Effect of Ti content on microstructure and properties of Ti_xZrVNb refractory high-entropy alloys

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Abstract: This study aimed to investigate the microstructure and mechanical properties of Ti_xZrVNb (x = 1, 1.5, 2) refractory high-entropy alloys at room and elevated temperatures. The TiZrVNb alloy consisted of the body-centered cubic (bcc) matrix with a small amount of V₂Zr phase. The $Ti_{1.5}ZrVNb$ and Ti_2ZrVNb alloys exhibited a single-phase bcc structure. At room temperature, the tensile ductility of the as-cast alloys increased from 3.5% to 12.3% with the increase in the Ti content. The Ti_xZrVNb alloys exhibited high yield strength at 600°C, and the ultimate yield strength was more than 900 MPa. Softening occurred at 800°C, but the ultimate yield strength could still exceed 200 MPa. Moreover, the Ti_xZrVNb alloys displayed low densities but high specific yield strengths (SYSs). The lowest density of Ti_xZrVNb alloys was only 6.12 g/cm³, but the SYS could reach about 180 MPa cm³·g⁻¹, which is better than those of most reported high-entropy alloys (HEAs).

Keywords: high-entropy alloys; mechanical properties; low density; elevated temperature

1. Introduction

In recent years, a new series of alloys called high-entropy alloys (HEAs) [1] or multi-principal element alloys [2] has become a research focus [3]; this is because of the excellent properties of the alloys, such as high strength [4–5], high ductility [6–7], high-temperature stability [5,8], oxidation resistance [9], wear [10] and corrosion resistance [11], and magnetic properties [12]. Such characteristics have made HEAs potentially valuable in industrial applications [13].

As a branch of HEAs, refractory high-entropy alloys (RHEAs), which are generally composed of refractory elements, such as Ti, Zr, Hf, Nb, V, Ta, Mo, and W [14], have shown potential industrial applications. Some RHEAs exhibit some remarkable properties [15], such as high strength at room temperature [16] and elevated temperature [17–18], low density [19–20], oxidation resistance [21], and radiation resistance [22]. Of these characteristics, the mechanical properties of RHEAs at elevated temperatures are the most remarkable and have made RHEAs replace super alloys in some applications such as turbine and aero-engine blade manufacture [23–27].

Nevertheless, RHEAs also have some disadvantages.

Most RHEAs have a body-centred cubic (bcc) structure [13] because most refractory elements are bcc-structured, which generally results in high strength but weak plasticity [28–29], especially at room temperature. The slip systems of a bcc structure are fewer than those of a face-centred cubic (fcc) structure. In addition, although some RHEAs, such as MoN-bTaW (13.75 g/cm³) [30] and TiZrHfNbTa (9.94 g/cm³) [31], have good mechanical properties, their densities are high. These disadvantages hinder the industrial application of RHEAs.

In this study, a new series of RHEAs, Ti_xZrVNb alloys, with low density and high specific yield strength (SYS) was designed, and the microstructure and mechanical properties at room and elevated temperatures were also studied.

2. Experimental

The purity of the raw materials (Ti, Zr, V, and Nb) was more than 99.99wt%. Vacuum arc melting was used to melt the alloys. The vacuum chamber during the melting process was evacuated to 3×10^{-3} Pa and backfilled to 0.05 Pa with high-purity argon gas. All the alloys were remelted at least six times and solidified in a water-cooled copper hearth to en-

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sure homogenization. The crystal structures of the alloys were identified using a Shimadzu 6000 X-ray diffractometer (XRD). The range of the scanning angle (2θ) was $20^{\circ}-100^{\circ}$, and the scanning speed was 4°/min. The microstructure and phase composition of the alloys were analysed using a JXA-8530F PLUS electron probe microanalyzer (EPMA) equipped with an energy-dispersive X-ray spectrometer (EDS). The transmission electron microscopy (TEM) test was processed using a Tecnai G20 instrument. Vickers hardness was measured using an MH-50 hardness tester under a load of 4.9 N for 15 s. The densities of samples were measured by the Archimedes method using a TOLEDO ME204E accurate electronic balance. The mechanical properties at room temperature were measured using a DNS-100 uniaxial compression tester. The compressive samples were cylindrical (5 mm in diameter and 10 mm in height). The tensile sample was dog bone-shaped, with gauge dimensions of 28 mm in length and 4 mm in width and thickness. The mechanical property at elevated temperature was processed using a Gleeble-3500 thermal simulation machine; the size of the sample was the same as that used for the room-temperature compressive test. The heating rate of the test temperature was 5 K/s, which was maintained for 5 min before the test. The strain rate of all the mechanical property tests was $1 \times 10^{-3} \text{ s}^{-1}$.

