New TITaNbZrMo high-entropy alloys for metallic biomaterials

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Keywords: alloy design, high-entropy alloys, mechanical property, biomaterials

Abstract

The advantages of high entropy alloy with good comprehensive properties provide a potential opportunity to explore and develop new alloys suitable for human implantation. In this experiment, TITaNbZrMo high entropy alloy was designed and prepared by alloy design and first principle. The calculation results predict that the phase composition of each high entropy alloy is BCC structure, and the designed high entropy alloy has structural stability; the non-equal atomic ratio TiNbTaZrMo high-entropy alloy has higher ductility than the equal atomic ratio TiNbTaZrMo high-entropy alloy; the B/G, Poisson’s ratio υ and (C_{12} - C_{44}) values of Ti_{30}(NbTaZr)_{60}Mo_{10} alloy are the largest, indicating that the toughness of this alloy is the best, and the Young’s modulus value is the smallest. The experimental results show that the yield strength of Ti_{30}(NbTaZr)_{60}Mo_{10} alloy is 1132 MPa, the plastic strain is 33%, and the wear resistance and corrosion resistance are good. The potential of Ti_{30}(NbTaZr)_{60}Mo_{10} in biological field is proved by calculation and experimental test, which provides an important basis for its industrial application in biomedical alloy.

1. Introduction

The development of science and technology and the improvement of living standards have made people pay more attention to physical health, which has promoted the development of social medical technology. A large number of patients with diseased or damaged hard tissues need to be replaced or repaired by surgery. In order to meet the needs of this field, there is an urgent need for biomedical materials with superior biocompatibility and mechanical properties. Due to the complicated shape of surgical implants, it is required that biomedical materials should be easy to process and form, easy to manufacture, and reasonably priced. Metal materials have become the earliest and most widely used medical materials due to their excellent properties [1–4]. At present, biomedical alloys used mainly include cobalt-based alloys, stainless steel, titanium and titanium alloys. In the physiological environment of human body, cobalt-based alloys and stainless steel are more likely to be corroded than titanium and titanium alloys, thereby dissolving Ni, Cr and Co ions that are toxic to the human body, and their elastic modulus (cobalt-based alloy: 240 Gpa, stainless steel: 210 Gpa) are much greater than that of human bone (20 ~ 30 Gpa). The biocompatibility and corrosion resistance of titanium alloy are better than those of cobalt-based alloys and stainless steel, and the elastic modulus is lower, but the wear resistance is lower than that of cobalt-based alloys [5, 6].

Due to the frequent occurrence of human injuries such as diseases and injuries, people pay more attention to new medical materials. High entropy alloys (HEAS) with multi-component (five or more elements) and equal or near equal atomic concentration have become one of the most potential medical new medical materials in recent years because of their excellent properties, which have been explored and studied by many scholars [7–11]. The existing alloy materials are designed by adding a small amount of other alloying elements to a single principal element, and this is often limited to the improvement of its comprehensive intrinsic properties. High-entropy alloys are alloys with multi-principal elements and high degree of confusion. The characteristic of multi
principal component high entropy makes it reflect ‘collective characteristics’ and tend to be disorderly arranged, so it is easy to form a simple phase [12–15]. In particular, biomedical high-entropy alloys with titanium as the main element have been rapidly developed. For example, Takao Hori et al. used thermodynamic calculations and established a binary phase diagram to design Ti-Nb-Ta-Zr-Mo alloy and proposed the possibility of this alloy as a biomaterial [16]; Yuan Yuan et al. conducted systematic experiments on all materials in Ti-Zr-Hf-Nb-Ta alloy and proved that all components are non-toxic and non-allergenic [17]; G. Popescu et al. used powder metallurgy to prepare Ti-Zr-Nb-Ta-Fe alloy. Through the study of structure, mechanical properties and corrosion properties, they proved that it has good mechanical biocompatibility [18]. The above studies show that high-entropy alloys are suitable as a new type of metal biomedical materials. In this study, based on the alloy design of HEAs and first-principles calculations, we took the metal elements Ti, Ta, Nb, Zr, and Mo with good biological indicators as the research objects, and designed a five-element HEA. The analysis of microstructure, mechanical properties and corrosion resistance provides a basis for the industrialization of biomedical alloys.

