Biocorrosion Evaluation on a Zr-Cu-Ag-Ti Metallic Glass

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Abstract. Metallic glasses are in high demand for fabrication of variety of innovative products, in particular surgical and biomedical tools and devices owing to its excellent biocompatible properties. In the present investigation, a novel Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆ metallic glass composition was synthesized using melt spinning technique. Potentiodynamic polarization studies were conducted to investigate bio-corrosion behaviour of Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆ metallic glass. The test were conducted in various simulated artificial body conditions such as artificial saliva solution, phosphate-buffered saline solution, artificial blood plasma solution, and Hank’s balanced saline solution. The bio-corrosion results of metallic glass were compared with traditional biomaterials. The study aims to provide bio-compatible properties of Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆ metallic glass.

1. Introduction

Amorphous nature in metallic glasses gives rise to noteworthy mix of physical and chemical properties, for example, high hardness, high yield strength, excellent corrosion and wear protection. Metallic glasses display low elastic modulus, which represses the shielding effect, is alluring for bio-embed applications.¹⁻³ The chemical and structural homogeneity in bulk metallic glasses of a single phase likewise support biocompatibility. These properties are promising qualities for bio-embeds, particularly for stack bearing applications. Therefore, extensive examinations on biological property assessment of bulk metallic glasses, particularly on Zr-based frameworks are being carried out.⁴⁻⁵ Additionaly, bulk metallic glasses have a high strength-to-weight proportion which in this way result in smaller implants and in this way limit the impact of foreign body response.⁶⁻⁸ Ni and Be are known to be cytotoxic and carcinogenic in natural solutions.⁹ the presence of such components in metallic glasses may diminish the biocompatibility. Consequently, there is more emphasis laid out on a blend of metallic glass that were free from such cytotoxic components. Similarly, a progression of Ni-and Be-free, Zr-based and Mg-based smooth BMG’s were created and considered for biocompatibility tests.¹⁰⁻¹² Liu and coworkers¹³⁻¹⁸ built up an arrangement of Ni-free lustrous compounds, for example, Zr-Nb-Cu-Pd-Al, Zr-TiCu-Fe-Al, Zr-Nb-Cu-Fe-Al, and Zr-Co-Al-Ag to think about their biocorrosion properties and cytotoxic impacts. These Zr-based polished alloys¹³⁻¹⁸ are accounted for to display excellent protection towards Biocorrosion in artificial body solutions in correlation with conventional bio-embed materials, for example, 316L stainless steel and Ti-6Al-4V compounds. After much consideration, we have set out on the union of lustrous compound free from such cytotoxic components which are natural constituents in many bulk metallic glasses.

In the present examination, a unique metallic glass synthesis Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆ is created. The biocorrosion assessment of liquefying spun Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆ is completed in different artificially prepared body liquids, and it is contrasted. It is imperative to decide biocompatibility of
Zr$_{39.5}$Cu$_{50.5}$Ag$_{4}$Ti$_{6}$ as the use of bulk metallic glasses (BMG’s) as biocompatible material is vastly increasing and henceforth an endeavor has been made in the present research work. The present research work aims to provide a thorough and detailed study on corrosion resistance in artificial body fluids of the Zr$_{39.5}$Cu$_{50.5}$Ag$_{4}$Ti$_{6}$ metallic glass.

2. Experimental

Alloy ingots with chemical composition Zr$_{39.5}$Cu$_{50.5}$Ag$_{4}$Ti$_{6}$ glassy alloy (at. pct). Are prepared by arc-melting pure mixtures of Zr, Cu, Ag, and Ti (>99.9 wt pct) in a Ti-gettered argon atmosphere. Alloy ingots were re-melted several times to ensure homogeneity. Zr$_{39.5}$Cu$_{50.5}$Ag$_{4}$Ti$_{6}$ rapidly solidified glassy ribbon samples with cross-sections (thickness nine widths) of 0.04x1.07 mm, were produced by melt spinning under argon flow on a Cu wheel with a moderate wheel speed of 20 m/s. X-ray diffraction (XRD) was performed using a PANalytical X’pert-Pro diffractometer with Cu-Ka (k = 0.154 nm) radiation on solid flat melt-spun ribbon surface.

