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The Perfect Mechanical Properties and Biomedical Compatibility of TiNbTaZrMo HEA, its Variants, and the TiHfTaZrMo Refractory HEA

Abstract

Investigating the high-entropy alloys TiNbTaZrMo and other variations such as TiNbTaZrMoHf revealed numerous beneficial properties, primarily a high yield strength of 1500 MPa, a tensile strength of 2250 MPa, and high ductility, with Young's Modulus being 153 GPa. Furthermore, it has been shown that through cold rolling, annealing, and changing the concentration of certain elements such as Mo or Ti can further increase or decrease the fracture toughness or strength, respectively. Introduction of elements such as oxygen and nitrogen was found to further strengthen these properties. Using stress induced martensitic phase transformation from the two initial BCC phases to a HCP phase can increase both the strength and ductility. Dislocations frequently cross-slip between {110} and {112} planes during plastic deformation caused by screw dislocations. Additionally, it has been shown to have both good biocompatibility and retain much of its strength at high temperatures, as well as high resistance to corrosion. TiNbTaZrMo has a wide range of medical usages, mainly due to its strong mechanical properties combined with its biocompatibility.

Introduction

High Entropy Alloys, or HEAs are a relatively new class of materials that contain five or more elements in equiatomic or near-equiatomic ratios which enhances stability, specifically at higher temperatures. Titanium has always been the superior material for mechanical designs due to its low density coupled with high yield strength. Specifically, the titanium-containing HEA TiNbTaZrMo was developed as a new metallic biomaterial for its corrosion, mechanical and wear behaviors.[1] TiNbTaZrMo has two body-centered-cubic solid solution phases, hardness of 500 HV, as well as compressive strength around 2,600 MPa.[2] Due to a decrease in Ti content, $Ti_{0.5}$ZrNbTaMo resulted in the greatest corrosive wear resistance because of a comparatively lower wear rate from both dry and wet sliding.[2] After cold-working the alloy maintained a single-phase microstructure, 1483 MPa tensile yield stress at room temperature, 1495 MPa peak true stress, and true fracture strain of 5 pct. [6]

316L stainless steel is known for good corrosion resistance and high creep strength at high temperatures and is often used for biomedical applications. In comparison to SS316L having tensile strength of 515 MPa and yield strength of 205 MPa, TiNbTaZrMo HEA possess drastically higher tensile and yield strength of 2250 MPa and 1500 MPa which makes this Titanium based HEA the more desirable material.[11] The TiNbTaZrMo high entropy alloy shows promise for a range of biomedical applications, for example, bone plates, hip joints, surgical instruments and dental implants.[2] Ti-based alloys are superior for their mechanical properties, biocompatibility, Young's modulus of 153 GPa and high corrosion resistance.[1] HEA's desirable properties are owed to their high entropy effect, sever lattice distortion, and the sluggish diffusion.[2]

Discussion

Body Centered Cubic Crystal Structure

The structure characterization of our HEA indicates that it comprises two BCC solid solution phases (BCC-1 and BCC-2). As described, BCC-1 contains “Ta-enriched main solid solution phase dendrite,” while BCC-2 contains “Ti-, Zr-, and Nb-enriched minor solid solution phase inter-dendrite matrix.”[2] It was also discovered that the same HEA with half as much Ti results in hardness of 500 HV and 2600 MPa of compressive strength. Due to the BCC structure, Ti-Zr-based HEAs present with higher hardness and resistance to wear, which decreases consequences of “wear debris disease.”[2] These capabilities enable implanted devices, like bone screws, to maintain enough strength for thinner screw rods and deeper threads while “resisting the plastic deformation and fracture under an applied stress.”[2] The main BCC has a lattice constant of 0.325 nm while the second BCC has a lattice constant of 0.333nm. Based on the XRD patterns analyzed, “the decrease in the fraction of Ti in the alloys, the peak position of the minor BBC-2 phase shifts to lower angles.”[2] This shift decreases the ratio between peak intensity of BBC-2 and BBC-1 phase. This structure correlates to overall high strength and low ductility.[2]

Slip System, Bands and Burgers Vector

A similar Ti-Zr- based HEA which includes Hf rather than Mo, shows persistent slipping. BCC metals frequently have cross-slipping dislocations, specifically between the {110} and {112} slip planes during plastic deformation.[7] In most Nb-Mo alloys, the slip plane is the same as the maximum shear stress plane at room temperature . The frequency of cross-slipping is altered by the solid solutes. Slip bands were found to be on the {110} plane when the crystal deforms and showed straight slip bands numerous times.[7] The slip bands within these dislocations tend to be straight. For a similar HEA TiZrNbHfTa, a study determined the slip direction of “[111] by evaluating the magnitude of cross-slipping by tracing slip bands” of bending tests.[7] A study looking at the same HEA variation, excluding Mo, discusses the deformation tendencies of the HEA single and polycrystals. The Burgers vector of dislocations is found to be “1/2 [111] and the dislocation line is nearly parallel to [111].”[5] The study concludes that 1/2<111> screw dislocations cause the specific deformation behavior.[5]

