 0.8	BCC	79	718	16.2
	x = 1	BCC	83	728	18.7
TaxNb _x HfZrTi	x = 0	HCP	111	822	13.6
	x = 0.2	HCP + BCC	71	480	32.5
	x = 0.4	BCC	78	800	10
	x = 0.5	BCC	85	850	13
	x = 0.6	BCC	73	880	19
	x = 0.8	BCC	93	890	18
	x = 1	BCC	103	1200	12

system. Figure 2(c) shows the comparison of tensile properties between our fabricated HEAs and the conventional biomedical titanium materials [11]. Noted that the Young's modulus of alloys 2, 3, 4 and Ta_{0.5}HfZrTi (red column in Figure 2(c)) is only half that of conventional biomedical titanium alloys such as Ti-15Mo (annealed) and Ti-35.3Nb-5.1Ta-7.1Zr whose Young's modulus is on the lower side among all titanium bio-implant alloys [11]. Therefore, the currently developed HEAs, especially alloys 2, 3, 4 and Ta_{0.5}HfZrTi, possess a good combination of low Young's modulus, high strength and ductility, in comparison with those of the conventional bio-implant titanium materials [11]. Particularly, Ti-Zr-Nb-Ta HEAs exhibit really decent mechanical properties under compression, i.e. high compressive strength (800–1200 MPa) and large compressive plasticity (> 40%) (Figure 2(b)).

Young's modulus has been known as one of the intrinsic nature of materials, and the crystalline structures have a dramatic effect on its value, e.g. the BCC structure generally has a lower Young's modulus in comparison with HCP structures in the same group [12]. Therefore, effects of crystalline structures on Young's modulus of the group IV (Ti, Zr, Hf) HEA alloys are worthy to be investigated at the first place. The valence electron concentration (VEC) is the dominant factor in controlling the phase structure and stability for many intermetallic

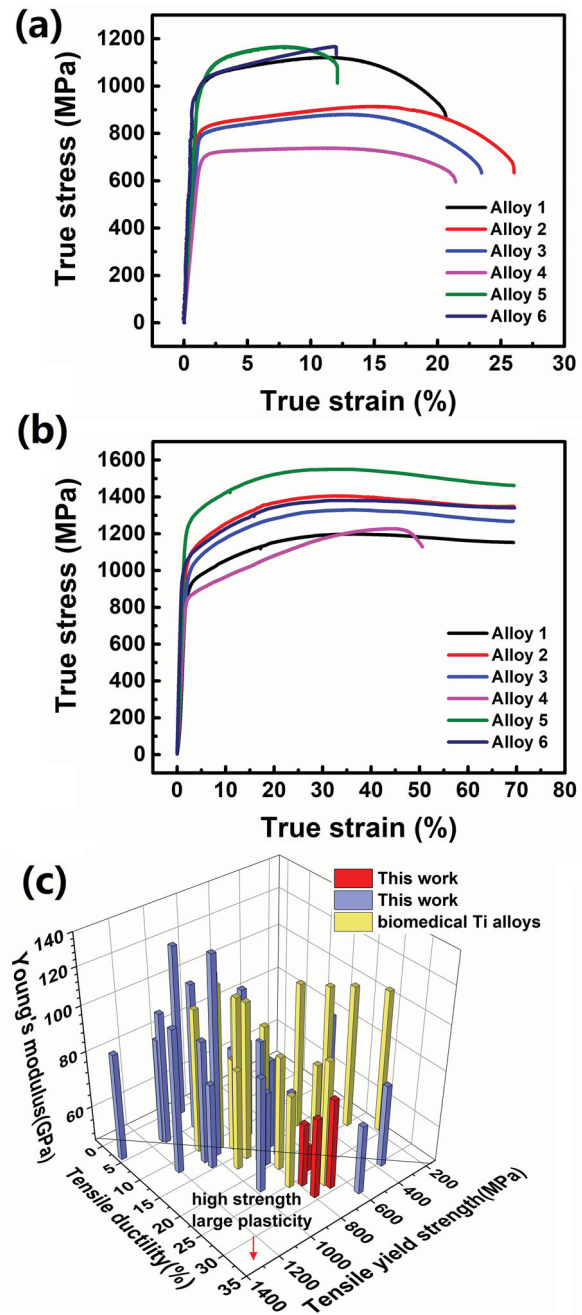


Figure 2. Room-temperature (a) tensile and (b) compressive true stress-strain curves of alloys 1–6. (c) The Young's modulus, tensile yield strength and tensile ductility of all the fabricated HEAs, in comparison with those of conventional biomedical Ti alloys [11].