3. Results and discussion

Fig. 1 shows the XRD patterns of the Ti_xZrVNb alloys. According to the patterns, all the alloys exhibited a typical single-phase bcc structure. The diffraction peak shifted to a lower angle with the increase in the Ti content, indicating the occurrence of lattice expansion. The values of the lattice constants of TiZrVNb, $Ti_{1.5}ZrVNb$, and Ti_2ZrVNb alloys were 0.3303, 0.3313, and 0.3317 nm, respectively, confirming the expansion of lattice with the increase in the Ti content.



Fig. 1. XRD patterns of Ti_xZrVNb alloys.

Fig. 2 shows the EPMA images of the Ti_xZrVNb alloys. Different from the XRD patterns, a small number of dots and

needle-like precipitation phases were observed in the TiZr-VNb alloy, and they represent the precipitation phase (about 4.9% in volume fraction), which was too small to be identified by XRD. The EDS results shown in Table 1 indicate that the precipitation phase (denoted by P) was rich in Zr and V. The closer the precipitation phase to the boundary, the larger its size. The solidification of the boundary region occurred later compared with that of the grain, which was beneficial to the growth of the precipitation phase. Composition fluctuation was also observed in the TiZrVNb alloy. Moreover, almost no precipitation phase was observed in the Ti₁₅ZrVNb and Ti2ZrVNb alloys. The composition fluctuations in the Ti_{1.5}ZrVNb and Ti₂ZrVNb alloys were much lower than that of the TiZrVNb alloy because the difference in melting temperature between the dendrite (denoted by D, the dark grey region in Fig. 2) and interdendritic (denoted by ID, the light grey region) region decreased with the increase in the Ti content. As presented in Table 1, the dendrite region was rich in Zr and Nb, and the interdendritic region was rich in V, while Ti was uniformly distributed in the dendrite, interdendrite, and precipitation phase regions. According to the V-Zr binary phase diagram [32], when the atomic ratio of V to Zr was closer to 1:1, the V₂Zr precipitation phase might have formed. According to the calculated isothermal section of the Ti–V–Zr system at different temperatures [33], the increase in the Ti content within a certain range could inhibit the formation of the V₂Zr precipitation phase during the solidification process. Therefore, almost no precipitation phase was observed in the Ti1.5ZrVNb and Ti2ZrVNb alloys.

Fig. 3 displays the TEM image of the TiZrVNb alloy. In agreement with the EPMA image, the TiZrVNb alloy exhibited a dual-phase structure composed of a matrix and a precipitation phase. According to the analysis of the $[1\bar{1}\bar{2}]$ zone axis (Z) in the selected-area electron diffraction (SAED) image, the precipitation phase was confirmed to be V₂Zr precipitation, which is consistent with previous findings. In addition, an elongated spot was also observed in the SAED image, which indicates stacking fault in the V₂Zr precipitation phase.

Fig. 4 shows the Vickers hardness of the Ti_xZrVNb alloys. The decrease in hardness linearly correlated with the increase in the Ti content. The densities of the Ti_xZrVNb alloys also decreased with the increase in the Ti content. That is, due to the increase in the Ti content, which had the lowest density (4.54 g/cm³) compared with the densities of the other elements in the Ti_xZrVNb alloy (6.49 g/cm³ for Zr, 5.96 g/cm³ for V, and 8.57 g/cm³ for Nb), the average density of the alloy reduced.

