A combinatorially developed Zr-Ti-Fe-Al metallic glass with outstanding corrosion resistance for implantable medical devices

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ABSTRACT

This paper explores a Zr-Ti-Fe-Al metallic glass, fabricated via combinatorial approach using magnetron co-sputtering. The paradigm of combinatorial synthesis is demonstrated via X-Ray Diffraction and Transmission Electron Microscopy. The metallic glass is probed electrochemically in contrast with a distinguished biomaterial, commercially pure titanium (cp-Ti). The metallic glass shows no susceptibility to pitting corrosion and manifests better corrosion resistance properties than cp-Ti in terms of roughly one order improvement in corrosion current density and charge transfer resistance, attributed to the combined role of homogeneous amorphous structure and chemically stable oxide film predominantly composed of ZrO2 and TiO2.

Keywords:
Metallic glass
Combinatorial development
Magnetron co-sputtering
XPS
Bioimplants

Metallic glasses are gaining ground as modern engineering materials [1–3]. They are multicomponent metallic materials, vitrified by rapid cooling in order to bypass their thermodynamically favorable transformation into crystalline state. They possess a chemically and structurally homogeneous, isotropic structure that impart excellent mechanical [4–7] and electrochemical properties [8–10], making them candidate materials for wide range of applications, notably, bioimplants [10–12].

In the area of bioimplants, the conventional biomaterials face some shortcomings. For instance, high Young’s modulus in case of stainless steel, Co-Cr and Ti-based alloys, that may cause stress shielding; leaching of bio-toxic elements Cr, Co, Ni that may lead to inflammatory cascades [13,14]; as well as poor wear resistance, for example β-Ti alloys [15]. Among these biomaterials, titanium is widely used for orthopaedic and dental implants, however, despite its excellent corrosion resistance, some studies have reported release of titanium ions and particles in-vivo, subsequently causing cytotoxicity [16,17]. Thus, while the existing biomaterials may possess one or another desired property, they may not be equipped with a combination of characteristics needed for bioimplants. Such multi-property attributes are, however, reported for several metallic glasses. For instance, Ida et al. [11] have reported a Zr-Ni-Cu-Al bulk metallic glass exhibiting superior mechanical properties, biocompatibility and biosafety compared with titanium, demonstrating its promise as a prospective biomaterial. Metallic glasses are widely reported to exhibit high corrosion resistance [9,10] ensuring less ions release; high mechanical strength [4–7] enabling smaller, thinner implant devices; high hardness [18] limiting the wear-induced degradation; and low elastic modulus [19,20] eliminating the problems of stress shielding.

Among the limitations faced by conventional biomaterials, corrosion plays a decisive role as it can prompt alloying elements to leach into the surrounding environment, which is unavoidable even in the case of highly corrosion-resistant biomaterials, and thus concomitantly induce bio-toxic effects and adverse biological reactions. That being so, corrosion may be considered a determinant of in-vivo biocompatibility [21]. Hence, trying to reduce such corrosion-induced-degradation arises the need of a material possessing superior corrosion resistance properties in order to endure the aggressive physiological conditions.

Metallic glasses offer such desirable corrosion–resistance properties, however their complex fabrication methods have hampered the development of novel metallic glass compositions [22]. Nonetheless, a novel robust technique is the combinatorial development via co-sputtering, that has recently caught attention for the development of metallic glasses [22–24] to identify systems having a combination of desired characteristics out of a vast compositional space. In this paper, a combinatorially developed Zr45Ti36Fe11Al8 metallic glass is explored via microstructural, surface and electrochemical characterization. The metallic glass shows excellent corrosion resistance properties in Phosphate Buffered Saline (PBS) solution demonstrating its potential for bioimplants.

Binary targets of Zr-Ti (50–50 at.%) and Fe-Al (60–40 at.%) are individually sputtered as well as co-sputtered using Nano-36 Sputterer (Kurt J. Lesker Company) on silicon wafers in a base pressure...
of $1 \times 10^{-6}$ Torr and working pressure of $8 \times 10^{-3}$ Torr to generate thin films (~325 nm). Grazing-Incidence X-Ray Diffraction (GI-XRD) is done using Rigaku SmartLab Diffractometer equipped with Ge-220 2-bounce monochromator. High-Resolution Transmission Electron Microscopy (HR-TEM) is conducted using JEM 3100R05 with double aberration correctors, operated in a scanning transmission electron microscopy (STEM) mode. The high-resolution images are further processed via Fast Fourier Transformation (FFT). X-ray Photoelectron Spectroscopy (XPS) is conducted using Kratos Axis Ultra DLD X-Ray Photoelectron Spectrometer with monochromated Al source. The electrochemical testing is carried out in PBS solution using a three-electrode-cell coupled with Gamry Potentiostat. The Saturated Calomel Electrode (SCE) and graphite are used as reference and counter electrode, respectively. Electrochemical Impedance Spectroscopy (EIS) is done using a potential perturbation of 10 mV$_{\text{rms}}$ (at DC 0 V, vs open circuit potential, OCP). Potentiodynamic polarization is conducted from OCP towards anodic polarization to an apex potential of 1.5 V followed by scan-reversal. Potentiostatic polarization is carried out at 0.3 V$_{\text{SCE}}$. The electrochemical tests are repeated three times to ensure reproducibility.

