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REVIEW ARTICLE

Biomedical Applications of Titanium and Aluminium-based High Entropy Alloys

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ABSTRACT

High entropy alloys are a subclass of metallic biomaterials whose biomedical applications are vigorously explored in recent times due to their excellent mechanical properties and biocompatibility. Most of the current biomaterials are a tradeoff between biocompatibility and mechanical properties or tribological properties. For overcoming this problem, high entropy alloys are introduced into the field of biomaterials. They arise because of development in modern technologies especially, processing technologies such as Arc melting, RF magnetron sputtering, powder metallurgy, vacuum arc melting, cold rolling, selective laser sintering, etc. The gross resultant properties of high entropy alloys are a function of the composition of the metals used, processing methods, compatibility between the alloys, and many other parameters. Hence, in the following review the factors that affect the overall properties of high entropy alloys that are made up of titanium and aluminum along with their mechanical properties, tribological properties are discussed for their application in many load-bearing areas in a human body.

Keywords: Aluminum alloys, Biomedical Applications, High Entropy Alloys, Orthopedic applications, Titanium alloys.

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INTRODUCTION

Biomaterials are materials that aid in the temporary or permanent replacement of damaged tissues or an injured organ.[1] They're employed in everything from scaffolding cells and tissues to joint replacements in the biomedical field. They are classified as synthetic or natural biomaterials depending on the material from which they are made. Metallic, ceramic, Polymeric and other composite biomaterials are examples of synthetic biomaterials. Natural biomaterials include natural silk, chitosan, and collagen.[2] However synthetic biomaterials gained popularity because of their simplicity and their ease of handling. The choice of material depends upon the location of the application because the biomechanics of the body is specific to each location. For instance, metals are used as biomaterials because of their excellent mechanical properties. Stainless steel, Co-Cr alloys, Titanium alloys, and other metals like platinum, palladium, rhodium, iridium, ruthenium, osmium, and tantalum are examples of the most used metallic biomaterials. The development of modern technology has led to the advancement of manufacturing and fabrication technologies of these biomaterials, which indeed opened the door for an even broader spectrum of biomedical applications.[3] One modern approach of metallic biomaterials is a combination of elements to produce multicomponent alloys which are called high entropy alloys. High entropy alloys are composite materials containing five or more elements in relatively 5–35% concentration to achieve the formation of stable solid alloy solution.[4] The concept of a high entropy alloy can be found in medical applications such as hip and joint replacements, dental implants, plates, and screws. The high entropy alloys are divided into two main categories to examine their deformation mechanism according to the crystallographic structure of the phase which includes FCC-based, BCC-based, HCP-based, amorphous, and intermetallic high entropy alloys. According to the phase types which include single-phase, dual-phase, eutectic, and multi-phase high entropy alloys (HEAs).[4] High-entropy alloys are well known for their distinctive microstructural characteristics which gave rise to enhanced properties when compared to conventional alloys. Thermodynamic high entropy effect, lattice distortion effect, sluggish diffusion effect, cocktail effect are the four remarkable properties of high-entropy alloys that assist in determining their solid solution phase, nanostructure, thermal stability, and other important properties. The Thermodynamic high entropy effect is mainly used in explaining the multi-principal-element solid solution. It helps in increasing the formation of the solution phase, with good strength and ductility which make the solution stiffer and better. The lattice distortion describes

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the high strength of HEAs, specifically the BCC-structured HEAs, along with tensile brittleness and slower kinetics. The Sluggish diffusion effect explains the nano-sized precipitation. It is mainly used in the casting process. The Cocktail effect is related to the mixing of multicomponent elements of HEA.[5] When compared to intermetallic compounds that achieve equilibrium states at high temperatures, the high mixing entropy is a multi-principal-element that displays less Gibbs free energy for irregular and partially ordered solid solutions. There is a highly significant difference in the enthalpy observed while mixing dissimilar atomic pairs, which gives rise to the formation of more than two phases. The atomic size difference parameter (δ) also plays an important role in the preparation of high entropy alloys and it is compared with the entropy of mixing (ΔS mix) as well as enthalpy of mixing (ΔH mix) which also explains setting phase selection rule and the order-disorder contesting in these alloys.[6] While designing any alloy, previous research focused mostly on the corners of a phase diagram to develop conventional alloy which usually occupies only a small portion of the design space. There are many strategies towards the designing approach that assist in shifting the focus towards the central portion of the design space.

