PREFACE

The present work deals with the alloy design, microstructure, mechanical behaviour, wear and corrosion, and biocompatibility of refractory metal based complex concentrated alloys (CCAs) for biomedical applications. The work embodied in this thesis is divided into nine chapters, followed by the scope of future work, references and list of publications.

Chapter 1 (Introduction) provides the background and motivation of the present work, describing the historical development of alloys and traditional biomaterials, as well as the advent of high entropy alloys (HEAs) or complex concentrated alloys. The possibility and necessity of research in the area of developing novel biomaterials such as new complex concentrated alloys is also discussed.

Chapter 2 (Literature Review) contains a comprehensive literature survey of high entropy alloys, particularly refractory HEAs and the state of the art with regard to development of refractory HEAs targeting biomedical applications. Through this detailed literature review, the research gaps or areas providing further scope for investigation are identified and summarized before formulating the objectives of the present work.

Chapter 3 (Experimental Procedure) concisely explains all the experimental methodology used to perform the various alloy fabrication and characterization. This includes the details of vacuum arc melting technique used to develop the alloys, and the various characterization such as optical microscopy, scanning and transmission electron microscopy (SEM and TEM, respectively), X-ray diffraction (XRD) for microstructural analysis; hardness and instrumented microindentation for mechanical response; potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) for

corrosion behaviour; wear testing and tribological behaviour; and MTT assay and confocal microscopy for in-vitro biocompatibility (cytocompatibility) behaviour.

Chapter 4 is the first results chapter which discusses the alloy design, microstructural, mechanical and corrosion behaviour of Ti-Nb-Mo-Fe-Cr based CCAs. Initially, ThermoCalc software was used to perform CALPHAD based modelling to design a number of Ti-Nb-Mo-Fe-Cr based compositions. Starting from both equiatomic and various non-equiatomic compositions, a $Ti_{10}Nb_{30}Mo_{20}Fe_{20}Cr_{20}$ alloy was selected for experimental development based on the predicted microstructural phases in the phase diagram.

The aforementioned alloy was fabricated by vacuum arc melting technique. The observed density and lattice parameters of the as-cast alloy are 7.821 g/cm^3 and 3.179 ± 0.003 Å, respectively, which were in line with the theoretical values obtained by the rule of mixture. The phase evolution, chemical composition, and microstructure in the as-cast condition, as well as after annealing treatment at 800ºC, 1000ºC, and 1200ºC, were investigated through XRD, TEM, and SEM-EDS. The XRD and TEM analyses confirmed the presence of BCC structure with minor amount of $TiCr_2$ type and $NbCr_2$ type C14 Laves phases. Instrumented micro-indentation and corrosion testing were performed in the as-cast and annealed specimens. The microhardness of the as-cast alloy was 825 HV and it increased to 1102 HV after annealing at 1200ºC for 20 h. This peak hardness was achieved after annealing at 1200ºC due to the presence of a large volume fraction of Laves phase. Potentiodynamic polarization tests of the as-cast and annealed specimens revealed outstanding corrosion resistance of the CCA compared to 316L stainless steel. This is attributed to better microstructural homogeneity and reduced elemental segregation after annealing.

Thus, in this chapter, we were able to develop an alloy with low density, high strength and good corrosion resistance. However, the elastic modulus of the alloy was quite high for

biomedical application. Therefore, it was concluded that the composition of the alloy needs further tuning.

Chapter 5 discusses the design, development and characterization (microstructure, mechanical and tribological behaviour) of a new $Ti_{35}Zr_{35}Nb_{15}Mo_5Fe_5Cr_5$ CCA. Once again, the alloy was designed by ThermoCalc and experimentally fabricated by vacuum arc melting. Subsequently, its microstructural evolution, mechanical properties, and wear behavior were systematically evaluated. The alloy has an experimentally measured density of 6.37 g/cm^3, suitable to fulfill the requirement of light weight. XRD analysis revealed that the as-cast and annealed specimens contain two BCC solid solution phases and a $TiCr_2$ type Laves phase. The average microhardness (H) and elastic modulus (E) of the as-cast CCA are 618.39 ± 9.26 HV and 97.32 ± 3.58 GPa, respectively. Moreover, the yield strength (YS) of the as-cast alloy, estimated from elastoplastic analysis of the microindentation data, is 1203.94 ± 30.28 MPa. However, the CCA annealed at 1100˚C exhibits a microhardness of 833.08 ± 7.58 HV and a YS of 1669.65 ± 24.79 MPa, with the elastoplastic stress-strain response revealing no significant loss of plasticity due to the increased hard Laves phase. The specific wear rate (SWR) of the as-cast CCA is 1.53×10^{-7} mm^3/N.mm at 30 min sliding time and 10 N applied load. After annealing treatment, the SWR of the CCA is significantly decreases (7.27×10^{-8} mm^3/N.mm), this enhancement of the wear resistance is due to increased hardness after annealing treatment.