alloys such as (Fe, Co, Ni)₃V [13] and NbCr₂-based Laves phase alloys [14]. In addition, VEC also plays a decisive role in the stability of Ti alloys [12] and some FCC and BCC solid-solution HEAs [15]. However, whether the VEC criterion holds in the current HEA systems still needs to be verified. VEC for a multi-component alloy can be defined as the weighted average from VEC of the constituent components: $VEC = \sum_{i=1}^n c_i (VEC)_i$, where $(VEC)_i$ is the VEC for the individual element (Table 2)

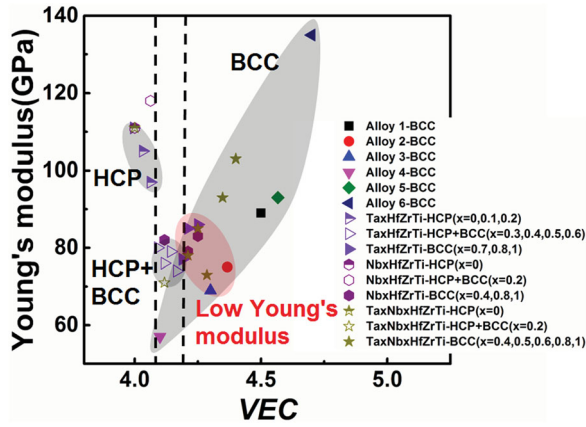


Figure 3. Dependence of Young's modulus and crystalline phase structure on VEC in all the HEAs investigated.

[16]. Figure 3 shows Young's modulus of the current HEAs as a function of VEC. A careful examination of Figure 3 suggests that the VEC criterion can be used to predict phase constitution in the current HEA system, i.e. from single HCP, to mixed HCP and BCC, and to single BCC with increasing BCC stabilizers of Nb and Ta. At $VEC \geq 4.18$, a single BCC phase was formed, whilst when $4.09 \leq VEC < 4.18$, mixed BCC and HCP phases co-existed and a single HCP phase would be formed at $VEC < 4.09$. It is evident that as the VEC value decreases from 4.18, the HCP structure stabilizes and its formation subsequently leads to an increase of Young's modulus, as shown in Figure 3. The single BCC structure forms in the area with $VEC \geq 4.18$, and in this regime, Young's modulus increases monotonically with increasing VEC. This trend is due to the fact that the Young's modulus in the $\langle 111 \rangle$ direction of BCC crystals is usually reduced by lowering $c_{11} - c_{12}$ [12] which is generally decreased with decreasing of d + s electrons (i.e. the valence electrons for transitional metals) in BCC metals [17]. Therefore, a low Young's modulus can be achieved by controlling the VEC value around 4.18 to obtain a small $c_{11} - c_{12}$ value while maintaining the BCC structure simultaneously.

Table 2 shows $\sigma_{0.2}$ values for pure elements at room temperature [18]. Yield strengths of the six Ti-Zr-Nb-Ta HEAs (alloy 1–6) estimated from rule of mixture of the yield strength of pure elements, i.e. $(\sigma_{0.2})_{\text{mix}} =$

Table 2. The valence electron concentration (VEC) [15], yield strength $\sigma_{0.2}$ [18], atomic radius r [20] and shear modulus G [18] of Ti, Zr, Hf, Nb, Ta metals.