PROPERTIES TO DESIGN ALLOYS

Properties such as enthalpy of mixing, the entropy of mixing, melting points, atomic size difference, and valence electron concentration are used in designing high entropy alloys through the phase formation rule. These rules and specifications allow us to design a high-entropy alloy with the specific features that appropriately suit their proposed application.[6-8]

Enthalpy and Entropy of Mixing

The entropy of mixing of an alloy is similar to that of an ideal gas when the equal atomic size and loose atomic packing are presumed and there is a comparison in the solid-state phases of an alloy, those are elemental phases, intermetallic compound phases, and solid solution phases (random/irregular solid solutions and partially ordered solid solutions).[6] The phase with very little free energy at a given temperature and pressure will be prevailing in the equilibrium state. If kinetic factors are not included in it, then phase formation is thermodynamically controlled by the Gibbs free energy,

$$\Delta G_{mix} = \Delta H_{mix} - T \times \Delta S_{mix},$$

(where, ΔH = enthalpy of mixing, ΔS mix= entropy of mixing, T= temperature)[6,7]

Ω Parameter

It gives the integrated effects of ΔS mix and ΔH mix on the stability of different components of solid solution, by taking these various components melting points into the discussion. The Ω and Tm specifications are defined by $\Omega = T_m . \Delta S_{mix} / |\Delta H_{mix}|$.[6,7]

Where, $\Delta S mix > 1.6R$ (R = gas constant) as a standard for high-entropy alloys, many researchers proposed if $\Omega > 1.1$, where higher the Ω value, the higher the chances of making a single-phase random solid solution in high-entropy alloy

Atomic Size Difference

The critical atomic size difference (δ) found for a solid solution to form high-entropy alloys is $\delta \leq 6.6\%$.[6,7]

Φ parameter

The individual parameters SC and SE with Tm and ΔHmix, give rise to the φ parameter, which defined as

$$\Phi = Sc\, |\Delta H_{mix}| = Tm / |SE|$$

(where, SC is equivalent to ΔSmix, SE= function of atomic composition).[6,7]

Both ΔSmix and **Ω** had remarkable expressions in their specific values introduced for the high-entropy alloys with various kinds of phases, and φ has shown to be good out of all other three specifications which discussed earlier, with a critical value of $\Phi c = 20$, where alloys with greater values of Φc shows single-phase solid solutions, and lower values show multiphase and amorphous solutions.

Valence Electron Concentration

The valence electron concentration (VEC) shows the type of structure that will be making high-entropy alloys, which are usually face-centered cubic (FCC), body-centered cubic BCC, or hexagonal close-packed (HCP) structures (6). The valence electron concentration, which directs the crystal structure of HEA, is involved in their creation. VEC (6.87) = BCC structure, (>8) = FCC structure, (3) = HCP structure are the stable electron concentrations (Figures 1 and 2).[6,7]

MATERIALS AND METHODS

There are many methods for preparing HEA that include Powder metallurgy where we prepare the alloying step by step

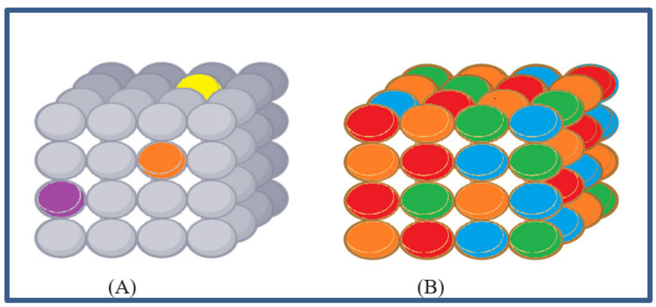

Figure 1: (A) conventional Alloys (B) High Entropy Alloys

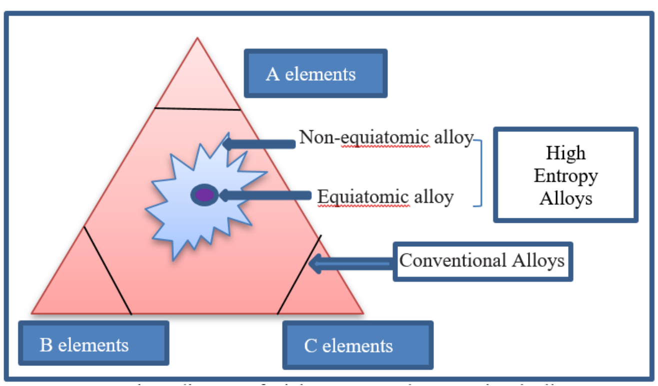

Figure 2: Ternary phase diagram of High Entropy and Conventional Alloys

using ball milling/mixing, pressing, sintering, and subsequent processing. The surface of the substrate is cladded with the alloy powder on the substrate in Laser cladding. Separate metal atoms off the surface of the target using direct current or radiofrequency in magnetron sputtering. Most HEA is prepared in bulk using ingot metallurgy, powder metallurgy, and selective laser melting techniques. However, laser cladding and magnetron sputtering methods are mostly used for synthesizing thin films or coatings of HEA.

