Abstract

CoCrMo (ASTM F75) alloys are clinically preferred as articulating surfaces for total joint arthroplasty; such as knee, shoulder, and hip prostheses. The alloy possesses high yield strength, excellent corrosion resistance, and good wear properties. However, patients have been reported to exhibit both local, and systemic toxicity when implanted with Co-Cr based hip prosthesis. Wear debris, accumulated in the periprosthetic tissue induces local toxicity, which results in adverse local tissue reactions (ALTR) such as necrosis, pseudotumor, accompanied by osteolysis, and ultimately, the implant failure. Conversely, in systemic toxicity metal ions leached in blood circulation and interacts with vital organs causing neurological disorders, cardiomyopathy, and hypothyroidism.

Therefore, in this work, two types of high entropy system based on composition TiMoNbTaWCr and TiMoNbZr were fabricated via vacuum arc melting technique for the intended application as articulating surfaces in total joint arthroplasty (TJA) and their mechanical, in-vitro wear, corrosion, and cytocompatibility were studied. Further, with an aim to enhance hardness, yield strength, and wear resistance, equiatomic TiMoNbZr MEA were micro-alloyed with carbon. This work adopts a multi facet approach combining both experimental, and atomistic (molecular dynamics) simulation to strengthen our existing understanding of concentrated bcc alloys, and further develop an insight on the rate limiting mechanism underlying their high yield strength.

We have investigated the dependence of Cr substitution on microstructural evolution, mechanical behaviour, and wear resistance in $(TiMoNbTaW)100_{-x}Cr_x$ (x=0, 5, 10, & 15 at%) based RHEAs. X-ray diffraction revealed single bcc crystal structure where lattice constant decreased upon Cr addition. The Cr addition resulted in a gradual increase in bulk hardness from ~4.9 GPa to ~7.1 GPa, and yield strength from ~1.3 GPa to ~1.9 GPa, attributed to lattice distortion induced misfit strain. Enhanced pitting resistance was seen upon Cr addition,

attributed to the presence of Cr_2O_3 on Cr enriched surface as confirmed by X-Ray photoelectron spectroscopy (XPS) analysis after anodic passivation. Similarly, TiMoNbZr based refractory medium entropy alloys (RMEAs) exhibited high compressive yield stress > 1500 MPa. Enriching Nb in solid solution impedes phase separation during casting yielding single bcc, while its plastic strain increased to more than 11 %. The investigated RMEAs possess low dissolution rate, 0.05-0.1 $\mu A/cm^2$, and exhibits a negative hysteresis loop. Higher polarization resistance (R) confirms RMEAs superior semi-conductive anti-corrosion nature of the passive film ($R_{equiatomic}$>$R_{Nb\ enriched}$> $R_{Ti\ enriched}$ RMEA). Furthermore, the close agreement of simulated yield stress with experimental, strengthens the role of edge dislocation in controlling yield strength in concentrated bcc random alloys. While studying deformation characteristics via molecular dynamics approach, it is inferred that in concentrated random bcc, at pinned regions activation barrier for kinks to propagate in that glide plane, may be even higher. And the activation barrier for a non-conservative movement of edge dislocation via climb in this rugged energy landscape may even be relatively lower at low temperature, and high stress regimes, against the established notion of thermally activated climb process only at high temperatures.

The high hardness in these alloys is attributed to severe lattice distortion, which imparts higher wear resistance. As in case of TiMoNbTaWCrx RHEAs, wear rate (mm^3/Nm) varied proportionally with hardness in order 10^{-5} to 10^{-7}, where Cr addition positively influenced its wear properties. While in TiMoNbZr based RMEAs, wet sliding wear rate were in ranges 7-9e^{-5} mm^3/Nm, where wear resistance followed the order Ti enriched>equiatomic>Nb enriched. In order to enhance tribological properties, carbon was microalloyed in a series of $TiMoNbZrC_x$ (x=0, 0.03, 0.05, & 0.09 wt%) RMEAs. RMEAs exhibited BCC as major phase with cubic carbide phases in C added samples. Increase in C content tend to refine microstructure attributted to Zenner pinning effect, and further enhanced its hardness (from

~610 to 727 Hv) and yield stength (from ~1668 MPa to 1990 MPa). The lean C (0.03 wt%) content enhanced *in-vitro* wear resitance by an order, while higher C addition accompanied an increase in wear rate ascribed to carbide assisted third body abrasion.

In terms of cytocompatibility, cell proliferation increased with increase in Cr content in TiMoNbTaWCrx based RHEAs and showed higher alkaline phosphatase activity (ALP) activity when Cr content was 10 at% or more. Similarly, TiMoNbZr based MEAs showed higher cell attachment, and proliferation attributed to the stable native oxide film that spontaneously forms on its surface, and supports better cell adhesion and growth. Although these results conclude non-cytotoxic nature of native surface on MEAs, these are still inconclusive about the behaviour of wear debris. Wear debris-bone cement mixture was systematically implanted inside rabbit femur for prolonged period of 3 months, and studied for any potential cytotoxicity. Histological analysis at the bone-wear particle interface after 30 days and 90 days of in vivo implantation confirms bone growth, and showed no tissue damage or necrosis, which emphasises bioinert nature of MEAs.

Keywords: High entropy alloys; Total joint arthroplasty; Wear; Corrosion; Molecular dynamics; Biocompatibility