2. Alloy design

In this study, Ti-Nb-Ta-Zr-Mo high-entropy alloy with excellent properties was selected as the starting alloy. According to Wang Shaoping’s research, it was found that Mo can cause embrittlement of TiZrNbTaMo alloy, but at the same time it will improve the corrosion resistance of the alloy [19]. In this study, the Mo atomic percentage in the alloy composition was selected as 10%, and the high-entropy alloy with excellent mechanical properties and biocompatibility was designed by changing the content of Ti. With the rapid development of high-entropy alloy research, more and more different kinds of high-entropy alloys have been developed. Therefore, predicting the structure of alloy phases can provide great convenience for the preparation of alloys. Researchers analyzed the formation law of the high-entropy alloy phase and found that the structure of the high-entropy alloy phase can be predicted by calculating the mixing entropy, mixing enthalpy, valence electron concentration and other parameters of the alloy [20]. In addition to practical experiments, modern scientific research will also conduct theoretical explorations with computer simulations and calculations. The advantage of first-principles calculations is that the electronic structure of the system can be calculated only by specifying the atomic type and arrangement order of the system, thereby predicting the various properties of the system [21, 22]. Based on this, the phase structure and properties of Ti(NbTaZr)0.89Mo0.11 high-entropy alloy are calculated through alloy design and first principle, and the best non equal atomic ratio TiZrNbTaMo high entropy alloy is selected for experimental comparison with equal atomic ratio TiZrNbTaMo alloy.

2.1. Phase structure prediction of high-entropy alloys

Zhang Yong et al. proposed three principles for the formation of solid solution phases in high-entropy alloys, namely: (1) the number of principal elements: n ≥ 5, and the mixing entropy $\Delta S_{\text{mix}} > 1.61 \ R$; (2) the difference in atomic size: $\delta < 4.6\%$; (3) The enthalpy of mixing ($\Delta H_{\text{mix}}$) satisfies: $-2.6858\sim-2.54 < -1.288 + 5.44 \text{ KJ mol}^{-1}$. Subsequently, its range was further expanded, namely: $12 < \Delta S_{\text{mix}} < 17.5\text{ KJ mol}^{-1}$, $\delta < 6.4\%$, $-20 < \Delta H_{\text{mix}} < 5\text{ KJ mol}^{-1}$ [23, 24]; Guo and other scholars put forward more relaxed formation conditions, namely: $11 < \Delta S_{\text{mix}} < 19.5\text{ KJ mol}^{-1}$, $\delta < 8.5\%$, $-22 < \Delta H_{\text{mix}} < 7\text{ KJ mol}^{-1}$ [25]. High-entropy alloys are simple disordered solid solutions composed of multiple principal elements. At present, there are mainly three common phase structures: body-centered cubic (BCC), face-centered cubic (FCC), and close packed hexagonal (HCP). In order to predict the crystal structure of high entropy alloys, theoretical criteria such as atomic size difference, valence electron concentration (VEC), mixing entropy and electronegativity are widely used. Zhang Yong et al. believe that the atomic radius of each principal element of high entropy alloy is not different, and the principal elements are easy to replace each other. When $\delta < 5\%$, the alloy principal elements can immediately occupy the lattice nodes to form disordered solid solutions, $5\% < \delta < 6.6\%$ form a disordered solid solution and an ordered solid solution mixed structure; Wang et al. proposed that the distribution of the largest and smallest atoms with the surrounding atoms $\lambda$ can also be used as a basis for the formation of disordered solid solution phases and intermetallic compounds in high-entropy alloys. It is believed that when $\lambda$ is less than 1.175, the alloy easily forms a single-phase BCC structure [26]. From the perspective of the outermost valence electrons, Guo et al. systematically explained the influence of the electronic structure on the crystal structure of the high-entropy aggregate solid solution. The phase structure type of the alloy was judged by the electron concentration. When the VEC is less than 6.7, the alloy phase structure is mainly BCC structure. When VEC is greater than 8, the alloy phase structure is mainly FCC. When VEC is between 6.7–8, a mixed solid solution of BCC and FCC is formed [27].

The calculation formulas for mixing enthalpy, mixing entropy, and integrated atomic radius are as follows [28]:

\[ \Delta H_{\text{mix}} = \sum_{i=1}^{n} \Delta H_{i} \]

\[ \Delta S_{\text{mix}} = \sum_{i=1}^{n} S_{i} \]

\[ \lambda = \frac{\text{atomic radius of largest atom}}{\text{atomic radius of smallest atom}} \]
The mixing enthalpy is:

$$\Delta H_{\text{mix}} = \sum_{i=1}^{n} \Omega_i C_i \Omega_{ij} = 4 \times \Delta H_{\text{mix}}^{\text{max}}$$

The mixing entropy is:

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

The comprehensive atomic radius is:

$$\delta = \sqrt[1/n]{\sum_{i=1}^{n} C_i \left(1 - \frac{r_i}{\bar{r}}\right)^2} = \sum_{i=1}^{n} C_i r_i$$

The $\lambda$ is:

$$\lambda = \left(1 - \sqrt[2]{\frac{(r_1 + \bar{r})^2 + (\bar{r})^2}{(r_1 + \bar{r})^2}}\right)$$

The valence electron concentration is:

$$\text{VEC} = \sum_{i=1}^{n} C_i \langle \text{VEC}i \rangle$$

Where $C_i$-the atomic percentage of component $i$ in the alloy; $C_j$-the atomic percentage of component $j$ in the alloy; $R$-gas constant (8.314 J/(mol·K)); $r_i$-the atomic radius of component $i$; $\bar{r}$-the average atomic radius of the multi-component alloy; $\langle \text{VEC}i \rangle$-the valence electron concentration of component $i$ in the alloy.