The behaviour of Zr$_{39.5}$Cu$_{50.5}$Ag$_{4}$Ti$_{6}$ glassy ribbons tests is conducted in different physiologically and biologically significant conditions by electrochemical polarization tests utilizing a VersaSTAT three potentialstat. This test was performed in a three-anode cell setup utilizing an immersed calomel reference terminal (SCE) (USCE = 241 mV) and platinum gage counter anode. Preceding electrochemical estimations, the examples were ultrasonically degreased with (CH$_3$)$_2$CO, flushed with distilled water, and dried with pulsed air. Tests were led in three artificially created body liquid (SBF) conditions, in particular, artificial blood plasma solution (ABP), artificial saliva solution (ASS), phosphate-buffered saline solution (PBS) at a constant temperature maintained at 310.15 K (37 °C). The material composition of which are recorded in Table I.

### Table I. Compositions (g/L) of Artificial Saliva Solution, Phosphate-Buffered Saline Solution, Artificial Blood Plasma Solution.

| Composition (g/L) | Artificial Saliva Solution (ASS) | Phosphate-Buffered Saline Solution (PBS) | Artificial Blood Plasma Solution (ABP) |
|------------------|---------------------------------|----------------------------------------|-----------------------------------------|
| NaCl             | 1.5                             | 8.0                                    | 8.036                                   |
| NaHCO$_3$        | 1.5                             | —                                      | 0.352                                   |
| Na$_2$HPO$_4$    | 0.5                             | 1.15                                   | —                                       |
| KCl              | —                               | 0.2                                    | 0.225                                   |
| KSCN             | 0.5                             | —                                      | —                                       |
| KH$_2$PO$_4$     | —                               | 0.2                                    | —                                       |
| Lactic Acid      | 0.9                             | —                                      | —                                       |
| Na$_2$HPO$_4$.3$H_2$O | —                   | —                                      | 0.238                                   |
| MgCl$_2$.6$H_2$O | —                               | —                                      | 0.311                                   |
| CaCl$_2$         | —                               | —                                      | 0.293                                   |
| Na$_2$SO$_4$     | —                               | —                                      | 0.072                                   |
| CaCl$_2$.2$H_2$O | —                               | —                                      | —                                       |
| MgSO$_4$.7$H_2$O | —                               | —                                      | —                                       |
| Na$_2$HPO$_4$.7$H_2$O | —                   | —                                      | —                                       |
| Glucose          | —                               | —                                      | —                                       |
All electrolytes were set up from analytical grade reagent chemicals utilizing distilled water. Potentiodynamic polarization tests were performed at a scan rate of 0.167 mV/s. The working cathode (WE) was presented just to a zone of 1 cm², while whatever is left of the example was implanted in a thermoplastic gum to provide electrical disengagement. The WE submerged in test arrangements was permitted to achieve a steady open circuit potential (~60 min). About 500mL of each artificial body liquids was created at the site and was utilized for each potentiodynamic polarization test. The polarization graphs were measured no less than three times to affirm reproducibility of the information. Polarization resistance of the material was calculated using the ratio of the applied and resulting current response which is a useful technique that enables the estimation of a corrosion rate under steady state conditions using Tafel extrapolations\(^{19}\)

3. Results And Discussion

![Fig. 1](image1.jpg)

**Fig. 1**

XRD pattern of Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆

Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆ bulk metallic glass was prepared by a melt-spinning technique to have been characterized by the XRD as shown in Figures 1, respectively. The presence of a broad diffused diffraction hump and the absence of various sharp crystalline peaks in both the XRD pattern confirm the noncrystalline, i.e., amorphous structure of Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆ bulk metallic glass.