TITANIUM-BASED ALLOYS

In recent years, many HEAs are used as medical implants, consisting of refractory elements with non-toxic and non-allergenic nature. Many of these alloys have desirable properties for biomedical applications, among which Titanium-based alloys show remarkable biocompatibility with low young modulus, good wear resistance, corrosion resistance, and low magnetic susceptibility.

Ti-Ta-Zr-Hf-Nb

Metallic biomaterials like 316L, Co-Cr-Mo and Ti-6Al-4V show low biocompatibility besides poor wear and corrosion resistance. To overcome this situation the concept of refractory high entropy alloy was introduced to synthesize novel biomaterials like -Ta-Zr-Hf-Nb and $Ti_{1\cdot5}ZrTa_{0\cdot5}Hf_{0\cdot5}Nb_{0\cdot5}$ exhibit superior wear resistance, wettability, corrosion resistance. Where the Ti-Ta-Zr-Hf-Nb system constitutes non-toxic, allergy-free, low young modulus, and low magnetic susceptibility. Ti-Ta-Zr-Hf-Nb is synthesized by Arc meting (Mixture of pure metal in Titanium getter high purity Argon atm.) and vacuum arc melting; Ti-Ta-Hf-Nb-Zr films are deposited by Radio Frequency magnetron sputtering (argon ions are accelerated by Radiofrequency electric field to hit a target made of the material to sputter) over Ti-6Al-4V substrates. Ti-6Al-4V shows less biocompatibility which is improved by deposition of Ti-Ta-Zr-Hf-Nb on it.

Mechanical properties of the alloys change rapidly when the alloy composition changes. Young modulus is one of the intrinsic natures of materials and its crystalline structure has a dramatic effect on its value. Alloy 1, 2, 3, 4, 5, 6 shows BCC structure having lower young modulus and high yield strength since BCC phase shows low young modulus than HCP Phase. On comparing (alloy 6) with $Ti_{1\cdot5}ZrTa_{0\cdot5}Hf_{0\cdot5}Nb_{0\cdot5,}$ the young modulus decreases, and strength increases as the composition is altered. Upon comparing equimolar $Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$ with $Ti_{31\cdot6}Zr_{31\cdot6}Nb_{31\cdot66}Ta_{5}$ (Alloy 2) it is evident that high young modulus also has high yield strength thereupon it leads to an increase in corrosion resistance. Compared to the bulk form of Ti-Ta-Hf-Nb-Zr, Ti-6Al-4V films show the increasing mechanical property in terms of young modulus (Table 1).[9-13]

Multi-principal-element (Ti-Zr-Nb-Hf-Ta) N [N= nitrides] and (Ti-Zr-Nb-Hf-Ta) C [C= carbide] protection coatings are be done by DC magnetron sputtering for biomedical applications. The (Ti-Zr-Nb-Hf-Ta) N film has a quasi-stoichiometric composition. However, the (Ti-Zr-Nb-Hf-Ta) C-1 and (Ti-Zr-Nb-Hf-Ta) C2 films are sub-stoichiometric; over stoichiometric respectively, there are remarkable differences between the (Ti-Zr-Nb-Hf-Ta) C-1 and (Ti-Zr-Nb-Hf-Ta) C−2 coatings. For the over-stoichiometric films, metal-containing carbon shows the presence of C–C bonds, and for the sub-stoichiometric film, C–C bonds were not detected. Carbide coating with the highest carbon content shows the best friction performance ($\mu = 0.12$) and the highest wear resistance in the tribological tests

Table 1: Comparison of mechanical properties between various titanium-based alloys

Ref	*Composite &concentration materials*	*Composite preparation technique*	*Youngs Modulus (Gpa)*	*Yield strength (MPa)*
(9)	$Ti_{25}Zr_{25}Nb_{25}Ta_{25}$ (Alloy1)	Arc meting (Mixture of pure metal in Ti getter high purity Argon atm.)	89	970
(9)	$Ti_{31.6}Zr_{31\cdot6}Nb_{31\cdot66}Ta_{5}$ (Alloy 2)	Arc meting	75	790
(9)	$Ti_{35}Zr_{35}Nb_{25}Ta_{5}$ (Alloy 3)	Arc meting	69	780
(9)	$Ti_{45}Zr_{45}Nb_{5}Ta_{5}$ (Alloy 4)	Arc meting	57	690
(9)	$Ti_{21\cdot67}Zr_{21\cdot67}Nb_{21\cdot66}Ta_{35}$ (Alloy 5)	Arc meting	93	1050
(9)	$Ti_{15}Zr_{15}Nb_{35}Ta_{35}$ (alloy 6)	Arc meting	135	970
(11)	$Ti_{1\cdot5}ZrTa_{0\cdot5}Hf_{0\cdot5}Nb_{0\cdot5}$	Arc meting	98.57 ± 4.18	800–1500
(10)	$Ti_{20}Zr_{20}Hf_{20}Nb_{20}Ta_{20}$	Arc meting	80	800–985
(12)	TiTaHfNbZr filmsTi-6Al-4V substrates	RF magnetron sputtering	181.3 ± 2.4	-
(13)	TaNbHfZrTi	Vacuum arc melting	131.6	-