Based on the above formula, we have carried out the corresponding calculation results for the alloy designed in this experiment, as shown in Table 1. It can be seen from Table 1 that the designed high-entropy alloys all meet the conditions of solid solution phase formation. By predicting that the high-entropy alloy phase composition of each component is BCC structure, and the designed high-entropy alloys have structural stability.

**Table 1.** Alloy parameters of $\Delta S_{\text{mix}}$ [J mol$^{-1}$ K$^{-1}$], $\Delta H_{\text{mix}}$ [kJ mol$^{-1}$], $\delta$ [%], $\lambda$, and VEC in the Ti$_x$(NbTaZr)$_{90-x}$Mo$_{10}$ and equiatomic TiNbTaZrMo alloys.

| Alloys                  | $\Delta S_{\text{mix}}$ | $\Delta H_{\text{mix}}$ | $\delta$ | $\lambda$ | VEC  |
|-------------------------|-------------------------|--------------------------|-----------|------------|------|
| Ti$_{10}$(NbTaZr)$_{30}$Mo$_{60}$ | 13.07                   | 0.1774                   | 4.225     | 0.8641     | 4.6662 |
| Ti$_{15}$(NbTaZr)$_{25}$Mo$_{60}$ | 13.07                   | 0.09056                  | 4.178     | 0.8495     | 4.632  |
| Ti$_{20}$(NbTaZr)$_{20}$Mo$_{60}$ | 12.89                   | 0                      | 4.113     | 0.8649     | 4.6    |
| Ti$_{25}$(NbTaZr)$_{15}$Mo$_{60}$ | 12.74                   | -0.096                   | 4.03      | 0.8653     | 4.566  |
| Ti$_{20}$Nb$_{20}$Ta$_{20}$Zr$_{20}$Mo$_{20}$ | 13.8                    | 1.76                     | 4.46      | 0.8658     | 4.8    |

**Figure 1.** Unit cell model of TiNbTaZrMo high entropy alloy.

2.2. First-principles calculation

Any performance of material is based on its structure, so it is necessary to construct the corresponding geometric structure model before calculating the various properties of the material; and in the first-principles calculation, the selection of calculation parameters is a very important prerequisite [29, 30]. At present, it is generally believed that high-entropy alloys are solid solution structures with stable mixed entropy. The mutual substitution of atomic positions in the crystal makes the crystal structure of high-entropy alloys more complex. Therefore, this paper is based on density functional theory and adopts the CASTEP module in material studio.
The ground state energy determines the electron density and deduces the properties of the ground state alloy. In the software, a model of the TiNbTaZrMo high-entropy alloy is approximated by virtual crystals. The geometric optimization of the unit cell model adopts the BFG algorithm, the k-space is $8 \times 8 \times 8$, and the truncation energy is 600 eV. The unit cell model is shown in the figure 1.

(1) Lattice constant

The lattice constant is an important basic parameter of the crystal structure, and it has a direct relationship with the bonding energy between atoms. The change of the lattice constant directly reflects the change of the internal composition and force state of the crystal. Figure 2 shows the lattice constants of the designed alloys of various components. It can be seen from figure 2 that the lattice constant of the non-equal atomic ratio TiNbTaZrMo high-entropy alloy decreases with the increase of the titanium element content, and the lattice constant of the non-equal atomic ratio TiNbTaZrMo high-entropy alloy is higher than that of the equal atomic ratio TiNbTaZrMo. The lattice constant of the alloy is small. The smaller the lattice constant of the high-entropy alloy, the greater the binding energy between atoms in the high-entropy alloy, and the more stable the structure.

(2) Elastic constant

Elastic property is the inherent property of material itself, which indicates the deformation of material under the action of external stress. The elastic constant of crystal reflects the macroscopic mechanical property constant of the material under the action of normal temperature or static load. It not only reflects the response mode to the applied stress or strain, but also reflects the bonding characteristics of near ground state. Therefore, the premise of studying solid properties is to study its elastic constant. Elastic modulus is one of the important performance parameters of materials. From the macro point of view, the elastic modulus is a measure of the ability of a material to resist elastic deformation, while from a micro point of view, it is the actual reflection of ionic, atomic or intermolecular bond strength. Table 2 shows the elastic constants $C_{ij}$ of TiNbTaZrMo high-entropy alloys with different compositions obtained by first-principles calculation.

