Combinatorial development and assessment of a Zr-based metallic glass for prospective biomedical applications

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ABSTRACT

In the quest of corrosion-resistant biomaterials, the emergence of metallic glasses is a welcome stimulus, however, their progress is potentially impeded by the complex fabrication routes. This paper explores a Zr$_{40}$Ti$_{35}$Ni$_{14}$Nb$_{11}$ metallic glass, developed through combinatorial magnetron co-sputtering. Structural characterization of the system via Grazing-Incidence X-Ray Diffraction and Transmission Electron Microscopy coupled with Fourier Transformation demonstrates single phase homogeneous amorphous structure. The metallic glass, upon comparative electrochemical examination in physiological solution, displays relatively better corrosion resistance properties than conventional biomaterials, i.e. stainless steel 316L and commercially pure titanium, by an order of magnitude lower corrosion current density, (17 nA/cm$^2$), lower passive current density (3.1 μA/cm$^2$), invulnerability to pitting corrosion and one-order higher charge transfer resistance (6.9 MΩ·cm$^2$). The superior corrosion resistance properties are ascribed to the synergistic effect of chemically and structurally homogeneous amorphous structure and protective passive film, enriched with chemically stable oxides of Zr and Ti. Mechanical characterization of the metallic glass via nanoindentation studies reveal high hardness (7.1 GPa) and fairly low elastic modulus (121.7 GPa), making it a candidate material for bioimplants.

1. Introduction

Metallic glasses have recently garnered substantial research enthusiasm and are emerging as quintessential engineering materials [1–4]. They are amorphous metallic materials having no long-range order, vitrified via rapid cooling in an attempt to suppress their transformation into crystalline state [1]. Metallic glasses are characterized by a compositionally and structurally homogeneous, isotropic structure down to atomic scale that usually impart superior strength [5–8] and corrosion resistance [9,10] properties. On the grounds of having unusual combination of chemical, physical, and mechanical properties, metallic glasses are emerging as candidate materials for high performance applications in various fields including structural materials [2,11], magnetic materials [3,12,13,14], catalysis [15–17] and most notably, bioimplants [10,18,19].

In the field of bioimplants, notwithstanding the fact that conventional biomaterials, i.e., Ti-based alloys and biomedical stainless steel are routinely employed for bioimplants, they, however, face some limitations, for instance, suboptimal biocompatibility, low corrosion resistance and poor mechnano-compatibility. The shortcomings comprise leaching of bio-toxic species Co, Cr and Ni for instance, resulting in inflammatory cascades [20,21]; unacceptably high Young's modulus possessed by stainless steel and Co-Cr systems, resulting in stress shielding effect and associated implant failure; as well as low wear resistance (e.g. β-Ti alloys [22]), enabling wear-induced-degradation. Among the aforementioned biomaterials, titanium is commonly utilized for bioimplants, however, it possesses lower strength than other metallic biomaterials, such as stainless steel [23], as well as low wear resistance [23]. Additionally, regardless of its superior corrosion resistance properties, some reports have demonstrated in-vivo release of titanium ions and particles, subsequently causing cytotoxicity [24,25].