	VEC	$\sigma_{0.2}$ (MPa)	r (pm)	G (GPa)
Ti	4	195	141.8	44
Zr	4	280	155.1	33
Hf	4	240	154.1	30
Nb	5	240	142.9	38
Ta	5	170	143.0	69

$\sum_{i=1}^n c_i (\sigma_{0.2})_i$, where c_i is the molar ratio and $(\sigma_{0.2})_i$ is yield strength value of each constituent element, is 221, 235, 235, 234, 214 and 215 MPa, respectively, which are much smaller than the experimental values (i.e. 970, 790, 780, 690, 1050 and 970 MPa, respectively). Senkov et al. [18] firstly attempt to predict solid-solution strengthening effect in the multicomponent TaNbHfZrTi HEA [19]. Here, the HEA is considered as a pseudo-binary solid solution. By doing so, atomic misfit and modulus misfit of the HEAs were estimated and finally their contribution to strength was determined theoretically. The atomic radius [20] and shear modulus [18] of the pure elements are given in Table 2. It should be noted that the BCC crystal lattice has eight nearest-neighbor atoms while the HCP crystal lattice has twelve nearest-neighbor atoms. Considering the largest difference in atomic size of Zr and Hf with the rest elements, to assess the contribution from lattice distortion, all the fabricated HEAs are taken as pseudo-binary solid solutions, defining the Ti, Nb, Ta as solvents and Zr plus Hf as solutes. For the calculation of modulus misfit, the largest modulus distortion appears in the vicinity of Ta element for the alloys containing Ta, while pairing of Ti atoms with other elements provides the largest modulus misfit for the alloys without Ta element, e.g. HfZrTi and Nb_xHfZrTi ($x = 0, 0.2, 0.4, 0.8$ and 1) HEAs. For clarity, we summarize a column chart (Figure 4) to directly show the strength contributions from lattice distortion $\Delta\sigma_a$, modulus distortion $\Delta\sigma_G$ and $(\sigma_{0.2})_{\text{mix}}$ based on the 'rule of mixtures' using the Senkov's model for all the fabricated single BCC and HCP HEAs. It is apparent that the calculated data $(\sigma_{0.2})_{\text{cal}}$ is in good agreement with the experimental values $(\sigma_{0.2})_{\text{exp}}$ (solid circle), especially for equiatomic HEAs. It can be easily seen from the chart that the solid strengthening from the modulus misfit and the atomic size misfit is almost the same in the currently developed HEA systems with less Ta addition. While the high yield strength in the HEAs with lots of Ta addition mainly associates

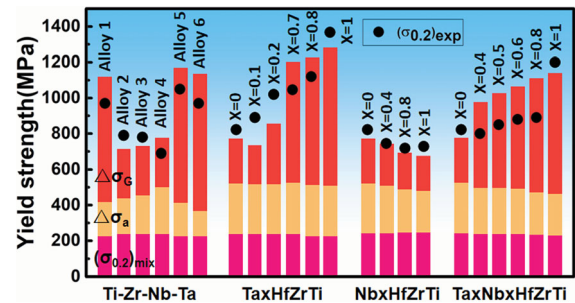


Figure 4. The calculated strength contributions from lattice distortion $\Delta\sigma_a$, modulus distortion $\Delta\sigma_G$ and $(\sigma_{0.2})_{\text{mix}}$ based on the 'rule of mixtures'. The solid circle represents experimental yield strength.

with the large modulus misfit, and therefore, to further increase the yield strength, addition of the elements with a larger modulus misfit with the constituent elements, such as Mo and W, should be considered. In addition, it has been reported previously [21], the yield strength of dual-phase (mixed HCP and BCC phases) HEAs depends on the constituent phase and their volume fractions, but here such aspects are not discussed.

Low magnetic susceptibility is required for biomaterials so that MRI diagnosis is not interfered. The magnetic variation versus the applied magnetic field of three typical HEAs (i.e. alloys 1, 4 and 6) at room temperature is shown in Figure 5(a), and the data of pure Zr is included for comparison. Similar to pure Zr, all the alloys show a linear trend, which is indicative of typical paramagnetic behavior. The magnetic susceptibility (χ) can be then derived from the slope by linear fitting of these data. Figure 5(b) shows the comparison of χ value of three HEAs ($\sim 2.45 \times 10^{-6}$, 2.58×10^{-6} and $1.71 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$, respectively) with that of representative conventional biomedical Co-Cr alloys (e.g. Co-Cr-Mo, $\sim 7.7 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) [2] and Ti-based alloys (e.g. Ti-6Al-4V, $\sim 3.5 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ and Ti-6Al-7Nb, $\sim 3 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) [2]. It is clear that the currently developed HEAs, especially alloy 6 possesses low magnetic susceptibility ($1.71 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$), similar to that