Table 2: Comparison of tribological properties between various titanium-based alloys

Ref	*Composite and concentration Material*	*Coefficient of friction*	*Wear rate (10^-4) mm^3/Nm*
(12)	Ta-Nb-Hf-Zr-Ti HEA film	0.1 to 0.2	0.5-1× 10−6 mm3N−1m−1
(13)	(Ti-Zr-Nb-Hf-Ta) C-1 coating	0.32	0.90 × 10−6mm3N−1m−1
(13)	(Ti-Zr-Nb-Hf-Ta) N coating	0.17	0.29 × 10−6 mm3N−1m−1
(13)	(Ti-Zr-Nb-Hf-Ta) C−2 coating	0.12	0.20 × 10−6 mm3N−1m−1

performed in simulated body fluids (SBFs). The Coefficient of friction is low and stable with the value ranging from 0.1 to 0.2 for TaNbHfZrTi HEA film (Table 2).[12,13]

Speaking of its biocompatibility, the cell adhesion to substrates is used in assessing cell surface interactions there upon evaluating its biocompatibility according to the literature. X-ray photoelectron spectroscopy (XPS) analysis gives the idea about the formation of a passive film composed of TiO_2, ZrO_2, HfO_2, Nb_2O_5, and Ta_2O_5 which is responsible for high bio-corrosion resistance of high entropy alloy, good adhesion, cell viability, cell proliferation behaviors of MC3T3-E1 pre-osteoblasts on the Ti-Zr-Hf-Nb-Ta HEA indicating well in In-vitro biocompatibility. Ti-Zr-Hf-Nb-Ta HEA is composed of five biocompatible elements Ti, Zr, Hf, Nb, Ta, which shows non-cytotoxic surface film character and high corrosion resistance, less release of corrosion products or ions during in-vivo implantation. Ti-Ta-Hf-Nb-Zr high entropy alloys are used in fetal bovine serum to assess their biocompatibility in presence of proteins so it has the potential to be used in orthopedic implant materials.[14]

Ti-Ta-Mo-Nb-Zr

A novel Ti-Ta-Nb-Mo-Zr composite is obtained from an equiatomic Ti-Ta-Nb-Zr alloy which is synthesized from arc melting. There are different types of composites of the Ti-Ta-Nb-Mo-Zr i.e., $Ti_{2.6}NbTaZrMo$, $Ti_{1.7}NbTaZrMo_{0.5}$, $Ti_{1.5}NbTaZrMo_{0.5}$, $Ti_{1.4}Nb_{0.6}Ta_{0.6}Zr_{1.4}Mo_{0.6}$ that show excellent biocompatibility. Among these composites, $Ti_{1.4}Nb_{0.6}Ta_{0.6}Zr_{1.4}Mo_{0.6}$ which is obtained by electrode induction melting gas has decreased melting point and enhanced ductility; its atomization of pre-alloyed rods. Mechanical properties like young modulus and hardness are evaluated using nano-indentation tests. However, stress, strain, and yield strength are obtained by a universal testing machine.

Ti-Ta-Nb-Mo-Zr alloy shows a lower young modulus and yield strength when compared to BCC1 phase alloy. As-cast Ti-Ta-Nb-Mo-Zr alloy consists of two phases BCC1 and BCC2 which are prepared by arc melting, the BCC1 phase shows high young modulus and yield strength than the BCC2 phase which means the BCC1 phase is harder and stiffer than the BCC2 phase. However, decreasing in young modulus and a decrease in yield strength observe in $Ti_{1.4}Nb_{0.6}Ta_{0.6}Zr_{1.4}Mo_{0.6}$ compared to Ti-Ta-Nb-Mo-Zr alloy. The Selective laser melting rapid solidification feature is successful in imparting excellent mechanical properties to $Ti_{1.4}Nb_{0.6}Ta_{0.6}Zr_{1.4}Mo_{0.6}$ alloy (Table 3).[15-18]

HEA under both dry and wet sliding conditions. The dry and wet wear rates of Ti-Zr-Nb-Ta-Mo are lower than Ti-6Al-4V which is $3.5*10^{-7}$ $mm^3mm^{-1}N^{-1}$ and $4.6*10^{-7}$ $mm^3mm^{-1}N^{-1}$. $Ti_{0.5}ZrNbTaMo$ shows a lower coefficient of friction and wear rate in both dry and wet conditions than TiZrNbTaMo alloy. Coefficient of friction and wear rate decrease when they are under wet sliding conditions (Table 4).[19,20]