Critically Resolved Shear Stress and Dislocations

A computational study of Refractory HEA, TaNbHfZr, did a series of simulations to obtain properties such as microstructual, strengthening, ductility and dislocation. Variation in a figure shows critically resolved shear stress (CRSS) for the TaNbHfZr R-HEA with respect to Monte Carlo structure evolution.The initial CRSS value of 435 rapidly increases within the first 10 swaps of Monte Carlo structure evolution. [4] The implied calculated yield strength reached a value nearing 2500MPa which was computed using the Taylor factor relation. Thus it can be determined that the calculated yield strength reaches a value roughly equal to 2500 MPa, computed using the Taylor factor relation. However the yield stress measured experimentally for as-synthesized TaNbHfZr R-HEA returned a value of 1315 MPa. “CRSS values obtained from the edge dislocation simulations indicate that the simulated yield strength of the alloy is within 1.5% accuracy of the experimental value for the random solid solution and within 7.6% of the experimental value for the 1-day annealed material.”[4] Further on in the study, under an application of 1500MPa for the 15MC swap structure, “the dislocation was completely broken and destroyed turning the crystalline structure into an amorphous configuration with a shear band.”[11] The failure can be explained by the dislocations inability to move under high shear stress within the structure. This behaviour “is expected for dislocation pile-ups and crack-tip shielding for ductile materials.” [4]

Strengthening Mechanisms: Cold Rolling and Annealing

The microstructure and tensile properties of HEA variant HfNbTaTiZr were explored after cold rolling and annealing the alloy. After cold rolling, the material’s thickness decreased to 89 pct without cracking. Following this process the alloy still had its single-phase microstructure, “tensile yield stress $\sigma(0.2)$ of 1438 MPa, peak true stress σ_P of 1495 MPa, and true fracture strain ε_F of 5 percent”[6] at room temperature. Since HfNbTa-TiZr alloys can be “heavily cold rolled to 86%,”[5] the microstructure can be maintained by heat treatments. However, HfNbTaTiZr alloys when cast show “strong solidifying segregation,”[5] affecting the mechanical properties.

The same study annealed the HEA at 800C for 256 hours and found precipitation of “Nb and Ta rich particles with a BCC crystal structure inside a Hf-and-Zr-enriched BCC matrix.”[6] In the two-phase material, “$\sigma(0.2)$ decreased from 1159 to 1071 MPa, and σ_P from 1174 to 1074 MPa, accompanied by an increase in particle diameter from 0.18 to 0.72 lm, while ε_F remained between 5 and 8 pct.”[6] Following heat treatment, the alloy was proven to be a “single-phase BCC structure with $\sigma(0.2)$ ranging from 1110 to 1115 MPa, σ_P from 1160 to 1195 MPa, and ε_F from 12 to 19 percent,” which came from a 1 hour annealing period.[6] A study exploring deformation behavior of HfNbTaTiZr HEA single crystals and polycrystals also experimented with annealing. The study found that the microstructure depended strongly on annealing temperature. “At 773-1073 K, phase separation into two BCC phases took place, while the hexagonal close-packed phase was precipitated at 773-973K.”[5] Severe plastic deformation is found after cold or hot working which is important to consider during practical applications.

SS316L Mechanical Properties Comparison

316L stainless steel is known for good corrosion resistance against most chemicals and high creep strength at higher temperatures. This makes it great for biomedical applications such as implants as well as marine applications and food applications. In comparison to TiNbTaZrMo HEA it has far lower tensile strength, yield strength, but a higher modulus of elasticity. The tensile strength of the SS316L is 515 MPa vs the HEA’s tensile strength of 2250 MPa. The yield strength of the SS316L is 205 MPa and the HEA’s is 1500 MPa. The modulus of elasticity for SS316L is 193 GPa and the HEA’s is 153 GPa. In summation the mechanical properties of TiNbTaZrMo HEA are superior to SS316L. The higher tensile and yield strength leads to a much stronger alloy overall.

SS316L Biomedical Properties Comparison

Conventional SS(316L) has far lower osteoblasts concentration compared to TiNbTaZrMo. The cells grown on the as-cast and annealed TiNbTaZrMo have widespread morphology as opposed to the relatively small spread morphology of the cells present on the SS 316 alloy. The spread of cells has a significant role in cellular functions, it affects migration proliferation and protein synthesis. The TiNbTaZrMo HEA had similar characteristics to CP-Ti and both metals have significant advantages compared to SS 316L in bone matrix formation. Cell density after 24hr was analyzed and it was found that TiNbTaZrMo HEA had significantly higher cell density compared to SS 316L and the HEA showed outstanding biocompatibility similar to CP-Ti. This could indicate that redistribution of constituent elements or the grain coarsening in the annealed TiNbTaZrMo HEA increased cellular adhesion of the osteoblasts. The formation of Ti oxide layers and Zr oxide layers in TNTZ alloys exhibit excellent biocompatibility and an increase in cell density over CP-Ti. It can be concluded that TiNbTaZrMo HEA is highly biocompatible and shows far greater promise as an alternative or replacement to biocompatible SS 316L.