Microstructural features of the three systems, i.e. Zr-Ti, Fe-Al and Zr-Ti-Fe-Al, are studied via GI-XRD and HR-TEM. From Fig. 1, the first binary system, Zr-Ti, shows a single phase solid solution of beta ($\beta$) zirconium (JCPDS 01-089-4792) [25]. The local atomic structure of this system via HR-TEM, selected-area-electron-diffraction (SAED) and FFT analysis is also presented that manifest a fully crystalline system, Fig. 1 (a-e). Despite a high-quench-rate deposition, the absence of amorphous structure in a sputter-deposited system may occur depending upon multitude of factors, such as deposition conditions [26] (i.e. adatom mobility, adatom arrival rate) and compositional factors (heats of mixing of constituents [27]). In terms of compositional factors, Inoue’s empirical rules [28] for glass formation may offer one possible explanation. In the case of Zr-Ti, it can be presumed that non-compliance to Inoue’s rules in the form of less than 3 constituents, lower atomic size differences (~8%) and nearly zero heat of mixing, might have favored beta solid solution rather than amorphous structure [27]. The second binary system, Fe-Al, shows a broad peak of iron (110), in the X-Ray diffraction

Fig. 1. (Left) GI-XRD of binary systems, Zr-Ti & Fe-Al, and quaternary system, Zr-Ti-Fe-Al. (Right) The HR-TEM images of the three sputtered systems, Zr-Ti (a-e), Fe-Al (f-j) and Zr-Ti-Fe-Al (k-o). STEM imaging (a, f, k), the SAED (b, g, l), the FFT (c, h, m), the inverse-FFT (d, i, n), and the filtered-FFT images (e, j, o) of the three systems.
pattern. The nanoscale structure via HR-TEM, SAED and FFT analysis demonstrates a crystalline configuration, Fig. 1(f-j).

The third system, Zr-Ti-Fe-Al, made via simultaneous co-sputtering, however, shows a fully amorphous state in accordance to Inoue’s rules [28], verified by both GI-XRD and HR-TEM, Fig. 1(k-o). Thus, both GI-XRD and HR-TEM manifest a single-phase amorphous structure of Zr-Ti-Fe-Al system (abbreviated as ZTFA).

Surface chemistry plays a key role in influencing electrochemical properties. The XPS survey spectrum of ZTFA, Fig. 2(a), displays peaks of Zr 3d, Ti 2p, Fe 2p, Al 2p, and O 1s. The high-resolution spectra of these constituents, Fig. 2(b), display mainly the oxidized states, i.e. Zr$^{4+}$ [29,30], Ti$^{4+}$ [31], Fe$^{2+}$/Fe$^{3+}$ [32], Al$^{3+}$ [29] and low-intensity peaks of metallic states, i.e. Zr$^{0}$ and Fe$^{0}$. O 1s is decomposed into two peaks, i.e. ‘OM’ denoting metallic oxides, and ‘OH’ representing non-lattice..
oxygen [12]. The high-resolution spectra demonstrate, predominantly, the presence of metallic oxides as principal species on the surface of ZTFA.

XPS depth profilometry is done to explore compositional transition from surface towards bulk, Fig. 2(c). Corresponding to the initial etching time, the concentration of Fe 2p and Al 2p are very low, which indicate the enrichment of the surface film with oxides of Zr and Ti. By calculating the integrated intensities, Zr$^{4+}$ and Ti$^{4+}$ constitute the main species of the surface oxide film. This predominance of Zr$^{4+}$ and Ti$^{4+}$ on the surface (upon air exposure) can be ascribed to the higher concentration of Zr/Ti species (as-deposited composition) and possibly preferential oxidation owing to their higher negative heat of formation of oxides, as reported in case Ti-Zr-Pd-Cu-Sn system [12].