Speaking of Biocompatibility, SLM-built $Ti_{1.4}Nb_{0.6}Ta_{0.6}Zr_{1.4}Mo_{0.6}$ with as-cast counterparts, commercially Pure Titanium, and SS316L all show osteoblast density adhered to the specimens when they were evaluated using Giemsa staining. The cell adhesion and proliferation behavior of MC3T3-E1 osteoblast on the surface of the equiatomic ratio of TaNbHfZrTi are not significantly different from Ti-6Al-4V alloy, indicating good biocompatibility due to high corrosion resistance of Mo than Hf in the body fluid.

Ti-Ta-Fe-Zr-Nb

The Ti-Ta-Fe-Zr-Nb, HEA were investigated for the influence of milling time, mechanical properties, compaction, and sintering. They are synthesized by cold rolling, powder metallurgy, arc melting, and thermal processing. Beta titanium alloys (beta-type Ti-based alloys) are a more flexible class of titanium alloys. They are generally used for manufacturing orthopedic and dental implants, as they show the greatest strength to weight ratios, low young modulus, a better combination of strength, toughness, and fatigue resistance, as compared to alpha+ beta type Ti-alloys. While manufacturing high entropy alloy hard coatings is done by high power

Table 3: Comparison of mechanical properties between various Ti-Ta-Mo-Nb-Zr alloys

Ref	*Composite &concentration materials*	*Composite preparation technique*	*Youngs Modulus (Gpa)*	*Yield strength (MPa)*
(15)	Ti-Ta-Nb-Mo-Zr	Arc melting	153	1390
(15)	$Ti_{15}Zr_{10}Nb_{20}Ta_{31}Mo_{24}$ (BCC1)	Arc-melted ingot, XRD for structure	161	2005
(15)	$Ti_{24}Zr_{43}Nb_{12}Ta_{8}Mo_{13}$ (BCC2)	Arc-melted ingot, XRD for structure	133	1668
(16)	$Ti_{1.4}Nb_{0.6}Ta_{0.6}Zr_{1.4}Mo_{0.6}$	Arc melting, selective laser melting	140 ± 9	1140

Table 4: Comparison of tribological properties between various Ti-Ta-Mo-Nb-Zr alloys

Ref	*Composite and concentration Material*	*Coefficient of friction*		*Wear-rate (10^{-4}) mm^3/Nm*	
		Dry	*Wet*	*Dry*	*Wet*
(20)	$Ti_{0.5}ZrNbTaMo$	0.75	0.61,	$2.22*10^{-7}$ mm^3mm^{-1}N-1	$1.52*10^{-7}$ mm^3mm^{-1}N-1
(20)	TiZrNbTaMo	0.94	0.64	$2.91\text{-}3.50*10^{-7}$$mm^3mm^{-1}$N-1	$1.85\text{-}4.60*10^{-7}$ mm^3mm^{-1}N-1
(20)	$Ti_2ZrNbTaMo$	0.84	0.71	$2.42*10^{-7}$ mm^3mm^{-1}N-1	$2.45*10^{-7}$ mm^3mm^{-1}N-1

impulse magnetron sputtering (HiPIMS) system, in which novel TiZrNbTaFe and TiZrNbTaFeN HEA coatings were produced with an equiatomic TiZrNbTaFe which focused on three different substrates involves 304 stainless steel (ss), 420 SS and P-type Si (100) wafer, using a HiPIMS system at different RN2 ratios. The best biomedical materials used in an orthopedic device with an extended period, need a combination of a low young's modulus, high strength, and approximately matches with the human cortical bone.

Alloys synthesized by powder metallurgy have lower young modulus and higher yield strength, but if they are manufactured using a high-power impulse magnetron sputtering (HiPIMS) system they show high young modulus. So, the milling process is important in synthesizing Ti-Nb-Zr-Ta-Fe alloy. If Ti-Nb-Zr-Ta-Fe alloy is coated with 32% concentration of nitrogen, young modulus increases. This is observed in the case of Ti-Nb-Zr-Fe-O alloy whereas young modulus slightly increases. Different compositions of Ti-Nb-Zr-Fe-O alloy under cold rolling and forged condition shows an increase in young modulus and yield strength compared with solution treatment. The addition of Fe and O into the Ti-Nb-Zr-Fe-O alloy enhances mechanical properties (Table 5).[21-25]