![Figure 2. Lattice constant of alloys.](image)

### Table 2. Elastic constant $C_{ij}$ of TiNbTaZrMo alloys.

| Alloys | $C_{11}$ | $C_{12}$ | $C_{44}$ | $C_{12} - C_{44}$ |
|--------|----------|----------|----------|------------------|
| Ti$_{20}$Nb$_{20}$Ta$_{20}$Zr$_{20}$Mo$_{20}$ | 186.94 | 126.90 | 52.97 | 73.93 |
| Ti$_{10}$Nb$_{30}$Ta$_{10}$Zr$_{10}$Mo$_{10}$ | 138.01 | 131.53 | 71.58 | 59.95 |
| Ti$_{15}$Nb$_{25}$Ta$_{25}$Zr$_{25}$Mo$_{10}$ | 233.86 | 228.65 | 94.49 | 134.16 |
| Ti$_{15}$Nb$_{30}$Ta$_{20}$Zr$_{15}$Mo$_{10}$ | 358.76 | 153.92 | 15.78 | 138.14 |
| Ti$_{15}$Nb$_{35}$Ta$_{15}$Zr$_{10}$Mo$_{10}$ | 328.41 | 150.56 | 16.67 | 133.89 |

The ground state energy determines the electron density and deduces the properties of the ground state alloy. In the software, a model of the TiNbTaZrMo high-entropy alloy is approximated by virtual crystals. The geometric optimization of the unit cell model adopts the BFG algorithm, the k-space is $8 \times 8 \times 8$, and the truncation energy is 600 eV. The unit cell model is shown in the figure 1.
According to the thermodynamic stability criterion of cubic crystal system: \( C_{44} > 0; C_{11} > |C_{12}|; C_{11} + 2C_{12} > 0 \) [31]. Combined with the data in table 2, it can be seen that TiNbTaZrMo high-entropy alloys are thermodynamically stable, which also shows that TiNbTaZrMo alloys have a stable crystal structure.

The elastic constant can be used as a criterion for judging the ductility of cubic crystals, using the so-called Cauchy pressure \((C_{12} - C_{44})\). Generally speaking, for materials with ductility, the Cauchy pressure is positive, and the greater the pressure value, the better the ductility; on the contrary, for brittle materials, the Cauchy pressure is negative. From the Cauchy pressure values listed in table 2, it can be seen that the non-equal atomic ratio TiNbTaZrMo high-entropy alloy has higher ductility than the equal atomic ratio TiNbTaZrMo high-entropy alloy (except for Ti20(NbTaZr)70Mo10 alloy). This may be because the ductility of titanium structure itself reduces the cutting effect of the alloy, reduces the stress concentration under load, and prevents the generation and propagation of cracks, Thus, the ductility of the alloy is increased, which is consistent with the research results of Wang Lanxin et al. [32]. The maximum Cauchy pressure of Ti30(NbTaZr)70Mo10 high-entropy alloy is 138.14. It can be seen that there is no intermetallic compound or complex phase that causes brittleness in the multi-component alloy.

Table 3. Elastic modulus of TiNbTaZrMo high entropy alloy.

| Alloys                     | B   | G   | E   | B/G | \(\nu\) |
|----------------------------|-----|-----|-----|-----|---------|
| Ti20Nb20Ta20Zr20Mo20       | 146.92 | 42.18 | 115.49 | 3.48 | 0.37    |
| Ti20(NbTaZr)70Mo10         | 41.68  | 86.87 | 153.78 | 0.48 | −0.11   |
| Ti25(NbTaZr)65Mo10         | 232.12 | 24.43 | 70.80 | 9.5  | 0.45    |
| Ti30(NbTaZr)60Mo10         | 222.20 | 13.74 | 40.39 | 16.17 | 0.47    |
| Ti35(NbTaZr)55Mo10         | 209.85 | 35.14 | 99.83 | 5.97 | 0.42    |

Figure 3. Relationship between elastic modulus and high entropy alloys of TiNbTaZrMo system with different components.

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According to the thermodynamic stability criterion of cubic crystal system: \( C_{44} > 0; C_{11} > |C_{12}|; C_{11} + 2C_{12} > 0 \). Combined with the data in table 2, it can be seen that TiNbTaZrMo high-entropy alloys are thermodynamically stable, which also shows that TiNbTaZrMo alloys have a stable crystal structure.