Electrochemical characterization of ZTFA metallic glass is conducted via impedance spectroscopy and polarization techniques, with cp-Ti as a reference. From the EIS Bode plot, Fig. 3(a), the ZTFA exhibits higher total impedance ($|Z_{mod}|$), indicative of the barrier characteristics of oxide film formed on ZTFA. From the Nyquist plot, Fig. 3(b), the

![Fig. 3.](image-url)
diameter of the semicircle (intercepts on Zreal axis if extrapolated to low-frequency), representing the charge transfer resistance, is also comparatively larger for ZTFA. In order to extract quantitative information from the EIS spectra, two equivalent electrical circuit (EEC) models are discussed as shown in Fig. 3(c). Model-A represents a porous and/or defective oxide film formed on the working specimen surface during open-circuit exposure to PBS solution, with ions migrating through the film from the surface of the working electrode, and the film acting as a barrier [33,34]. Model-B is a simple one-time-constant representation of the impedance behavior at the electrode/electrolyte interface. By comparison, Model-A may explain the impedance behavior of ZTFA system, characterized by an oxide layer (not completely sealed) formed under open-circuit conditions. However, owing to the involvement of one relaxation time constant as apparent from the Bode plot, Fig. 3(a), the possibility of using Model-A is disregarded. Based on the significant variation in the phase angle at medium and low frequency regime, it is suggested that parallel combination of charge transfer resistance (Rct, corresponding to faradaic processes) and double layer capacitance (CPEdl, corresponding to non-faradaic processes) could demonstrate the electrochemical activity at the electrode/electrolyte interface (i.e. Model-B). Constant Phase Element (CPE), following the equation \( Z_{CPE} = \frac{Q}{\omega^{n}} \), that represent a deviation from the ideal capacitor due to non-uniform distribution of currents and/or oxide defects, is used to represent the capacity of the double layer (CPEdl). From the quantitative information extracted via EEC model fitting, approximately one-order higher Rct of ZTFA (6.6 MΩ-cm² vs 0.24 MΩ-cm² for cp-Ti) is evident which suggests the relatively better corrosion resistance properties of ZTFA metallic glass.

Potentiodynamic polarization of ZTFA demonstrates a small active anodic region, followed by a transition into passive state signifying the formation of a barrier layer, Fig. 4(a). Under similar conditions, the ZTFA registers smaller current than cp-Ti (in the active region) and passivates at lower current density, (see comparison in Fig. 4(b)). Zr, Ti and Al can spontaneously passivate due to the high chemical stability of their corresponding oxides in PBS solution, therefore, the formation of a passive barrier film may quickly dominate the corrosion-dissolution process. The low passive current density, (\( I_{pass} \), 3.5 μA/cm²) registered by ZTFA corresponds to better barrier characteristics of the passive film formed on ZTFA surface compared to cp-Ti. In the wide potential range of full-passivity (~320–1240 mV vs SCE), the dissolution current is independent to the applied anodic potential, which is equivalent to the limited dissolution rate of oxide film [35]. Electron transfer across the passive oxide film can occur via electron tunnelling (allowing redox electron transfer), but no ionic tunnelling can happen (no ion transfer), thus creating a barrier layer between the underlying metallic system and corrosive environment [35].

Zr-based metallic glasses are well-known for excellent corrosion resistance properties, however, they are found vulnerable to pitting corrosion, especially in chloride containing solutions [36–39]. The cyclic
polarization scan of ZTFA, conducted to assess the susceptibility to localized corrosion, shows negative hysteresis and registers a lower anodic reverse-scan current density (in comparison to forward-scan), Fig. 4(c). This indicates that the metallic glass is not susceptible to localized corrosion under the given test conditions.

The formation of a passive oxide layer on ZTFA surface and its compact property is further investigated via potentiostatic polarization, Fig. 4(d). The continuous decay of current density with time suggests the stable growth of passive film on ZTFA surface [40]. In the log-log plot, Fig. 4(d), inset, a nearly zero slope in the beginning indicates a competitive dissolution versus film-formation processes followed by a second region with a slope of $-1$ that indicates a high-field controlled growth of passive film. The slope of $-1$ suggests a highly compact protective passive layer. Additionally, current spikes or micro transients, that are indicative of film breakdown and/or formation of metastable pits, are not observed in the given test conditions, that further validate the stability of the passive film and good pitting resistance of ZTFA metallic glass.