Using high power impulses magnetron sputtering system (HiPIMS), one TiZrNbTaFe and three TiZrNbTaFe N coated were manufactured in presence of gas flow ratios (RN2). TiZrNbTaFe HEA has less coefficient of friction, but a high wear rate. nitrogen coating on TiZrNbTaFe HEA provides a good wear rate as well as coefficient of friction. As coating concentration is high, the wear rate and coefficient of friction are less i.e., having good capacity towards wear and corrosion resistance (Table 6).[24]

Speaking of biocompatibility, there is a concern related to Fe although all other elements such as Ti, Ta, Nb, Zr show excellent biocompatibility and biological response. Fe is genotoxic and cytotoxic which may be prone to corrosion, so Ti-Ta- Nb-Fe was developed to improve biocompatibility and corrosion resistance properties. Corrosion resistance test is carried out while developing biocompatible HEA with superior characteristics along with an appropriate selection of suitable elements. Confocal micrographs performed on the alloys, along with Ti control, with SOS-2 osteoblast-like cells were observed under seven-day incubation. MTS assays were also performed to show a more quantitative analysis of cell proliferation and survival ability. When the level of confidence is reduced to 90%, the Ti–10Ta–4Fe alloy indicates a slight reduction in cellular response, particularly in comparison to the empty well control; even so, and at this reduced level, such an alloy was distinct from the C.P. Ti control, implying that all examined alloys at least rival existing materials in terms of cellular response.[26]

Table 5: Comparison of mechanical properties between various alloys of-Ta-Fe-Zr-Nb

Ref	*Composite & concentration materials*	*Composite preparation technique*	*Youngs Modulus (Gpa)*	*Yield strength (Mpa)*	*Ultimate tensile strength (MPa)*
(21)	Ti-Nb-Zr-Ta-Fe	powder metallurgy (PM) route	52	2425	-
(22)	Ti-Nb-Zr-Fe-O	Cold rolling + solution treatment, thermal processing program	60-107	-	903 - 1370
(22)	Ti-20Zr-10Nb-3Ta-1Fe-1O (ST)	solution treatment	50	784	-
(22)	Ti-35.3Nb-5.7Ta-7.3Zr-2Fe-0.4O (forged)	Cold rolling	107	817	1130
(24)	Ti-Zr-Nb-Ta-Fe	Powder metallurgy (PM) the route, high power impulse magnetron sputtering (HiPIMS) system	135± 9	-	-
(24)	TiZrNbTaFe N1 (32.0 at. % nitrogen)	Powder metallurgy (PM) the route, high power impulse magnetron sputtering (HiPIMS) system	206 ± 2	-	-
(24)	TiZrNbTaFe N3	Powder metallurgy (PM) the route, high power impulse magnetron sputtering (HiPIMS) system	265 ± 3	-	-

Table 6: Comparison of Tribology properties between various alloys of Ti-Ta-Fe-Nb-Zr

Ref	*Composite and concentration Material*	*Coefficient of friction*	*Wear rate (10^-4) mm^3/Nm*
(24)	TiZrNbTaFe	0.40 ± 0.08	9.50 ×10−6mm3N−1m−1
(24)	TiZrNbTaFe N1	0.75 ± 0.04	3.55 ×10−6mm3N−1m−1
(24)	TiZrNbTaFe N7	0.79 ± 0.06	1.63 × 10−6mm3N−1m−1
(24)	TiZrNbTaFe N10	0.69 ± 0.05	2.65 × 10−6mm3N−1m−1

ALLOY BASED ON ALUMINUM

In these alloys, aluminum is the most common metal. Aluminum alloys offer high specific strength, excellent casting properties, and a low cost. However, it has low biocompatibility and poor wear and corrosion resistance, making it ineffective for biomedical applications. This can be solved by using micro-arc oxidation (MAO) in the fabrication process, which enhances wear and corrosion resistance. These aluminum-based alloys have been modified for use in orthopedic implants.

Al-Co-Cr-Fe-Ni

The use of multi main elements from diverse elements such as 3d transition elements (Fe, Co, Cr, Cu, Ni) and metals such as Aluminium is one of the novel techniques for the design of HEA. At ambient and cryogenic temperatures, a 3d transition metal derived from a single-based FCC structure exhibits good ductility, high strength, and fracture toughness. At room temperature, the high-strength body-centered-cubic (BCC) AlCoCrFeNi alloy has different structures and characteristics. Transmission and scanning electron microscopy were used to analyze the microstructure of these alloys. With increasing Al content, the crystalline structure changes, and multiple phase structures arise, ranging from a single face-centered cubic (fcc) structure to a duplex fcc plus body-centered cubic (bcc) structure to a single bcc structure. After that, there's a single bcc structure. Arc melting, powder metallurgy, cold rolling, and spark plasma sintering are used to create the alloy's composition.