Chapter 6 discusses the corrosion and biocompatibility behaviour of the novel $Ti_{35}Zr_{35}Nb_{15}Mo_5Fe_5Cr_5$ CCA described in Chapter 5. Corrosion test was conducted in a simulated body fluid (SBF) solution, and the corrosion resistance of the as-cast and annealed $Ti_{35}Zr_{35}Nb_{15}Mo_5Fe_5Cr_5$ CCA was found to be superior compared to CP-Ti and 316L SS. Also, the corrosion resistance increased with increasing annealing temperature due to better

microstructural homogeneity. The SEM corroded surface morphology showed that the as-cast CCA exhibited fewer pits, while the CCA annealed at 1100˚C showed almost no corrosion pits. This indicates that the CCA annealed at 1100˚C possesses a very strong passive film, which prevents the release of metallic ions. The in-vitro cell culture experiments (MTT assay, AO/EtBr staining, Rh-123 staining, and DCFH-DA staining) revealed that both the as-cast and 1100˚C annealed CCA demonstrated good cell adhesion and proliferation along with high cell viability. These findings indicate that the CCA has significant potential for biomedical applications.

Chapter 7 attempts to delve into the underlying mechanisms of the observed biocompatibility response of the $Ti_{35}Zr_{35}Nb_{15}Mo_5Fe_5Cr_5$ CCA. In this chapter, the crystallographic texture dependence of the biocompatibility of the aforementioned novel $Ti_{35}Zr_{35}Nb_{15}Mo_5Fe_5Cr_5$ CCA in the as-cast and annealed states was investigated. In-vitro cell culture experiments using MG-63 cells demonstrated that the cell viability and proliferation of the annealed CCA were superior compared to the as-cast CCA. SEM images also showed higher cell adhesion (higher number density of adhered cells) on the annealed CCA sample. EBSD and X-ray texture measurements were performed to obtain the micro- and macro-texture evolution, respectively, in order to unravel the effect of crystallographic texture on the biocompatibility behavior of the as-cast and annealed CCA samples. The higher biocompatibility in the annealed specimen is related to texture evolution during annealing. While standard texture components were not distinctly observed in the as-cast specimen except some rotated Cube component, the annealed specimen showed the presence of γ-fiber, ε-fiber and Brass components in addition to Cube component. The cell adhesion is sensitive to texture, with a greater number of cells attaching to grains that are crystallographically oriented with their <111> normal to the surface exposed to the cells. This preferential cell

attachment along <111> accounts for the enhanced biocompatibility of the annealed CCA specimen as compared to the as-cast specimen.

Chapter 8 is the final results chapter that discusses the application of high pressure torsion deformation to reduce the elastic modulus of the $Ti_{35}Zr_{35}Nb_{15}Mo_5Fe_5Cr_5$ CCA to make it further bone compatible. In this chapter, the biocompatible $Ti_{35}Zr_{35}Nb_{15}Mo_5Fe_5Cr_5$ CCA is subjected to severe plastic deformation through high-pressure torsion (HPT) at 1, 3, 5, and 7 turns. The effect of HPT on microstructure, mechanical response, corrosion behaviour, and cytotoxicity was thoroughly investigated. XRD analysis shows two BCC solid solution phases along with a C14 type Laves phase in all the specimens of the HPT deformed alloy. Also, as the number of HPT turns increases, the crystallite site decreases (from 25.74 to 8.29 nm). Correspondingly, the lattice strain increase from 4.36×10^{-3} to 10.32×10^{-3} and the dislocation density increases from 3.21×10^{15} /m^2 to 17.50×10^{15} /m^2. TEM analysis additionally reveals an ordered FCC phase along the $[\bar{2}33]$ zone axis, which was not detected by XRD. The hardness of the CCA increases with increasing number of HPT turns (with variation from center to periphery also) while the elastic modulus decreases from 97.32 ± 3.58 GPa to 68.37 ± 5.16 GPa. Potentiodynamic polarization and EIS experiments indicate improved corrosion resistance after HPT, attributed to a more homogeneous microstructure and the presence of nano-grains, which act as nucleation sites for oxide film formation. HPT deformation also enhances the biocompatibility of the alloy, including cell viability and proliferation. Confocal microscopy images of MG-63 cells stained with AO/EtBr, Rh-123, and DCFH-DA confirmed that the HPT-deformed CCA exhibits better biocompatibility compared to the as-cast CCA. In summary, HPT significantly enhances the hardness, reduces the elastic modulus, improves corrosion resistance, and enhances cytocompatibility,

demonstrating the considerable potential of the HPT processed CCA for biomedical applications.

Chapter 9 (Conclusions) illustrates the overall goals achieved through the research work embodied in the thesis, besides providing a point-wise summary of the significant conclusions of the overall work.

The scope of future work is also briefly discussed after the Conclusions chapter, followed by references and list of publications.