Table 1 summarizes the quantitative corrosion parameters from which it can be concluded that ZTFA possesses better corrosion resistance properties than cp-Ti in PBS solution.

| Sample ID | $E_{corr}$ (mV (SCE)) | $i_{corr}$ ($10^{-7}$ A/cm²) | $i_{pass}$ ($\mu$A/cm²) | $R_i$ (Ω·cm²) | $CPE_{dl}$ | $Q$ ($\mu$F cm⁻²) | $R_{ct}$ (MΩ·cm²) | $|Z_{mod}|_{0.01}$ (MΩ·cm²) |
|-----------|-----------------------|-----------------------------|-------------------------|--------------|-----------|----------------|----------------|----------------|
| cp-Ti     | $-$326                | 1.6                         | 7.6                     | 21           | 0.92      | 67.9           | 0.37           | 0.24           |
| ZTFA      | $-$323                | 0.52                        | 3.5                     | 28           | 0.93      | 25.3           | 6.6            | 0.54           |

The generally higher corrosion resistance exhibited by metallic glasses has been attributed to various factors, i.e., the role of chemical composition, the role of homogeneity (both structural and compositional) and the role of intrinsic amorphous structure. Role of chemical composition in the corrosion behavior of metallic glasses is a well-known perspective [12,41,42]. Role of structural and compositional homogeneity is also a widely reported explanation; however, this factor alone may not be sufficient to explain the higher corrosion resistance of metallic glasses. For instance, based on the homogeneity perspective, a Zr-Ni metallic glass and its single-crystal counterpart (both compositionally and structurally homogeneous), should offer similar corrosion resistance. However, this is not the case in a study conducted by Wang et al. [43] where the higher corrosion resistance of Zr-Ni metallic glass is attributed to the role of amorphous structure influencing the composition and compactability of passive film. Apart from compositional and homogeneity perspective, the role of intrinsic amorphous structure is also influential in governing electrochemical properties of metallic glasses, as the growth mechanism of passive film is sensitive to amorphous structure [43]. To further shed light on the role of intrinsic amorphous structure, a likely explanation is put forward by Tang et al. [34], in terms of atomic mobility. According to this approach, metallic glasses, unlike crystalline materials, are thermodynamically in a metastable state exhibiting higher energy, and therefore higher atomic mobility. Therefore, the atoms in metallic glasses are electrochemically more active leading to faster passivation. Nonetheless, the role of structure on corrosion behavior is also controversial as competing studies exist [37,43–46].

Given these competing studies, instead of relying on individual role, a composite effect may be considered to be operative in case of ZTFA. Role of chemical composition stems from the fact that the majority of matrix forming species (Zr & Ti) possess very high oxygen affinities as well as high thermodynamic stabilities of their respective oxides in aqueous solution [47,48]. Role of structural and compositional homogeneity may be explained in terms of the very low $i_{corr}$, registered in potentialdynamic polarization before the formation of a barrier oxide layer, and the high $R_i$ from EIS conducted at OCP. However, separating this role from the compositional role is challenging. Intrinsic role of amorphous structure in case of ZTFA may be linked to the preferential oxidation and earlier passivation ensured by, most likely, the higher activity of Zr & Ti in the amorphous matrix leading to rapid enrichment of their respective oxides on the surface (Fig. 2(c)). Furthermore, it may also be linked to the formation of a barrier-type oxide layer following anodic polarization and its stability at high anodic potentials that may be linked to a less-defective nature of the oxide film formed on ZTFA as reported elsewhere [43]. Importantly, though the role of chemical composition is clear in case of ZTFA, confirming the role of homogeneity and intrinsic amorphous structure may necessitate a direct comparison with crystalline counterpart. Therefore, further investigations may be conducted.

In summary, a Zr₄₅Ti₃₃Fe₁₅Ni₃ metallic glass is successfully developed via combinatorial approach using magnetron co-sputtering. GI-XRD and HR-TEM demonstrate a fully crystalline configurations for the binary deposited systems and a single-phase amorphous structure in case of co-sputtered ZTFA. XPS manifest the presence of an oxide film on the surface of ZTFA, predominantly composed of ZrO₂ and TiO₂ that in combination with homogeneous amorphous structure, endows the system with excellent corrosion resistance properties. ZTFA is invulnerable to pitting corrosion and displays better corrosion resistance properties than cp-Ti in terms of lower $i_{corr}$ (0.52 $\times$ $10^{-7}$ A/cm² versus 1.6 $\times$ $10^{-7}$ A/cm² for cp-Ti), lower $i_{pass}$ (3.5 $\mu$A/cm² versus 7.6 $\mu$A/cm² for cp-Ti) and one-order higher $R_i$ (6.6 MΩ·cm² versus 0.24 MΩ·cm² for cp-Ti). The metallic glass, after rigorous biocompatibility investigations, may have prospective applications for biomaterials.

### Table 1

Summary of the quantitative information extracted from Tafel extrapolation of potentiodynamic polarization scans and EEC model fitting of EIS spectra.

### References