Therefore, it is safe to presume that while the conventional biomaterials are endowed with certain distinguishing characteristics, they may not possess a blend of features required for the acceptable performance of bioimplants. The combination of such requisite characteristics are, nonetheless, described in numerous metallic glasses. For example, Liu et al. [16] have reported a Zr-Cu-Fe-Al-Ag metallic glass, possessing a combination of excellent corrosion resistance, biocompatibility and low elastic modulus. Recently Ida et al. [18] have explored a Zr-Ni-Cu-Al metallic glass possessing excellent biocompatibility, biosafety, and mechanical properties, in comparison to a
distinguished biomaterial, titanium, signifying its potential as a prospective biomaterial. In a comparative ion-release study of Zr-Ni-Cu-Al metallic glass, stainless steel and titanium incubated for 7 days, Ida et al. [18] have shown that there is almost no ions released from the metallic glass. Metallic glasses are commonly reported to possess excellent corrosion resistance [9,10] reducing the in-vivo ions-release; superior mechanical strength [5–8] permitting smaller, thinner biodevices; high hardness [26] reducing the wear-induced degradation; and lower Young’s modulus [27,28] diminishing the stress shielding effects. Furthermore, they are endowed with a distinguishing polymer-like formability and ease of nano/micro imprinting [3,4,29] that offers a unique opportunity to fabricate complex implants and biodevices [30]. Metallic glasses also show a unique compositional flexibility, as opposed to crystalline systems, in terms of no thermodynamical constraints, or solid solubility limits. Driven by such attributes, research is gaining ground in the development and electrochemical characterization of metallic glasses for biomedical applications mainly in three classes, i.e. Ti-based [19,31,32], Zr-based [10,18,33] and Fe-based [34–36] systems. Among these, Zr-based metallic glasses are prominent for their relatively higher glass forming ability, excellent corrosion resistance, biocompatibility, and lower elastic modulus [10,18].

Out of the several limitations faced by existing biomaterials discussed earlier, corrosion resistance, inarguably, plays a fundamental role. Poor corrosion resistance can result in species leaching into the physiological environment, that is inescapable even in the case of prominent corrosion-resistant biomaterials. This may, subsequently, result in bio-toxic effects and adverse biological reactions during long-term implantation. That being the case, corrosion resistance may be considered to strongly govern the in-vivo biocompatibility [31] and mechanical integrity of bioimplants. Therefore, striving to impede such corrosion-induced-degradation and its adverse effects arises the need of a material having excellent corrosion resistance properties, capable of enduring the aggressive physiological environment.

Metallic glasses display such desirable anticorrosion characteristics, but the Achilles heel is their complex fabrication routes—very cumbersome as well as time- and resource-consuming—that have obstructed the development of novel metallic glasses [37]. Nevertheless, a novel technique that is on the rise is the combinatorial development via co-sputtering, where multiple components are simultaneously sputtered to fabricate amorphous systems with desired compositions. Combinatorial development via co-sputtering, characterized by a vapor-solid transition, is gaining ground for the development of novel metallic glasses [37–39], in order to avoid the strict experimental conditions that are otherwise encountered in conventional methods characterized by liquid-solid transition. In this technique, the compositional tuning can be easily channelled via controlling the sputtering parameters. On top of that, this technique inherently possesses high quench rates [40], and thus has the prospect to accelerate modern developments in metallic glasses [37,39,41,42].

In this work a Zr$_{40}$Ti$_{35}$Ni$_{14}$Nb$_{11}$ metallic glass with optimized composition, developed via magnetron co-sputtering, is explored. Combinatorial synthesis via co-sputtering and the structural characteristics of metallic glass are studied using X-Ray Diffraction and Transmission Electron Microscopy. The metallic glass is further studied for its corrosion resistance properties in comparison with stainless steel (SS 316L) and commercially pure titanium (cp-Ti), in Phosphate Buffered Saline (PBS) solution via different electrochemical techniques. Additionally, mechanical properties of the metallic glass are assessed via nanoindentation studies. The metallic glass, in a comparative study, reveal excellent electrochemical and mechanical properties suitable for biomedical applications.