Table 1: Critical values interpreted from various graphs.[1][2]

K_Q	18.7 MPa√m at 20% Mo
Yield strength	1500MPa
Tensile strength	2250MPa
ductility	Young's modulus: 153GPa

Ductility and the Affects of Additional Mo

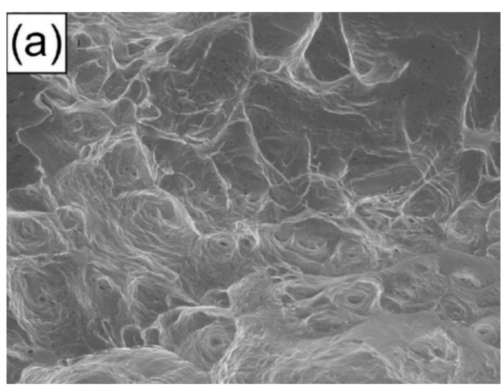
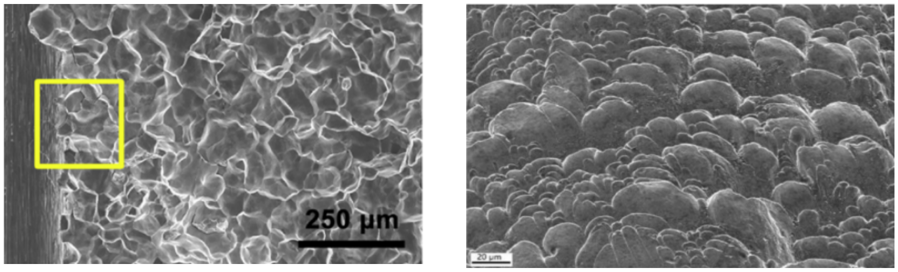


Figure 1: Fracture surface of TiZrHfTa annealed at 1473K for 1h.[5]

The ductility the HEA largely depend on both the annealing temperature,[14] as well as the amount of Mo present.[14] Additionally, The Brittle-ductile transition (BDT) temperature also depends on the amount of Mo present in the alloy.[14] The larger the amount, the higher the BDT temperature is.[14] It is also possible that in a variant of the alloy with 8 at% Mo the ductility is completely removed. In addition,

Notch Fracture Toughness and Creep Resistance



(a) (b)

Figure 2: (a) Micrograph of fractured surface at beginning of notch;[14] (b) Micrograph of dimples formed in TaNbHfZrTi after a strain rate of $2600s^{-1}$ was applied under 77K.[3]

The Notch fracture toughness also depends on the amount of Mo present.[2] If no Mo is present, the notch hardness value (K_Q) is 28.5 MPa $m^{1/2}$.[2] However, with 20 at% Mo present K_Q is reduced to 18.5 MPa $m^{1/2}$.[2] Perhaps this has to do with the rise in BDT temperature.

The RHEA TaNbHfZrTi has a relatively high strain rate of $2600s^{-1}$ at 293K. However, it can be much lower depending on the temperature of.[3] Additionally, its sensitivity to change in temperature decreases with an increase in temperature above room temperature (293K).[3]

Eutectic and Invariant Reaction in TiNbTaZrMo and more Generally

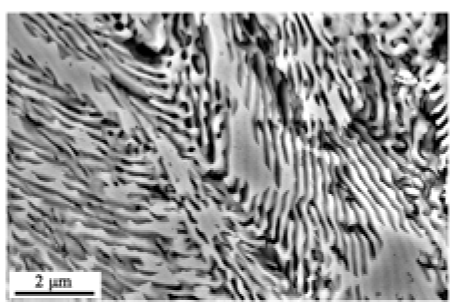


Figure 3: CoCrFeNiMo Eutectic Reaction[10]

TiNbTaZrMo does not show a point of eutectic reaction through its phases. A eutectic reaction for CoCrFeNiMo is shown in figure 3, a eutectoid with one shared element. In the pseudo-binary tables shown in figure 4, multiple points of invariant reactions can be seen, such as at about 1000C at 90 mole% Ti in the Mo-Ti diagram. 1000 degrees celsius is also observed as an invariant reaction point for about 95 mole% Zr in the Mo-Zr diagram. 1000C is a critical temperature in the synthesis of the alloy.[12]