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(3) Elastic modulus

The elastic modulus represents the relationship between the stress and strain of the material, and it mainly includes Young’s modulus, shear elastic modulus, bulk elastic modulus, poisson’s ratio, etc. The elastic modulus is the general term for these moduli. The modulus of elasticity can be regarded as a measure of the difficulty of the material to produce elastic deformation. The greater the modulus value, the greater the stress required for elastic deformation, that is, the smaller the elastic deformation of the material under certain stress. Because biomedical materials require materials to have a Young’s modulus similar to that of bone tissue to reduce the ‘stress shielding effect’, thereby reducing the absorption and aseptic loosening of the bone tissue around the prosthesis. Therefore, the young’s modulus is given priority when selecting the appropriate TiNbTaZrMo high entropy alloy according to the first principal calculation results. Table 3 lists the elastic modulus of TiNbTaZrMo high entropy alloys with different compositions, and figure 3 shows the relationship between elastic modulus and alloy composition.

The bulk elastic modulus B reflects the ability of the crystal to resist volume deformation under external pressure, the shear modulus G is the measure of the crystal’s resistance to reversible deformation under shear
stress, and the young’s modulus $E$ is the physical quantity characterizing the compression or tension of the crystal within the elastic limit. It can be seen from table 3 that the bulk elastic modulus $B$ of the alloy is distributed between $41 \sim 232$ GPa, and the shear modulus $G$ is from 13 to 86 GPa. Young’s modulus $E$ is between $40 \sim 150$ GPa. With the increase of Ti content, the bulk elastic modulus $B$ first increased and then decreased, the shear modulus $G$ and Young’s modulus $E$ first decreased and then increased, and the young’s modulus of Ti30(NbTaZr)60Mo10 was the smallest. Therefore, with the increase of Ti content, the resistance to volume deformation of TiZrNbTaMo high entropy alloy is gradually weakened, while the resistance to reversible deformation and compression in the elastic range are improved.

Brittle-ductile is a very important property of materials. It is used to describe the ability of materials to absorb energy and carry out plastic deformation before fracture. Usually, the ratio of bulk elastic modulus and shear modulus $B/G$, Poisson’s ratio $\nu$ and $(C_{12}-C_{44})$ are used to predict the brittleness and toughness of the alloy. When the alloy satisfies $B/G > 1.75$, $\nu > 0.26$ and $(C_{12}-C_{44}) > 0$ at the same time, the alloy exhibits toughness characteristics, otherwise it is brittle. It can be seen in figure 3 that except for Ti20(NbTaZr)70Mo10 alloy which is brittle (where Poisson’s ratio $\nu = -0.11 < 0.26$), the other alloys all exhibit obvious toughness characteristics. And with the increase of Ti content, the $B/G$ curve and Poisson’s ratio $\nu$ curve change the same. Among them, the $B/G$, Poisson’s ratio $\nu$ and $(C_{12}-C_{44})$ values of Ti30(NbTaZr)60Mo10 alloy are the largest, indicating that the toughness of this alloy is the best, and the Young’s modulus value is the smallest. Therefore, this component is selected for experimental comparison with TiZrNbTaMo alloy with equal atomic ratio.

3. Experimental procedures

High-purity metals Ti, Ta, Zr, Mo and Nb (purity $\geq 99.9\%$) are selected, and the alloy master ingot is configured according to the atomic molar ratio, and the composition is Ti30(NbTaZr)60Mo10 and Ti20Zr20Nb20Ta20Mo20. High entropy alloy ingots were prepared by magnetic levitation melting and melted repeatedly for 4 times to ensure the stability of chemical composition in the alloy. The melted ingot is prepared by wire cutting mechanism $\phi 7$ mm $\times$ 4 mm cylindrical sample for XRD analysis. The test conditions are as follows: the tube voltage is 50 kV, the tube current is 50 mA, the scanning speed is 3° min$^{-1}$, the scanning step is 0.02, and the scanning angle is 10 $\sim$ 90°. The HF-HNO3 etching solution with a ratio of 4:1:5 was used to corrode the sample and conduct metallographic analysis. The room temperature compression test is completed on the electronic universal material machine, the sample size is $\phi 3$ $\times$ 6 mm, and the test compression strain rate is