2. Experimental procedure

2.1. Magnetron sputtering

Binary sputtering targets of Zr-Ti (equi-atomic, 99.9% pure) and Ni-Nb (60/40 at.%, 99.995% pure) from Kurt J. Lesker Company are individually sputtered as well as co-sputtered using magnetron sputterer (Nano-36, Kurt J. Lesker Company) on silicon wafers (100) (universitywafers.com). The silicon wafers are mounted on a disk rotating with 20 rpm angular speed to ensure deposition uniformity. Gun-to-substrate throw distance is kept constant at 7 cm in all cases. The sputtering chamber is first evacuated to a base pressure of $\sim$1 x $10^{-6}$ Torr and then filled with high purity Argon with a working pressure of $\sim$8 x $10^{-7}$ Torr. The powers of DC gun (Zr-Ti) and RF gun (Ni-Nb) are kept at 200 and 100 W respectively to deposit the respective systems. Before deposition, a 10-min pre-sputtering is carried out in closed-shutter configuration to remove the airborne surface oxides on the targets. Deposition is carried out for 20 min in all three cases, under ambient substrate temperature (though the substrate self-heated via particle impact during operation). Thickness of the co-sputtered quaternary system ($\sim$590 nm) is calculated via DektakXT stylus profiler (Bruker). Energy Dispersive X-ray Spectroscopy (EDS, coupled with Hitachi Scanning Electron Microscope) of the quaternary system is done in an area scan to reveal the composition: Zr (40%), Ti (35%), Ni (14%), and Nb (11%), in atomic percent.

2.2. Grazing-incidence X-ray diffraction

Grazing-Incidence X-Ray Diffraction (GI-XRD) is conducted for the three deposited systems (Zr-Ti, Ni-Nb and Zr-Ti-Ni-Nb) using Rigaku SmartLab Diffractometer, equipped with 1.54 Å Cu Kα source and Ge-220 2-bounce monochromator, operated at 40 kV, 30 mA. GI-XRD is done in a grazing incidence 2θ-u mode, using a scan rate of 1°/min. ‘u’ is set at 1° in order to avoid interference from silicon substrate by minimizing the X-Ray penetration depth. The diffraction patterns are smoothed via Fourier Transformation and interpreted using PANalytical XPert HighScore.

2.3. High-resolution transmission electron microscopy

High-Resolution Transmission Electron Microscopy (HR-TEM) is carried out using JEM 3100R05 with double aberration correctors operated at 300 kV acceleration voltage, in a scanning transmission electron microscopy (STEM) mode. The lens settings are set to define a probe size of $\sim$1.5 Å for both imaging and EDS elemental mapping. High-resolution imaging and selected-area-electron-diffraction (SAED) are done to reveal the nanoscale structure of the co-sputtered Zr-Ti-Ni-Nb system. Sample for TEM study is made via focus ion beam (FIB) in-situ lift-out method (FEI Helios FIB/SEM system) to prepare a cross-sectional view of the film-substrate system. The high-resolution HR-TEM images are processed via Fast Fourier Transformation (FFT), inverse-FFT and filtered-FFT using Gatan Microscopy Suite. EDS elemental mapping is conducted using a JEOL SSD X-ray detector ($\sim$60 mm$^2$).

2.4. X-ray photoelectron spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is done using Kratos Axis Ultra DLD X-Ray Photoelectron Spectrometer with monochromated Al source (having energy resolution of $\sim$0.6 eV at 20 eV pass energy) in a chamber pressure < $10^{-8}$ mbar. The photoelectrons emitted from the surface are analyzed at a take-off angle of 45°. Survey spectra (0–1000 eV) of the Zr-Ti-Ni-Nb system is acquired for quantitative analysis while high-resolution spectra are obtained to characterize the chemical states of different species on the surface. The high-resolution spectra are deconvoluted using Gaussian-Lorentzian-Cross function. Background subtraction of the high-resolution spectra is carried out using Shirley (for Nb 3d) [43], Tougaard (for Ni 2p, Ti 2p and O 1s) [44] and linear (for Zr 3d) methods. NIST X-ray Photoelectron Spectroscopy Database is used for binding energy values in the analysis of deconvoluted spectra. Depth profilometry is done using in-situ Argon-ion beam sputtering. Casa XPS is used to extract the relative
concentration profiles of the constituent elements from the in-situ depth profiling data.

