Mechanical properties of bio-resorbable and non-resorbable bulk metallic glasses

Shangmou Yang^{1a}, Paul. P. Conway¹ and Carmen Torres-Sanchez¹

¹Multifunctional Materials Manufacturing Laboratory, Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough LE11 3TU, UK

as.yang@lboro.ac.uk

Abstract. In this study, cylindrical samples of Ca-Mg-Zn and Ti-Zr-Cu-Pd bulk metallic glasses (BMGs) were manufactured by induction melting and arc melting, respectively, followed by copper mould casting. The mechanical properties including compressive strength, Young's modulus, plasticity and hardness of these alloys were systematically evaluated.

Introduction

Bulk metallic glasses (BMGs) show potential as biomedical materials because they exhibit superior mechanical properties and good corrosion resistance due to their unique long-range disordered atomic structure and the absence of lattice defects [1]. Among a wide range of amorphous alloy systems, extensive efforts have been devoted to the investigation of Ca, Mg and Zn-containing BMGs because when they get reabsorbed, a retrieval surgery is not needed [2]. However, one major drawback of existing Ca-rich BMGs is that their corrosion rate in a physiological environment is still too fast to be tolerated by the human body due to the high bio-reactivity of their elements. A rapid corrosion rate generates drastic changes in pH and evolution of H₂ gas which causes cellular decay and death. In this context, many efforts have focused on the development of new Ti-based BMGs with good biocompatibility and high corrosion resistance in biological environment [3]. Without any potentially cytotoxic elements such as Al, Ni or Be, Ti-Zr-Cu-Pd BMGs are considered as promising candidates in orthopaedics, which can eliminate the risk of allergic or chronic inflammatory reactions due to toxic ions or wear debris that are released into the human body when utilised for permanent medical implants. However, the high cost of noble elements (e.g., Zr and Pd) have driven research efforts to develop BMGs with reduced noble metal content without compromising their desirable properties. This study introduces a novel composition of Ti₄₂Zr₈Cu₄₀Pd₁₀ BMG with a reduced concentration of noble elements compared to the most commonly studied composition (i.e., Ti₄₀Zr₁₀Cu₃₈Pd₁₂, at.%). The raw materials cost of the new designed BMG is significantly reduced by 14%. The mechanical properties, including yield strength, Young's modulus, plasticity and hardness of bioresorbable Ca62.49Mg18.19Zn19.32 and non-bioresorbable Ti-Zr-Cu-Pd BMGs, were systematically investigated.

Materials and Methods

Ca-Mg-Zn samples were manufactured by induction melting high purity elements (>99.9%) of Ca, Mg and Zn followed by copper mould casting under Ar atmosphere using a REITEL INDURET induction casting unit at IFW Dresden, Institute for Complex Materials, Germany. Ti-Zr-Cu-Pd alloys were prepared by arc melting the mixture of pure elements (purity≥99.9%, ThermoFisher Scientific, UK) under a Zr-gettered Ar atmosphere followed by vacuum die casting in a water-cooled copper mould (MAM-1 Edmund Bühler Compact Arc Melter, Germany). Pure Ti samples were prepared and used as control for comparison purposes. The diameter of all samples is 3 mm. Uniaxial quasi-static compression testing was conducted with a 3369 universal testing machine (Instron, Mass, USA) equipped with a load cell of 5kN for Ca-Mg-Zn BMG and 50 kN for Ti alloys, in line with ASTM E9 standard [4]. The cylindrical samples with aspect ratio of 2:1 were carefully polished to ensure that both top and bottom surfaces were flat and perpendicular to the compressive axis. A LVDT extensometer (2601, Instron, USA) was mounted axially to measure the strain accurately and maintain a constant strain rate of 10⁻⁴ s⁻¹. Young's modulus was calculated from the slope of the elastic region when plotting stress vs strain. Microhardness tests were performed on a Vickers Hardness tester (Zwick/Roell, Germany). A pyramid-shaped diamond indenter (Φ: 10 mm) with face angles of 136° was applied to the sample under a load of 300 gf (HV0.3) and a holding time of 10 s. All the tests were assessed in triplicate to confirm the reproducibility.