of pure Zr ($1.67 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$), indicating the present HEAs have great potential to suppress artifacts in MRI measurements. It is noted that the small deviation between our experimental result ($1.67 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) and literature reported χ value ($1.33 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$) for pure Zr [22] may be due to experimental errors such as elemental purity, experimental method and testing environment. To better understand origins of magnetization behavior, it is interesting to verify whether the magnetic susceptibilities obey Vegard's rule of mixture, i.e. whether a given magnetic susceptibility of the 'mixture' χ_{mix} is a compositional average of the properties χ_i of the constituent elements, $\chi_{\text{mix}} = \sum_i c_i \chi_i$. The magnetic susceptibility at 20 °C of pure Ti [22], Zr [22], Nb [22] and Ta [22] is 3.35×10^{-6} , 1.33×10^{-6} , 2.30×10^{-6} and $0.85 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$, respectively. Deviation of the experimental values χ_{exp} from the ROM values χ_{mix} can thus be calculated using the expression $\Delta\chi/\chi_{\text{mix}} = (\chi_{\text{exp}} - \chi_{\text{mix}})/\chi_{\text{mix}}$ as 25, 14 and 6% for alloy 1, 4 and 6, respectively, suggesting that the rule of mixture does not hold for the magnetic susceptibility in the present HEAs. This observation implies that in addition to compositional average of magnetic susceptibilities, there may exist strong complex coupling effects from the multiple constituents in the disordered structures.

4. Conclusions

A series of HEAs with different lattice structures, from a single HCP, to a mixture of HCP + BCC, and finally to a BCC structure were designed in the TiZrHfNbTa HEA systems. Highly biocompatible HEAs with a unique combination of low Young's modulus, high strength and ductility, and low magnetic susceptibility were developed. Our analyses indicate that VEC plays an important role in phase stability and Young's modulus of these HEAs: single HCP or BCC phase was formed when $\text{VEC} < 4.09$ and > 4.18 , respectively, and the mixed HCP and BCC phases were formed in-between. A low Young's modulus can be achieved by controlling the value of VEC around 4.18 and simultaneously maintaining the BCC structure. Large modulus misfit based on solid solution model was found to mainly contribute to the significantly enhanced yield strength. The low magnetic susceptibility of the developed HEAs is related to the chemical disordering and lattice distortion. Current understanding and implications governing biocompatibility provide important guidelines for developing promising biomedical HEAs with enhanced overall properties.

Disclosure statement

No potential conflict of interest was reported by the authors.

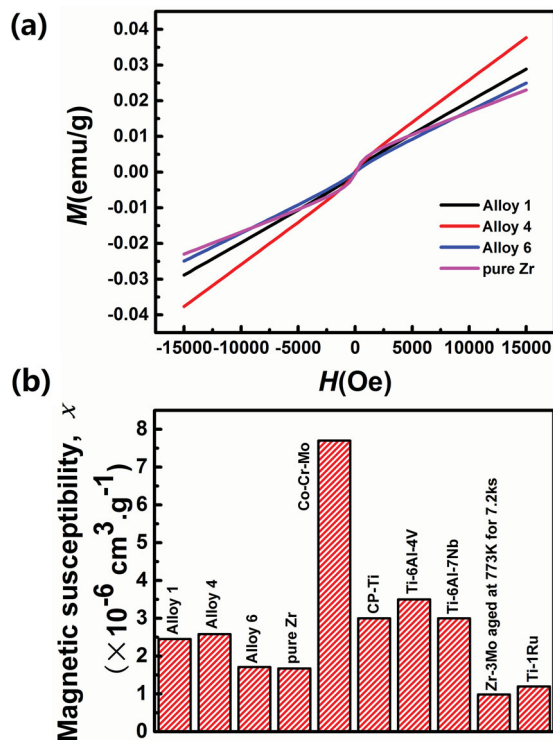


Figure 5. (a) The magnetization variation as a function of applied magnetic field at room temperature for alloys 1, 4, 6 and pure Zr. (b) Comparison of magnetic susceptibilities of alloys 1, 4, 6 and pure Zr with the alloys commonly used in medical devices.

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