ABSTRACT

The long-term clinical success of ceramic and Co-Cr alloy articulating surfaces in total joint replacement (TJR) is limited by brittleness and metal ion toxicity, motivating the development of alternative materials for bearing surfaces. Refractory high entropy alloys (RHEAs) have recently emerged as promising candidates due to their superior mechanical properties, excellent corrosion resistance, and biocompatibility. However, achieving an RHEA that simultaneously offers high strength, ductility, wear resistance, corrosion resistance, and biocompatibility remains a challenge. Therefore, the present work aims to design and develop RHEAs suitable for TJR surfaces, using a multifaceted approach that integrates experimental characterization with atomistic simulations. Guided by atomic-scale design principles, the TiTaNbZrMo system was selected, and the Ti/Ta ratio was systematically tuned to improve mechanical performance, corrosion resistance, and biocompatibility.

As a proof-of-concept, the effects of partial substitution of Ta with Ti in a series of $Ti_xTa_{2-x}NbZrMo$ (x = 0.25, 0.5, 0.75, 1) RHEAs on phase stability and mechanical properties were investigated through density functional theory (DFT), CALPHAD calculations, and experimental characterization. DFT predicts that the present alloys stabilize a BCC structure, with enthalpy of formation calculations indicating enhanced phase stability with increasing Ta content. CALPHAD predictions and experimental observations confirm the coexistence of BCC1 and BCC2 phases, with Ta enrichment increasing the stability and volume fraction of the BCC1 phase. Ta-rich alloys exhibit coarser microstructures with Ta segregation in BCC1 and Zr segregation in BCC2, accompanied by increased lattice parameters. Theoretical predictions of elastic modulus and hardness show excellent agreement with experimental results, with errors within 15%. Experimentally, Vickers hardness and elastic modulus increase by 22% and 10%, respectively, from equiatomic to Ta-rich compositions. Electronic structure analyses based on density of states and crystal orbital Hamilton population (COHP) reveal that enhanced mechanical properties originate from stronger directional metallic bonding and a higher fraction of occupied bonding states with increasing Ta content.

The preliminary study on the $Ti_xTa_{2-x}NbZrMo$ RHEAs reveals that the Ta-rich alloy exhibits good phase stability and enhanced mechanical properties compared with the equiatomic RHEA. However, the correlation between the observed mechanical properties and the underlying micromechanical deformation mechanisms remains unclear. Therefore, in a subsequent study, the deformation behaviour and strengthening mechanisms of the BCC phases in TiTaNbZrMo (Ta_1) and $Ti_5Ta_{35}Nb_{20}Zr_{20}Mo_{20}$ ($Ta_{1.75}$) RHEAs were investigated using nanoindentation experiments and molecular dynamics (MD) simulations. A fitted embedded atom method interatomic potential was first validated for the constituent BCC phases of the RHEAs. Both experiments and simulations reveal that $Ta_{1.75}$ exhibits higher hardness (14%) and elastic modulus (10%) than Ta_1. MD simulations indicate that increased lattice distortion in $Ta_{1.75}$ suppresses atomic migration and increases kink density, thereby hindering dislocation nucleation and mobility. During indentation, dislocation loop interactions lead to the formation of a sessile dislocation, which further contributes to hardening in $Ta_{1.75}$. ICOHP analysis confirms that increased Ta content enhances bonding states, raising the barrier for dislocation nucleation and propagation. Moreover, during unloading, $Ta_{1.75}$ exhibits little relaxation of the dislocation network, a smaller plastic zone, and a higher density of sessile dislocations. These features reflect reduced dislocation mobility in $Ta_{1.75}$ compared with Ta_1, resulting in increased hardness.

Further, to capture bulk mechanical behaviour beyond localized deformation, the compressive response of $Ti_xTa_{2-x}NbZrMo$ (x = 0.25, 0.5, 0.75, and 1) RHEAs was evaluated experimentally, and correlated with DFT and MD simulations. Compression tests reveal that increasing Ta content significantly enhances both the compressive yield strength (28%) and plastic strain (36%). DFT analysis attributes these improvements to modulus misfit-induced lattice distortion and a higher fraction of occupied bonding states. MD atomistic simulations further demonstrate that sessile dislocations and dislocation loop formation during compression synergistically contribute to enhanced strength and ductility, highlighting the ability of Ta-rich RHEAs to overcome the conventional strength-ductility trade-off.

The suitability of the developed alloys for TJR applications was further assessed through tribological, corrosion, and biocompatibility studies. Wet tribological tests in Hank's balanced salt solution reveal a tenfold reduction in wear and friction with increasing Ta content, attributed to the formation of a softer and lubricious Ta_2O_5-rich surface layer that suppresses adhesive and abrasion wear. *In vitro* corrosion studies show a 77% reduction in corrosion rate with Ta enrichment, resulting from the formation of a stable passive film. Electrochemical impedance spectroscopy and Mott-Schottky analyses demonstrate a significant increase in polarization resistance (67%) and a decrease in defect density (64%), due to enrichment of Ta_2O_5 in the surface film, consistent with XPS analysis. *In vitro* studies using MC3T3 cells reveal enhanced cell proliferation, osteogenic differentiation, and viability with higher Ta fractions, indicating good cytocompatibility. Moreover, *in vivo* evaluation using a rabbit femur model shows no evidence of tissue necrosis around the implants, while improved osseointegration and new bone formation are confirmed through histological and fluorochrome labeling analyses.

Overall, this comprehensive study demonstrates that the Ta-rich $Ti_5Ta_{35}Nb_{20}Zr_{20}Mo_{20}$ RHEA exhibits a combination of high hardness, elastic modulus, strength, and ductility, along with superior wear and corrosion resistance and excellent biocompatibility. These attributes effectively address the limitations of conventional articulating surfaces, positioning $Ta_{1.75}$ alloy as a promising candidate for next-generation TJR applications.

Keywords: Orthopedic implants; Refractory high entropy alloys; Atomistic simulations; Mechanical behaviour; Wear and corrosion; Biocompatibility