The yield strength $(\sigma_{0.2}^{cal})$ of the bcc-structured HEAs prepared by vacuum arc melting could be roughly calculated using Eq. (1) [15]:

$$\sigma_{0,2}^{\text{cal}} = \sigma_{0,2}^{\text{mix}} + \Delta \sigma \tag{1}$$

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Fig. 2. EPMA images of Ti_xZrVNb alloys: (a) TiZrVNb; (b) TiZrVNb at high magnification; (c) Ti_{1.5}ZrVNb; (d) Ti₂ZrVNb (M—Matrix).

Table 1.	Chemical compositions of	different regions i	in <mark>Fig. 2</mark> foi	r TiZrVNb, Ti _{1.5} Zr	VNb, and Ti ₂ ZrVNb alloys	at%
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Alloy	Region	Ti	Zr	V	Nb
	D	24.46	35.95	23.61	15.98
TiZrVNb	ID	25.26	24.30	28.65	21.79
	Р	20.46	33.64	31.91	13.99
T: 7-WNIL	D	34.65	18.72	24.02	22.61
$\Pi_{1.5}$ ZIVINU	ID	35.11	23.24	22.85	18.80
Ti ₂ ZrVNb	М	40.59	20.59	20.32	18.50

where $\sigma_{0.2}^{\text{mix}}$ is the yield strength calculated using the mixture rule, and $\Delta \sigma$ is the solid solution strengthening (SSS) of the alloy, which can be calculated using Eq. (2):

$$\Delta \sigma = \left(\sum \Delta \sigma_i^{3/2}\right)^{2/3} \tag{2}$$

where $\Delta \sigma_i$ is the SSS caused by the *i*th element. The parameters required in the calculation were according to those used in previous studies [15,34–35]. The yield strengths of the Ti_xZrVNb alloys calculated by simultaneous Eqs. (1) and (2) were 1381, 1265, and 1116 MPa for TiZrVNb, Ti_{1.5}Zr-VNb, and Ti₂ZrVNb, respectively. The reduction in lattice distortion and the weakening of SSS due to the decrease in atomic radius difference (4.80%, 4.71%, and 4.61% for TiZr-VNb, Ti_{1.5}ZrVNb, and Ti₂ZrVNb, respectively) were the main causes of the decrease in yield strength. Fig. 5 displays the tensile engineering stress–strain curves of the Ti_xZrVNb alloys at room temperature. According to the curves, with the increase in the Ti content, the strength decreased slightly but ductility increased significantly. The yield strength of TiZrVNb (1116 MPa) was greater than that of Ti₂ZrVNb (1058 MPa), by about 5.2%. The ductility of TiZrVNb (3.5%) was less than that of Ti₂ZrVNb (12.3%), by about 251%. The values of density, hardness, and mechanical properties of the Ti_xZrVNb alloys are presented in Table 2.

The trends of the experimental yield strength and the calculated yield strength with the increase in the Ti content were consistent. However, the experimental values were lower than the calculated values. The ratios of the experimental strength to the calculated yield strength were 80.8%, 87.0%, and 94.8% for TiZrVNb, $Ti_{1.5}ZrVNb$, and Ti_2ZrVNb alloys, respectively. The reason for the discrepancy between the calT.D. Huang et al., Effect of Ti content on microstructure and properties of Ti_xZrVNb refractory ...



Fig. 3. TEM image of bright field of the TiZrVNb alloy. Inset shows the SAED image of the precipitation phase (P).



Fig. 4. Vickers hardness of Ti_xZrVNb alloys.

culated and the experimental yield strengths is as follows: TiZrVNb alloy is a dual-phase structure composed of a matrix and a V_2Zr phase; therefore, the aforementioned equation is not completely applicable to the TiZrVNb alloy. For the Ti_{1.5}ZrVNb and Ti₂ZrVNb alloys, the composition fluctu-



Fig. 5. Tensile engineering stress–strain curves of Ti_xZrVNb alloys at room temperature.

ation should be the main reason; therefore, the experimental strength of the Ti_2ZrVNb alloy, which had less composition fluctuation, was closer to the calculated yield strength than that of the $Ti_{1.5}ZrVNb$ alloy. Moreover, the error of the equations also needs to be considered. The improvement in ductility was due to the decrease in stress concentration caused by the disappearance of the needle-like V_2Zr phase and the increase in component uniformity.