2.5. Electrochemical testing

The electrochemical testing of Zr-Ti-Ni-Nb, stainless steel (SS 316L) and commercially pure titanium (cp-Ti) is carried out in a three-electrode-cell coupled with Gamry Potentiostat (Reference 1000). The Saturated Calomel Electrode (SCE, +244 mV vs SHE) and graphite are used as reference and counter electrode, respectively. cp-Ti, (onlinemetals.com) and SS 316L (onlinemetals.com) are incorporated for a comparative study. The working samples of SS 316L and cp-Ti are ground through successive grades of SiC papers up to 1200 grit size. The samples are subsequently degreased via ultrasonication in acetone and dried under a high-pressure stream of Nitrogen gas. Open circuit potential (OCP) measurements of the three systems are registered for two hours in PBS solution (Thermo Fisher Scientific) under naturally aerated conditions to achieve a relatively steady state. The chemical composition of PBS solution is presented in Table 1.

OCP measurements are followed by potentiodynamic polarization where a potential sweep rate of 1 mV/s is used, starting from ~500 to 1500 mV (versus OCP). The corrosion current density and corrosion potential are extracted via standard technique, i.e., the application of Tafel analysis by linear fitting of strong polarized zone, i.e. ±100 mV around the OCP [45]. Cyclic-anodic polarization is conducted in PBS solution with a 1 mV/s sweep rate, starting from OCP followed by anodic polarization to an apex potential of 1.5 V or apex current density of 25 mA. At this point the scan direction is reversed and terminated at the previously registered OCP. Electrochemical impedance spectroscopy (EIS) is done using a sinusoidal potential perturbation of 10 mVrms (at DC 0 V, vs OCP) in the frequency range of 100 kHz to 0.01 Hz, after 2-h immersion in PBS solution. The impedance data is analyzed using Gamry Echem Analyst to obtain the electrical parameters describing the electrode/electrolyte interface. The electrochemical tests of Zr-Ti-Ni-Nb are repeated in triplicate for the purpose of reproducibility.

2.6. Nanoindentation

TribolIndenter, TI 980 Performech II (Bruker) with a Berkovich Diamond indenter is used for the nanoindentation testing. Two different modes, i.e. quasi-static and dynamic, are conducted to assess the mechanical properties of metallic glass. In the quasi-static mode, the indenter is driven into the surface until a peak load of 10 mN is held for 2 s and then unloaded to zero (trapezoidal-shaped load-unload cycle). In the dynamic test, a contextual stiffness measurement (CSM) mode is performed on the sample by superimposing a 220 Hz oscillating load on top of quasi-static load. The phase and amplitude of the oscillations are used to continuously measure the stiffness during the loading segment. Mechanical properties, i.e. elastic modulus and hardness are extracted from CSM mode by averaging in the range of 30–60 nm of contact depth (~5–10% of film thickness) to avoid substrate interference. For each sample, indentations are made at 18 different locations to ensure reproducibility.

3. Results and discussion

3.1. Structural characterization

Structural examination of the three sputtered systems, i.e. Zr-Ti, Ni-Nb and Zr-Ti-Ni-Nb, is carried out using Grazing-Incidence X-Ray Diffraction (GI-XRD). However, to further validate the nanoscale structure of the quaternary Zr-Ti-Ni-Nb system, aberration-corrected High-Resolution Transmission Electron Microscopy, selected-area-electron-diffraction and Fast Fourier Transformation are additionally conducted.