![Figure 4. X-ray diffraction patterns of Ti30(NbTaZr)60Mo10 and Ti20Zr20Nb20Ta20Mo20 high entropy alloys.](image-url)
0.8 × 10⁻² s⁻¹. Carry out the hardness test on the micro-Vickers hardness tester, the equipment model is TMVS-1. The test load is 500 g, and the load holding time is 10 s. 11 points are tested on each sample, the maximum and minimum values are rounded off, and the average value of the remaining nine test values is the hardness value of the alloy. The wear test was performed on the cut 4 × 4 × 12 sample on the friction and wear tester. The parameters were set as follows: load 1000 g, rotation speed 200 r min⁻¹, friction radius 12.5 mm, and experiment time 30 min. In this experiment, the cutting disc method was used, and the sample was fixed on the support for grinding with 45 steels. An electrochemical workstation was used to measure the polarization curve and AC impedance spectrum of each sample. The electrolyte used in the experiment is Phosphate buffer solution. Potential polarization curve test potential range is −1 ∼ 1 V, scanning speed is 0.001 mV s⁻¹; set electrochemical impedance spectroscopy test frequency range is 10⁻² ∼ 10⁵ Hz, signal amplitude is a sine wave of 10 mV. During the test, a constant temperature water bath was used to keep the electrolyte at 37 °C.

4. Results and discussion

Figure 4 shows the XRD analysis images of two high-entropy alloys. It can be clearly seen from the figure that the high-entropy alloys of the two systems show sharp diffraction peaks. And there is no order peak formed at the low angle position, so it can be seen that the system structure is composed of a single disordered BCC solid solution phase. At the same time, the XRD pattern also confirmed the formation of a hexagonal crystal system without any intermetallic compound phase or an ordered phase, indicating that no other phases were formed during the smelting process, which was consistent with the results of the above simulation calculation. In addition, it can also be seen from figure 4 that the high-entropy alloy of this system has a strong diffraction peak, which indicates that the crystallinity of the alloy crystal of this system is very good.

Figure 5 shows the microstructure photos of two high-entropy alloys with non-equal atomic ratio and equal atomic ratio. Figures 5(a) and (b) are metallographic photos of Ti₃₀(NbTaZr)₆₀Mo₁₀ alloys before and after corrosion. Figures 5(c), (d) are photos of Ti₂₀Zr₂₀Nb₂₀Ta₂₀Mo₂₀ alloy before and after corrosion.
figures 5(b), (d), we can see the obvious dendritic morphology, two phases with distinct colors and morphologies (bcc1 and bcc2, as shown by the red cross in the figure). Among them, the dendrite stem and dendrite arm regions are composed of bcc1 phase, and the inter dendritic stem and inter dendritic arm regions are composed of bcc2 phase, which corresponds to the bcc phase diffraction peaks of the two lattice constants in figure 4. And it can be seen from the morphology that the grains of the non-atomic ratio high-entropy alloy (Ti30(NbTaZr)60Mo10) are larger than those formed by the equal-atomic ratio high-entropy alloy (Ti20Zr20Nb20Ta20Mo20). The small grain size of Ti20Zr20Nb20Ta20Mo20 indicates better strength and hardness.

Combining the XRD analysis results (figure 4), SEM micrograph (figure 6) and the atomic percentage analysis within and between the grains (table 4), it can be determined that bcc1 is the main constituent phase in grains and bcc2 is the secondary constituent phase between grains. According to the data in table 4, the chemical composition expression of bcc1 phase of Ti30(NbTaZr)60Mo10 alloy is Ti26Zr8Nb21Ta35Mo10; the expression of the bcc2 phase is Ti43Zr26Nb14Ta9Mo8. The chemical composition expression of the bcc1 phase of Ti20Zr20Nb20Ta20Mo20 alloy is Ti14Zr4Nb22Ta27Mo33; the expression of the bcc2 phase is Ti26Zr46Nb12Ta7Mo9. Among them, Nb, Ta, and Mo elements are more distributed in the dendrite stem and dendrite arm region, and Ti and Zr elements are more distributed in the dendrite stem and inter dendritic arm region, this is consistent with the research results of Wang Shaoping et al [33]. Firstly, the melting points of Nb, Ta, and Mo elements are much greater than those of Ti and Zr elements. During the cooling process, the refractory metals Nb, Ta, and Mo solidify before other elements in the dendrite stems and arms, and have no time to diffuse to the dendrite stem gap and dendrite arm gap, resulting in a substantial decrease in the contents of Nb, Ta, and Mo, which leads to an increase in the contents of Ti and Zr. Secondly, the mixing enthalpy of Ti and Zr is 0, which indicates that random solid solutions are easily formed between the two elements, and the remaining mixing enthalpy is not 0, the separation of the elements may occur, that is, when the cooling rate is too fast, tree branches are formed. In the process of crystal segregation, Ti and Zr separate and segregate and form a more stable bcc2 structure with the remaining Nb, Ta and Mo elements. Furthermore, the atomic radius of the Zr element is large, and the alloy