Fig. 6 presents scanning electron microscope (SEM) images of the tensile fracture surfaces of the Ti_xZrVNb alloys at room temperature. Tearing edges and river patterns were observed in the TiZrVNb alloy, indicating that the fracture of the TiZrVNb alloy was quasi-cleavage one. Different from the TiZrVNb alloy, tearing edges, cleavage planes, and dimples were observed in the Ti1.5ZrVNb and Ti2ZrVNb alloys, indicating that the fractures of the Ti15ZrVNb and Ti₂ZrVNb alloys were mixed fractures. Thus, the strength and ductility of the Ti₁₅ZrVNb and Ti₂ZrVNb alloys were higher than those of the TiZrVNb alloy. Table 3 presents the EDS results of different regions in the tensile fracture surfaces of the Ti_xZrVNb alloys; the tearing edge regions of the Ti_{1.5}ZrVNb and Ti₂ZrVNb alloys (denoted by B and D) were rich in Zr, indicating that the segregation of the Zr element reduced the ductility. The dimple region was rich in Nb (denoted by C and E), but the segregation degree was lower than that of the Zr element in the tearing edge region.

Table 2. Density, hardness, and mechanical properties of $Ti_x ZrVNb$ alloys at room temperature

Alloy	Density / $(g \cdot cm^{-3})$	Hardness, HV	Tensile yield strength / MPa	Tensile fracture strength / MPa	Tensile ductility / %
TiZrVNb	6.45	434.9	1116	1447	3.5
Ti _{1.5} ZrVNb	6.22	383.1	1101	1401	11.2
Ti ₂ ZrVNb	6.12	350.4	1058	1305	12.3

Fig. 7 displays the compressive engineering stress–strain curves of the TiZrVNb, $Ti_{1.5}ZrVNb$, and Ti_2ZrVNb alloys at room temperature, 600°C, and 800°C. At room temperature, with the increase in the Ti content, the yield strength of TiZr-VNb (1229 MPa) was slightly higher than that of Ti₂ZrVNb

(1086 MPa), by about 11%. The room temperature compression ratio of the TiZrVNb alloy was about 35.2%, but no fractures occurred in the $Ti_{1.5}ZrVNb$ and Ti_2ZrVNb alloys until compression deformation exceeded 50%. At 600°C, all the Ti_xZrVNb alloys still maintained high strengths, about



Fig. 6. SEM images of the tensile fracture surfaces of $Ti_xZr-VNb$ alloys at room temperature: (a) TiZrVNb; (b) $Ti_{1.5}Zr-VNb$; (c) Ti_2ZrVNb .

Table 3. EDS results of the tensile fracture surfaces in Fig. 6for TixZrVNb alloysat%

Region	Ti	Zr	V	Nb
Α	26.63	24.36	23.95	25.05
В	32.91	28.38	19.36	19.35
С	32.42	19.73	21.98	25.87
D	37.31	26.29	19.91	16.49
Е	39.63	18.43	18.67	23.27

75% of those at the room temperature. When the temperature was increased to 800°C, the strengths of the Ti_xZrVNb alloys significantly decreased. Moreover, a serrated curve was also observed at 800°C due to the alternating softening deformation and recrystallization. The values of compressive mechanical properties at elevated temperatures are listed in



Fig. 7. Compressive engineering stress-strain curves of Ti_xZrVNb alloys at different temperatures: (a) TiZrVNb;
(b) Ti_{1.5}ZrVNb; (c) Ti₂ZrVNb (RT—Room temperature).

Table 4. The table shows that all the Ti_xZrVNb alloys maintained a high strength until the temperature reached 600°C. The yield strengths of the Ti_xZrVNb alloys with different Ti contents were almost the same at the same temperature, implying that the increase in the Ti content could not change the properties at high temperatures, but improve the ductility at room temperature.

The compressive SYSs and compressive strains of Ti_xZr -VNb alloys and some typical HEAs at room temperature [17,19,36–47] are summarized in Fig. 8. Some HEAs with T.D. Huang et al., Effect of Ti content on microstructure and properties of Ti_xZrVNb refractory ...