![Fig. 2](image2.jpg)

**Fig. 2**

Potentiodynamic polarization graphs of Zr₃₉.₅Cu₅₀.₅Ag₄Ti₆
The corrosion conduct of liquefy spun Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ BMG in various artificial body liquids is examined utilizing potentiodynamic polarization tests. Tafel extrapolation of polarization bends is used to decide corrosion current density ($i_{corr}$) and consumption potential ($E_{corr}$) values. (Figure 2) Demonstrates the polarization bends for Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass. The polarization curve for Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ test indicates passive conduct in which the metallic glass oppose any further active disintegration process. The estimations of $i_{corr}$ and $E_{corr}$ for Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass were resolved from Figure 2 and appeared in Table II.

In ASS media Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ composite is appeared to show a very low $i_{corr}$ esteem (0.9232E-6A/cm$^2$) and $E_{corr}$ esteem (-0.186) in the examination and a polarization resistance of (59.247kΩ) demonstrating a high resistance of the material towards ASS solution which is highly desirable. These findings propose extremely high corrosion protection of Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass with the corrosion rate in the order of E-5 which is a very important characteristic possessed by metallic glasses further it even shows a high polarization resistance of the order of E6. In ASS media, the $E_{corr}$ values of Co-Cr, AISI 304 and Low-Cu Amalgam are -0.40, -0.385, -0.505 V respectively [20] which shows that Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass shows a high stability which is highly important for a given biomaterial.

Table II. The Corrosion Potential ($E_{corr}$), Polarization Resistance(kΩ), Corrosion Current Density ($i_{corr}$) and Corrosion rate for Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ Glassy Alloy in Different Simulated Body Fluids

| Type of Solution | $i_{corr}$ (µA/cm$^2$) | Polarization resistance(kΩ) | $E_{corr}$(V vs. SCE) | Corrosion rate(mm/year) |
|------------------|------------------------|-----------------------------|-----------------------|-------------------------|
| PBS              | 6.647                  | 5.1538                      | -0.254                | 0.092990                |
| ASS              | 0.9232                 | 59.247                      | -0.186                | 0.013750                |
| ABP              | 3.9719                 | 3289.8                      | -0.193                | 0.00005                 |

Figure 2 demonstrates polarization bend for Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ in ABP Solution. Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass demonstrates a passive district, current thickness increments to a not so high incentive after $E_{corr}$ is reached. This insight that the specimen experiences a meager rate of disintegration process in ABP medium. The estimations of $i_{corr}$ and $E_{corr}$ for Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass were resolved from Figure 2 and appeared in Table II. Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ composite is appeared to show a moderate $i_{corr}$ esteem (3.97E-6A/cm$^2$) in the examination. These findings propose extremely high corrosion protection of Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass with the corrosion rate in the order of E-5 which is a very important characteristic possessed by metallic glasses further it even shows a high polarization resistance of the order of E6. Polarization resistance of the order of E7 shows an incredible resistance of the material towards ABP solution which is desirable.

The polarization bend for Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ in PBS arrangement is displayed in Figure 2. The polarization bend for Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ shows an extensive passive area, subsequently implying high protection of composite to disintegration process. Be that as it may, the polarization bends show effective corrosion protection of Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass. The estimations of $i_{corr}$ and $E_{corr}$ in PBS medium decided from Figure 2 are appearing in Table II. The $i_{corr}$ estimates of Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass are observed to be 6.647E-6 A/cm$^2$.

The $E_{corr}$ values of Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ exhibits an $E_{corr}$ value of -0.25 V signifying it to be more stable than existing biomaterials, for instance, Ti-6Al-4V, 316L SS [21] are reported as -0.55 and -0.3, respectively.
4. Conclusion

A unique Zr$_{39.5}$Cu$_{50.5}$Ag$_4$Ti$_6$ metallic glass is found to display a very good protection from corrosion in SBF conditions. Additionally it exhibits a very high polarization resistance and in this manner can be a promising possibility for biomedical applications. Further studies will be done on the surface morphologies and the cytotoxic effects of the bulk metallic glass.

5. References

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