| Alloys Position | Ti (atomic percentage) | Zr (atomic percentage) | Nb (atomic percentage) | Mo (atomic percentage) | Ta (atomic percentage) |
|----------------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| Ti30(NbTaZr)60Mo10 intracrystalline | 26 ± 1     |  8 ± 1     | 21 ± 1     | 10 ± 1     | 35 ± 1     |
|           | 43 ± 1     | 26 ± 1    | 14 ± 1    | 8 ± 1      | 9 ± 1      |
| Ti20Zr20Nb20Ta20Mo20 intracrystalline | 14 ± 1     | 4 ± 1     | 22 ± 1    | 27 ± 1     | 33 ± 1     |
|           | 26 ± 1     | 46 ± 1    | 12 ± 1    | 9 ± 1      | 7 ± 1      |

| Alloys          | Ti (atomic percentage) | Zr (atomic percentage) | Nb (atomic percentage) | Mo (atomic percentage) | Ta (atomic percentage) |
|----------------|-----------------------|------------------------|------------------------|------------------------|------------------------|
| Ti30(NbTaZr)60Mo10       | 31.8%            | 18.52%                | 18.92%                | 9.97%                  | 20.78%                |
| Ti20Zr20Nb20Ta20Mo20     | 21.27%           | 22.05%                | 18.48%                | 19.09%                | 19.10%                |
material will shrink macroscopically during the cooling process, which will further compress the microscopic space, which makes part of the Zr element precipitate and gather at the grain boundary.

The results of the regional energy spectrum analysis of the two alloys are shown in table 5. The data in the table shows that the atomic percentage of the alloy smelted in this experiment is very close to the percentage designed in the experiment, indicating that there is no volatilization of components in the melting process of the alloy. Figure 7 is the element distribution diagram of the experimental high-entropy alloy. From the perspective of the density of the different color points in the figure, the element distribution in the matrix region is uniform and closer to the nominal alloy composition. Overall, this indicates that the alloy after smelting has reached a homogeneous state.

Figure 8 shows the normal temperature compressive stress-strain curves of the two high-entropy alloys in the experiment. Table 6 compares the mechanical properties of the two high-entropy alloys and other medical alloys in this experiment [34–36]. It can be seen from figure 8 that both alloys have experienced the elastic deformation stage, the plastic deformation stage, and the failure fracture stage. It can be seen from table 6 that the yield strength of Ti_{30}(NbTaZr)_{60}Mo_{10} alloy is 1132 MPa. In contrast, Ti_{20}Zr_{20}Nb_{20}Ta_{20}Mo_{20} alloy has a higher yield strength, but the plastic deformation rate of Ti_{30}(NbTaZr)_{60}Mo_{10} alloy is 33%, which is 10% higher.
than Ti20Zr20Nb20Ta20Mo20 alloy, indicating that Ti30(NbTaZr)60Mo10 alloy has good shaping, this is consistent with the research results of Takao Hori et al. At the same time, compared with other medical alloys, Ti30(NbTaZr)60Mo10 alloy has good mechanical properties, and Mo element enhances the hardness of TiNbZrTa high-entropy alloy.

Figure 9 is a graph showing the change of friction coefficient of non equiatomic and equiatomic alloys under dry and wet grinding. It can be seen that the friction coefficient curve can be roughly divided into two stages: the initial friction stage and the friction stable stage. In the initial stage, the friction coefficient increases due to the increase of the contact area between the sample and the friction pair and the damage to the alloy surface due to friction. The friction coefficient of Ti30(NbTaZr)60Mo10 alloy is higher than Ti20Zr20Nb20Ta20Mo20 alloy whether it is dry grinding or wet grinding in human body fluids. The wear resistance of the alloy is inversely proportional to the friction coefficient, indicating that Ti20Zr20Nb20Ta20Mo20 alloy has better wear resistance under the same conditions. In the liquid environment, the friction coefficient of the alloy has been significantly reduced and the fluctuation of its value has become much smoother. This is mainly because the surface of the alloy is covered with a water film in a liquid environment, and water molecules fill the surface pits, reducing the surface roughness during friction. Moreover, from the wear rate of dry and wet wear in figure 10, it can be found that the wear rate of Ti30(Zr20Nb20Ta20Mo20 alloy is lower, and the wear rate of wet grinding is lower than that of dry grinding. The comparison shows that Ti30Zr20Nb20Ta20Mo20 alloy has better wear resistance, but Ti30(NbTaZr)60Mo10 alloy still has good wear resistance compared with other medical alloys. This fully proves that the TiZrNbTaMo high-entropy alloy has good wear resistance, which is consistent with the hardness and friction and wear results.