Temperature	Compressive property	TiZrVNb	Ti _{1.5} ZrVNb	Ti ₂ ZrVNb
	Yield strength / MPa	1229	1119	1086
Room temperature	Compressive strength / MPa	2287	—	_
	Compressive ductility / %	35.2	>50	>50
	Yield strength / MPa	768	778	834
600°C	Compressive strength / MPa	923	886	922
	Compressive ductility / %	>50	>50	>50
	Yield strength / MPa	227	233	204
800°C	Compressive strength / MPa	233	236	211
	Compressive ductility / %	>50	>50	>50

Table 4. Compressive properties of Ti_xZrVNb alloys at different temperatures



Fig. 8. Compressive SYSs and compressive ductilities of $Ti_x ZrVNb$ alloys and some typical HEAs at room temperature.

high SYSs, such as $Ti_{30}Al_{20}V_{20}Nb_{20}Mo_{10}$ and AlCoCrFeNi, had poor compressive ductilities. Some other HEAs with high compressive ductilities, such as CoCrFeNi, had low SYSs because of the high density. Nevertheless, the $Ti_{1.5}Zr$ -VNb and Ti_2ZrVNb alloys exhibited good SYSs with high compressive ductilities. Both alloys showed great application potential at room and elevated temperatures. The values of density, compressive SYS, and compressive ductility of the Ti_xZrVNb and typical HEAs listed in Fig. 8 are presented in Table 5.

Table 5.	Densities, compressive SYSs, a	nd compressive ductilitie	es of Ti _x ZrVNb alloys and	d some typical HEAs	at room temperature
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Alloy	Density / $(g \cdot cm^{-3})$	SYS / (MPa \cdot cm ³ \cdot g ⁻¹)	Compressive strain /%	Refs.
TiZrVNb	6.45	191	35.2	This work
Ti _{1.5} ZrVNb	6.22	180	>50	This work
Ti ₂ ZrVNb	6.12	177	>50	This work
NbTiV ₂ Zr	6.34	145	>50	[19,36]
CrNbTiZr	6.67	189	6	[19,36]
CrNbTiVZr	6.57	198	3	[19,36]
Ti ₂ ZrHf _{0.5} VNb	6.47	179	>50	[37]
$Ti_{40}Al_{10}V_{20}Nb_{20}Mo_{10}$	6.10	147	>50	[38]
$Ti_{35}Al_{15}V_{20}Nb_{20}Mo_{10}$	6.03	161	>50	[38]
$Ti_{30}Al_{20}V_{20}Nb_{20}Mo_{10}$	5.88	202	11	[38]
TiNbHfZr	9.94	93	>50	[39]
NbMoTaW	13.75	77	2.6	[17,40]
VNbMoTaW	12.36	101	1.7	[17,40]
CoCrFeNi	8.13	19	>50	[41]
AlCoCrFeNi	7.00	197	22.7	[42-43]
AlCoCrCuFeNi	7.10	183	9.9	[44-45]
AlNbTiVZr _{0.5}	5.64	263	>50	[46]
Al _{0.5} CrNbTi ₂ V _{0.5}	5.76	215	>50	[47]

4. Conclusions

(1) The TiZrVNb alloy comprised a bcc matrix and a small amount of V_2Zr precipitation phase. The $Ti_{1.5}ZrVNb$ and Ti_2ZrVNb alloys exhibited a single-phase bcc structure. The precipitation phase disappeared with the increase in the Ti content.

(2) At room temperature, the mechanical properties significantly increased with the increase in the Ti content; the tensile ductility of TiZrVNb (3.5%) was less than that of Ti_2ZrVNb (12.3%).

(3) The Ti_xZrVNb alloys exhibited high strength at 600°C; the yield strengths of TiZrVNb, Ti_{1.5}ZrVNb, and Ti₂ZrVNb alloys were 923, 886, and 922 MPa, respectively. Softening occurred at 800°C; the yield strengths of TiZrVNb, Ti_{1.5}Zr-VNb, and Ti₂ZrVNb alloys were 233, 236, and 211 MPa, respectively.

(4) The Ti_{1.5}ZrVNb and Ti₂ZrVNb alloys exhibited good SYSs (180 MPa·cm³·g⁻¹ and 177 MPa·cm³·g⁻¹, respectively) with high compressive ductilities (>50%) at room temperature. Therefore, both alloys have great application potential.

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