It was observed that, (Fe-Co-Ni-Cr-Mn) 100_xAlx (x = 0–20 at. %), (Al < 8%) and (Fe-Co-Ni-Cr-Mn) 100_xAlx (x = 0–20 at. %) 8% < Al < 16% alloys yield strength and ultimate tensile strength increases as concentration of aluminum increases. Depending on ductility it shows that, decrease in ultimate strength with an increase in ductility in Al-Co-Cr-$Fe-Ni_{2.1}$ alloy. As compare (Fe-Co-Ni-Cr-Mn) 100_xAlx with $Al_{0.5}$-Co-Cr-Cu-Fe-Ni (FCC + B2 and σ precipitate) and $Al_{0.7}$-Co-Cr-Fe-Ni (FCC + B2) shows that, a sudden increase in yield strength and ultimate tensile strength in Al0.5CoCrCuFeNi composition. And again, a slight decrease in $Al_{0.7}CoCrFeNi$ alloy as we see the decrease in the composition of alloy with an increase in yield strength and ultimate tensile strength. Equimolar $Al_{25}Co_{25}Cr_{25}Fe_{25}$ have highest yield strength than $Al_{+}Cr_{20}Co_{20}Fe_{20}Ni_{20}$. There is insufficient data about the young modulus of this type of HEA (Table 7).[27-32]

Table 7: Comparison of mechanical properties between various alloys of Al-Co-Cr-Fe-Ni

Ref	*Composite & concentration materials*	*Composite preparation technique*	*Youngs Modulus (Gpa)*	*Yield strength (Mpa)*	*Ultimate tensile strength (MPa)*
(27)	(FeCoNiCrMn) 100_xAlx (x = 0–20 at. %), (Al < 8%),	arc-melting	-	~220	~ 500
(27)	(FeCoNiCrMn)100_xAlx (x = 0–20 at. %) 8% < Al < 16%	arc-melting	-	832	1174
(28)	$AlCoCrFeNi_{2.1}$ (ductility 18 ± 2 %.)	a vacuum induction melting furnace	-	-	1100 ± 50 MPa
(28)	$AlCoCrFeNi_{2.1}$ (ductility 15.4%)	a vacuum induction melting furnace	-	-	1351 MPa
(29), (30)	$Al_{0.5}CoCrCuFeNi$ (FCC + B2 and σ precipitates)	Arc-melted, cast annealed, quenched, cold-rolled	225.69	1284	1344
(30)	$Al_{0.7}CoCrFeNi$ (FCC + B2)	Arc-melted, cast annealed, quenched, cold-rolled		780	1040
	$Al_{25}Co_{25}Cr_{25}Fe_{25}$	powder metallurgy, spark plasma sintering		3500	
	$Al_{20}Cr_{20}Co_{20}Fe_{20}Ni_{20}$	powder metallurgy, spark plasma sintering		2400	
	$Al_{10}Co_{30}Cr_{20}Fe_{35}Ni_{5}$	powder metallurgy, spark plasma sintering		1890	

Table 8: Comparison of Tribology properties between various alloys of Al-Co-Cr-Fe-Ni

		Coefficient of friction						*Wear rate (10^-4) mm^3/Nm*					
	Composite and concentration	*As- cast*			*nitrided*			*As-cast*			*nitrided*		
Ref	*Material*	*air*	*water*	*Acid rain*	*air*	*water*	*Acid rain*	*air*	*water*	*Acid rain*	*air*	*water*	*Acid rain*
(33)	AlCoCrFeNi	0.429	0.321	0.302	0.512	0.681	0.213	1.8	1.6	0.7	0.39	0.32	0.28
(34)	$Al_{25}Co_{25}Cr_{25}Fe_{25}$	-						11 ×10−6 (mm^3 /Nm) ± SD 0.3					
(34)	$Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$	-						241 ×10−6 (mm^3 /Nm) ± SD 10					
(34)	$Al_{10}Co_{30}Cr_{20}Fe_{35}Ni_{5}$	-						3.6 ×10−6 (mm^3 /Nm) ± SD 1.1					
(34)	$Al_{15}Co_{30}Cr_{15}Fe_{40}Ni_{5}$	-						0.4 ×10−6 (mm^3 /Nm) ± SD 0.05					

SD: Standard Deviation

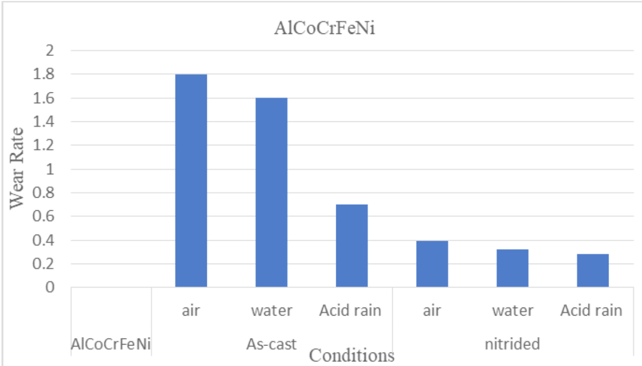

Figure 3: Wear rate of AlCoCrFeNi in different conditions.