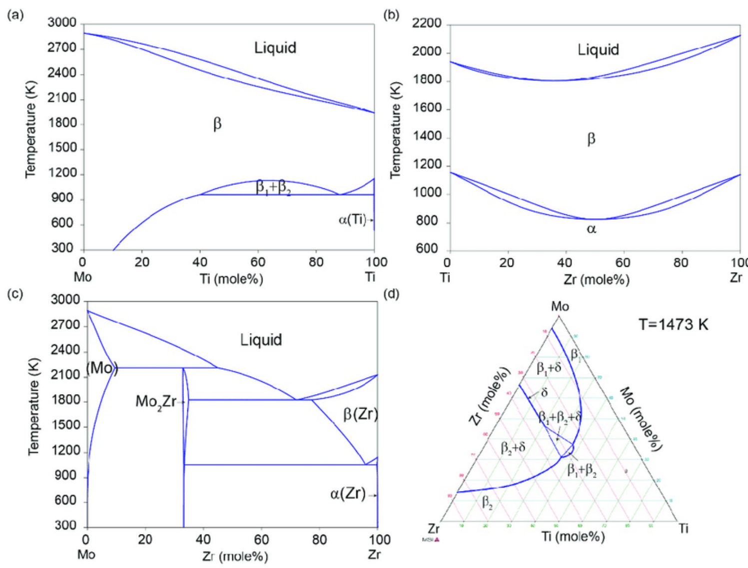


Figure 4: Pseudo-Binary and ternary phase diagrams for Mo, Ti, and Zr.[12]

Critical Temperatures to the HEA's Properties

HfNbTaTiZ exhibits a single phase BCC structure at and above 1000C, and shows multiple phases below this mark.[6] The BCC structures at temperatures below tend to be rich in Nb and Ta.[6] This alloy also increased in yield stress from 820 MPa and 1145 MPa and in fracture strength from 9.5% to 10% upon cold rolling by a thickness reduction of 86 percent and a 2 hour annealing at 1000C.[6] From these changes consistently occurring at this temperature, 1000C appears to be a critical temperature regarding the HEA's properties.[6] By increasing yield stress and fracture strength the alloy will be more resistant to deformation and failure in its real-world usages. Additionally, annealing at 800C resulted in the precipitation and coarsening of second-phase particles.[6] This precipitated phase had a BCC crystal structure, as seen in the main structure.[6] Four hours of this annealing caused a decrease in room temperature tensile yield stress to 1159 MPa, peak true stress to 1174 MPa, and true stress to 1127 MPa, with the fracture strain remaining constant.[6] One of the phases at the lower temperatures, at 500C, is a hexagonal phase riched in Hf and Zr, which was found in the alloy when treated with high pressure torsion.[6]

Phase Differences within the HEA

In HfNbTaTiZr, an FCC phase different from the typical BCC seen in the HEA, was found with nitrogen and oxygen within the structure.[8] This FCC structure exhibits a higher hardness than the BCC structure.[8] Investigations showed that when this HEA was annealed at 700C for 2.5 hours, it was mainly decomposed into three phases: BCC, a Ta-Nb rich BCC precipitate, and a Zr-Hf rich hexagonal-close-pack precipitate.[8] Another example of phase property differences is in TiZrHfNbO HEAs given solid solution treatment for 0.5 hours at 1000C.[15] The addition of

Oxygen to its phases successfully maintained its plasticity while significantly increasing the yield strengths.[15] However, the yield strengths were reduced and the plasticity was deteriorated when this process was followed by 100 hours of aging at 600C.[15]

Phase Transformations

For this specific HEA, there is a process called Strain-induced Martensitic Transformation (SIMT), which is often found in various steel and titanium alloys. It is often used to not only increase yield and tensile strengths of materials but can do so without deterioration of ductility.[9] In this case it is used on the RHEA TiZrHfTa where the "severe lattice distortion in Ta14 is a key factor for this SIMT".[9] More generally in HEA's, transformations occur more slowly than in traditional alloys or metals due to there much lower rate of diffusion.[13]

Conclusions

TiNbTaZrMo is a very strong option for manufacturing use, especially due to its extensive uses in medical equipment. Titanium has become a frequently used element for mechanical applications due to its relatively light weight and strong properties, and this specific HEA TiNbTaZrMo is very resistant to corrosion and has good biocompatibility, helping lead to its effectiveness for use in medical settings. The strong mechanical properties this HEA exhibits include high tensile strength, yield strength, ductility, true stress, and tensile yield stress. Strengthening mechanisms can be employed to improve these qualities as well, including cold rolling and annealing. The properties can be adjusted between phases based on the concentration of the materials and the addition of substances such as oxygen and nitrogen. Its ability to maintain its strong characteristics at a wide range of temperatures is another reason why this, along with other HEAs, are a strong choice for manufacturing use.

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