Results

Fig. 1 shows the compressive stress-strain curves of the as-cast Ca-Mg-Zn BMG, pure Ti loaded until yield and Ti-Zr-Cu-Pd BMGs loaded until fracture. The amorphous Ca-rich alloys were shattered progressively from free surfaces, which eventually exploded into numerous small pieces. It displays a compressive strength (σ) of 102.1 MPa and a relatively low Young's modulus (E) of 23.0 GPa. The value of stiffness is comparable to that of human bones (10-30 GPa), which is useful to minimize the stress shielding effect. The two Ti-Zr-Cu-Pd BMGs exhibit similar bulk properties under compression, including high yield strength of ~2000 MPa and Young's moduli of ~77 GPa, superior to those of pure Ti, making them as promising candidates for load-bearing biomaterials (Table 1). The plastic strain of Ti₄₀Zr₁₀Cu₃₈Pd₁₂ BMG (2.7%) is larger than that of Ti₄₂Zr₈Cu₄₀Pd₁₀ alloy (1.1%). The plastic deformation of BMGs is mainly dominated by the

initiation and rapid propagation of shear bands because of their lattice order-free amorphous structure. The serrated deformation indicates that abundant shear bands are activated during plastic flow. The Ti₄₂Zr₈Cu₄₀Pd₁₀ BMG exhibits a slightly higher Vickers microhardness than Ti₄₀Zr₁₀Cu₃₈Pd₁₂ BMG, more than twice as hard as pure Ti. This can be attributed to a denser atomic packing of Ti₄₂Zr₈Cu₄₀Pd₁₀ alloy.

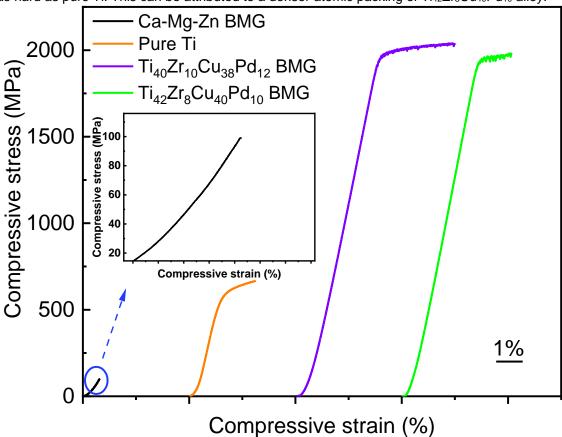


Fig. 1. Compressive stress-strain curves of the as-cast Ca-Mg-Zn, pure Ti and Ti-Zr-Cu-Pd BMGs.

Table 1: The mechanical properties of bioresorbable and non-bioresorbable BMGs.

	Yield strength [MPa]	Plastic strain [%]	Young's modulus [GPa]	Hardness [HV0.2]
Ca-Mg-Zn BMG	102.1 ± 2.9	-	23.0 ± 3.2	170.0 ± 6.2
Pure Ti	600 ± 26	-	67.5 ± 1.1	253.3 ± 3.1
Ti ₄₀ Zr ₁₀ Cu ₃₈ Pd ₁₂	1962 ± 21	2.7	77.7 ± 1.0	629.7 ± 1.9
Ti ₄₂ Zr ₈ Cu ₄₀ Pd ₁₀	1975 ± 8	1.1	77.2 ± 1.5	658.0 ± 3.3

Conclusion

This study summarised the results of compression testing and Vickers hardness measurements for bioresorbable Ca-Mg-Zn and non-bioresorbable Ti-Zr-Cu-Pd BMGs. Additionally, the effects of alloy composition on the mechanical properties of Ti-based BMGs were investigated. The outcomes of this study could pave the way for high-performance and cost-effective BMGs in biomedical applications.

Acknowledgement

This work was supported by Alloyed Ltd, Wolfson School Bursaries and EPSRC (EP/V007335/1). The authors are grateful to Prof. Julia Hufenbach from IFW for the Ca-Mg-Zn sample preparation.

References

- [1] Ida, H., Seiryu, M., Takeshita, N., Iwasaki, M., Yokoyama, Y., Tsutsumi, Y., Ikeda, E., Sasaki, S., Miyashita, S., Sasaki, S. and Fukunaga, T., 2018. Biosafety, stability, and osteogenic activity of novel implants made of Zr70Ni16Cu6Al8 bulk metallic glass for biomedical application. *Acta biomaterialia*, 74, pp.505-517.
- [2] Wang, Y.B., Xie, X.H., Li, H.F., Wang, X.L., Zhao, M.Z., Zhang, E.W., Bai, Y.J., Zheng, Y.F. and Qin, L., 2011. Biodegradable CaMgZn bulk metallic glass for potential skeletal application. *Acta biomaterialia*, 7(8), pp.3196-3208.
- [3] Lin, B., Yang, K., Bao, X., Liu, J., Guo, Q., Zhang, L., Wang, Q. and Hua, N., 2022. Enhanced wear, corrosion, and corrosive-wear resistance of the biocompatible Ti-based bulk metallic glass by oxidation treatment. *Journal of Non-Crystalline Solids*, *576*, p.121231.
- [4] Standard, A.S.T.M., 2019. E9-09 (1995) Standard test methods of compression testing of metallic materials at room temperature. ASTM International, West Conshohocken.