ELECTROCHEMICAL BEHAVIOR AS AN INDICATOR OF FUNCTIONAL PERFORMANCE CONTROL IN BULK METALLIC GLASSES

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Ti-Cu-(Pd) bulk metallic glasses (BMGs) offer high strength-to-stiffness ratios, but their biocompatibility is compromised by their high copper content, which affects cytocompatibility and corrosion resistance. Two BMGs, $Ti_{47}Zr_{7.5}Cu_{38}Fe_{2.5}Sn_2Si_1Ag_2$ and $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$, were studied in a phosphate buffer solution (PBS, pH 7.4, 37 °C) in free corrosion and anodic polarisation conditions. The first alloy exhibited poor passive film stability and pit repassivation ability, whereas the second alloy demonstrated higher pitting resistance with corrosion products enriched in Cu, Zr, and Pd. To improve biocompatibility, both alloys underwent a pseudo-dealloying process to create nanoporous Ti/Zr oxide layers. This treatment suppressed chloride-induced pitting, achieving corrosion resistance comparable to that of cp-Ti and rendering the alloy promising for use in implants.

Keywords: Ti-based metallic glasses, biocompatibility, pitting corrosion, nanoporous oxide layers

Introduction. Ti-based BMGs offer superior mechanical properties (E = 80–100 GPa, σ_{max} = 1680–2640 MPa) compared to conventional Ti alloys, making them promise for biomedical implants. However, their high Cu content, essential for glass-forming ability, raises biocompatibility concerns due to cytotoxicity and susceptibility to chloride-induced pitting corrosion. Two key alloys – $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ and $Ti_{47}Zr_{7.5}Cu_{38}Fe_{2.5}Sn_2Si_1Ag_2$ – were studied in simulated body fluid. Surface treatments like electrochemical "pseudo-dealloying" in HNO_3 create nanoporous Ti/Zr-oxide layers, improving corrosion resistance. Pd enhances passivation, while Cu accelerates localized degradation. These findings guide alloy design and surface modification strategies for implant applications [1].

Materials and Methods. $Ti_{47}Zr_{7.5}Cu_{38}Fe_{2.5}Sn_2Si_1Ag_2$ and $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy ribbons were prepared via melt-spinning (Ar atmosphere, 41 m/s Cu wheel) and characterized by XRD/DSC. Electrochemical surface treatment in 5 M HNO_3 (60°C, 1 V/60 min) induced pseudo-dealloying, forming nanoporous Ti/Zr-oxide layers. Corrosion behaviour was tested in PBS via OCP, LVA, and EIS. The Pd-containing alloy showed higher pitting resistance, while Cu-rich surfaces required modification for biomedical use. SEM/EDX/XPS revealed Cu depletion and oxide formation post-treatment, improving corrosion resistance [2,3].

Results and Discussion. $Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2$ and $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ glassy alloys were studied in PBS (Fig. 1). OCP measurements revealed metastable pitting in Cu-rich $Ti_{47}Zr_{7.5}Cu_{38}Fe_{2.5}Sn_2Si_1Ag_2$, while Pd-containing $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ showed higher stability [1]. Potentiodynamic tests confirmed early pitting in $Ti_{47}Zr_{7.5}Cu_{38}Fe_{2.5}Sn_2Si_1Ag_2$ (E_{pit} = −0.054 V) versus delayed pitting in $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Sn_2$ (E_{pit} = 0.462 V). SEM/EDX revealed Cu-enriched corrosion products and nanoligament formation. Electrochemical “pseudo-dealloying” in 5 M HNO_3 (60°C, 1 V/60 min) created nanoporous Ti/Zr-oxide layers, suppressing pitting in $Ti_{47}Zr_{7.5}Cu_{38}Fe_{2.5}Sn_2Si_1Ag_2$ but not in Pd-rich alloys due to inhomogeneous oxide growth. EIS indicated thicker passive films (16 nm vs. 8 nm) on $Ti_{47}Zr_{7.5}Cu_{38}Fe_{2.5}Sn_2Si_1Ag_2$ post-treatment. These findings highlight Cu's role in corrosion and Pd's stabilizing effect, guiding surface modification strategies for biomedical applications [2,3]. This work was funded by the DFG (projects no. 458057521 and the DFG Mercator Fellowship (V. Shtefan).

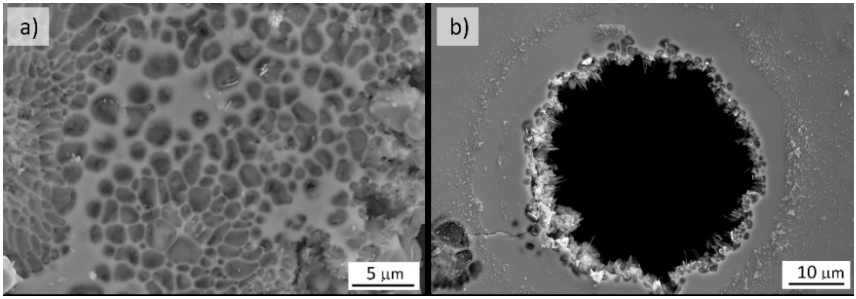

Fig. 1. SEM images showing characteristic morphologies of pits generated at the $Ti_{47}Cu_{38}Zr_{7.5}Fe_{2.5}Sn_2Si_1Ag_2$ alloy surface (a) after potentiodynamic polarisation and (b) after galvanostatic polarisation in PBS solution at 1 μA/cm^2.

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