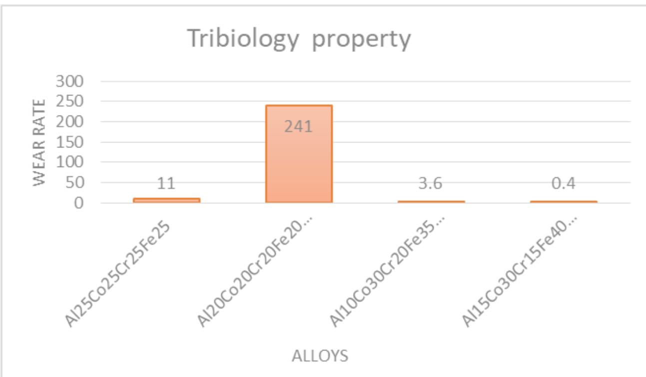

Figure 4: Wear rate of different compositions of Alloys

The plasma nitriding process was used to create a nitrided layer on an AlCoCrFeNi high-entropy alloy. When compared to other alloy compositions. The wear rate of the alloys in deionized water and acid rain was lower than in air, indicating that the lubricating effect of liquid was responsible for the decrease in wear rate and friction coefficient. The friction coefficient of the nitrided alloy in air and deionized water shows higher than that of the as-cast alloy. The tribological characteristics of high entropy alloys with non-equilibrium element concentrations were excellent if compared with equiatomic $Al_{20}Co_{20}Cr_{20}Fe_{20}Ni_{20}$. And, the non-equilibrium alloys show high hardness and less ductility according to wear rate. And according to the literature, the rate of wear is proportional to the alloy hardness (Figures 3 and 4) (Table 8).[33,34]

BIOMEDICAL APPLICATIONS

Metallic alloys are used in the preparation of plates, pins, screws, etc. They possess enough rigidity and strength if provided with enough corrosion resistance. Hence, Titanium-based alloys have the potential to perform closest to the cortical bone. They are mainly used for orthopedic devices such as hip joints, bone screws, knee joints, spinal fusion cages, shoulder and elbow joints, and bone plates and scaffolds. It is inert in the human body and can resist attack by body fluids. It is compatible with bone, strong, and has a low young's modulus, higher fatigue strength; that is why it is an outstanding material for orthopedic implants. Most total hip femoral stem, shoulder arthroplasty stems, intramedullary rods are made of a titanium alloy. When titanium is implanted, it is likely to oxidize. The oxidized titanium coats the implant in a very thin coating of oxidized titanium. This layer has no biological value. Aluminum alloys have a high specific strength, superior casting capabilities, and low cost when compared to Titanium alloys, which are extensively used in bone implants. However, poor wear resistance, corrosion resistance, and insufficient biocompatibility limit their usage in bone replacements.

CONCLUSION

Mechanical properties like Young's modulus, yield strain, and yield stress are measured using a nano-indentation method, where the values change considerably when the composition of the alloy is altered. Especially, Titanium based alloy i.e., Ti-Ta-Zr-Hf-Nb, Ti-Zr-Nb-Ta-Mo, Ti-Zr-Nb-Ta-Fe. Among them, elements like Zr, Nb, Ta have a huge contribution towards corrosion resistance of materials. Equiatomic Ti-Ta-Zr-Hf-Nb alloy with low young modulus 80Gpa, low magnetic susceptibility, yield strength 800-985 Mpa, Ti-Zr-Nb-Ta-Fe it shows low young modulus with high strength but Fe elements having some limitations regarding corrosion resistance. The novel titanium-based alloy shows superior mechanical properties to conventional Titanium alloy. Aluminum-based alloys like Al-Co-Cr-Fe-Ni show better mechanical properties. As the amount of aluminum in the solution increases, the phase shifts from crystalline single FCC to duplex FCC + BCC, and finally to single BCC. However, elements such as aluminum, cobalt, and chromium have limited clinical uses for long-term implant use, and they can cause an immunological response in the human body. As a natural cortical bone, it has a low young modulus and yield strength, which is similar to that of Titanium-based alloys rather than aluminum-based alloys. Finally, as compared to aluminum alloy, the titanium-based alloy has superior mechanical qualities, good biocompatibility, and tribological properties.

DECLARATION OF COMPETING INTEREST

The authors declare that no work in this paper is influenced by any financial interests or personal relationships.

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