Figure 11 shows the electrochemical corrosion polarization curve of TiZrNbTaMo high entropy alloy. It can be seen from the figure that in the corrosion process, they all go through the initial cathodic polarization stage, and the current decreases with the increase of scanning potential until the anodic polarization begins. With the continuous increase of voltage, the activation passivation transition zone begins to appear, and enters the passivation zone with the continuous increase of potential. Then the current hardly changes with the increase of voltage. Table 7 lists the electrochemical corrosion parameters of TiZrNbTaMo high-entropy alloys, and compares them with TC4, 316LSS and CoCrMo alloys. It can be seen that Ti30(NbTaZr)60Mo10 alloy has significantly better corrosion resistance than other alloys, and its self-corrosion potential Ec20 is −0.09 V. The current density Icorr is 1.69 × 10⁻⁸ A cm⁻² [33]. More Ti elements are enriched in the dendrite area to generate

Figure 9. Curve of friction coefficient of high entropy alloy with sliding time.

Table 6. Mechanical properties of high entropy alloy.

| Alloys                  | Yield strength (MPa) | Breaking strength (MPa) | Plastic deformation rate (%) | Hardness (HV) |
|------------------------|----------------------|-------------------------|-----------------------------|---------------|
| Ti30(NbTaZr)60Mo10     | 1132                 | 1488                    | 33                          | 487           |
| Ti30Zr20Nb20Ta20Mo20    | 1356                 | 1647                    | 23                          | 619           |
| CP-Ti                  | 692                  | 785                     | 20                          | 230           |
| Co-Cr-Mo               | 515                  | 725                     | 9                           | 780           |
| 022Cr17Ni12Mo2         | 750                  | 950                     | 41                          | 189           |

than Ti30Zr20Nb20Ta20Mo20 alloy, indicating that Ti30(NbTaZr)60Mo10 alloy has good shaping, this is consistent with the research results of Takao Hori et al [16]. At the same time, compared with other medical alloys, Ti30(NbTaZr)60Mo10 alloy has good mechanical properties, and Mo element enhances the hardness of TiNbZrTa high-entropy alloy.
TiNb phase, which reduces the Zr content in the bcc1 phase, prevents the corrosion micro-battery formed by the TiNbZr phase, which is beneficial to the improvement of the corrosion resistance of the alloy and the self-corrosion potential of the alloy.

5. Conclusions

In order to find a medical high entropy alloy with better performance, firstly, the composition ratio of tizrnbtaam high entropy alloy is determined through alloy design and first-principal calculation, and this composition is selected for experimental comparison with TiZrNbTaMo alloy with equal atomic ratio. The following conclusions are obtained:

| Alloys             | E_d (Volts) | I_d (Amp/cm²)    |
|--------------------|-------------|------------------|
| Ti_30(NbTaZr)Mo_20 | -0.09       | 1.69 × 10⁻³      |
| Ti_30Zr_30Nb_20Ta_20Mo_20 | -0.31       | 3.09 × 10⁻⁴      |
| TC4                | -0.57       | 0.96 × 10⁻⁶      |
| 316LSS             | -0.23       | 0.83 × 10⁻⁶      |
| CoCrMo             | -0.32       | 0.42 × 10⁻⁶      |
(1) The TiZrNbTaMo high-entropy alloy designed in this experiment is composed of a single-phase BCC solid solution structure. The Ti50(NbTaZr)30Mo10 alloy has the lowest Young’s modulus through calculation. The atomic percentage of the smelted alloy is consistent with the experimental design, and there is no lack of composition or the appearance of new phases. The equal atom ratio high-entropy alloy has finer grains and has a better hardness value.

(2) The yield strength of Ti20Zr20Nb20Ta20Mo20 alloy and Ti50(NbTaZr)30Mo10 alloy are 1356 MPa and 1132 MPa, respectively, and the plastic strain is 23% and 33% respectively. Therefore, Ti50(NbTaZr)30Mo10 alloy has better comprehensive mechanical properties.

(3) Whether dry grinding or wet grinding in human body fluid, Ti30Zr20Nb20Ta20Mo20 alloy has lower friction coefficient and wear amount, but Ti50(NbTaZr)30Mo10 alloy still has good wear resistance compared with other medical alloys. Wet grinding can significantly reduce the friction coefficient and wear of the alloy.

(4) Ti50(NbTaZr)30Mo10 alloy has good corrosion resistance, the self-corrosion potential Ecorr is −0.09 V, and the corrosion current density Icorr is 1.69 \times 10^{-8} \text{ A cm}^{-2}.

The Ti50(NbTaZr)30Mo10 alloy has proved its potential in the biological field through calculations and experimental tests. It can be further explored through supplementary experiments such as heat treatment, deformation, and cytotoxicity test.

Acknowledgments

This work was supported by scientific research fund project of Shaanxi Polytechnic Institute (serial number: 2020-10) and Science and technology innovation project of Shaanxi Polytechnic Institute (serial number: 2021YKZX-001).

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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