3.1.1. Grazing-incidence X-ray diffraction

Fig. 1 shows the diffraction patterns of the three sputtered systems, i.e. Zr-Ti, Ni-Nb and Zr-Ti-Ni-Nb. The diffraction pattern of binary Zr-Ti system demonstrates a solid solution of β-zirconium (JCPDS 01-089-4792) [46]. Despite the fact that magnetron sputtering is a powerful tool for the synthesis of amorphous films [37,39,47], it may not always ensure completely amorphous state, as observed in Zr-Ti. Whether or not the sputter-deposited system will be amorphous, depends on several factors. Among those factors, sputtering conditions [40] (i.e. adatom arrival rate, adatom mobility on the substrate etc.) and compositional factors (enthalpy of mixing among the constituents [48], for instance) can influence the structure of the deposited system. In terms of compositional factors, Inoue’s rules [49] formulated for glass formation (i.e. > 3 constituent elements, > 12% atomic size differences and negative heats of mixing) may provide one explanation. In the case of Zr-Ti, it can be maintained that non-compliance to the aforementioned Inoue’s rules in the form of lower atomic size differences (Zr, 1.6 Å and Ti, 1.48 Å, difference of ~8%) and zero heat of mixing, might have played a dominant role in the formation of beta solid solution rather than amorphous structure [48]. The diffraction pattern of the second binary system, Ni-Nb, shows a single sharp peak alongside a broad maximum, indicative of predominantly amorphous structure. In this case, however, the highly negative heat of mixing (~30 kJ/mol) may favor amorphization as seen in Fig. 1.

The combination of the two binary systems via simultaneous co-sputtering, however, steers the system towards completely amorphous state in agreement to Inoue’s rules [49]. The ease of glass formation in this case may also be explained in terms of Confusion Principle [50], according to which the higher the number of constituents involved, the lower the probability that the alloy can select viable crystal structures, and therefore, the greater the chances of glass formation. However, this principle is basically put forward for liquid-solid transitions. The diffraction pattern of Zr-Ti-Ni-Nb system, Fig. 1, shows no sharp Bragg’s diffraction peak and the broad maximum validate a single-phase amorphous structure.

The combinatorial development strategy is exploited for compositional tuning to arrive at an optimized chemical composition, in
accompanying with the rules of glass formation put forward by Inoue [49] and Lindsay Greer [50]. The probability of glass formation is usually higher in case of sputter deposition, where a vapor-solid transition takes place, having orders of magnitude higher quench rates [40], in comparison to the widely employed synthesis methods for bulk metallic glasses (characterized by liquid-solid transitions). This higher probability gives flexibility in going against the familiar rules of glass formation for incorporating species having desirable features for specific application. For instance, species having positive enthalpy of mixing can be added where amorphization is thermodynamically unfavourable. This presumption is validated by studies where amorphization in highly immiscible binary systems are reported, for instance, Cu-Nb [51], Ag-Fe [52], and Cu-Ta [53]. In the present work, the elemental species are selected and their chemical compositions optimized keeping in view a concoction of features implanted in the same system, including glass forming abilities, oxide forming tendencies, chemical stabilities in simulated physiological conditions and biocompatibility properties. A full-scale compositional-to-property correlation among the selected species is not, however, covered in this work.

3.1.2. Transmission electron microscopy

To reinforce the results of GI-XRD in manifesting amorphous structure in case of Zr-Ti-Ni-Nb system, HR-TEM is employed to further explore the nanoscale structure.

Fig. 2 shows the HR-TEM images, selected-area-electron-diffraction (SAED) and Fast Fourier Transformation (FFT) of Zr-Ti-Ni-Nb system, taken in cross-sectional view. The HR-TEM image of Zr-Ti-Ni-Nb, Fig. 2(b), shows no indication of any ordered arrangements that could have appeared during the fabrication process or as a result of any post-synthesis devitrification. The corresponding SAED pattern in the inset, shows concentric diffused ring, characteristic of amorphous structure. To further explore the nanoscale structure, FFT analysis is carried out, Fig. 2(c, d). FFT can extract information regarding local periodicities, as any small-scale periodicity in the HR-TEM image is susceptible to this analysis [54]. FFT represents the reciprocal space, equivalent to the diffraction pattern of the image, while inverse-FFT carries out an inversion back into the real space. As demonstrated, the inverse-FFT, Fig. 2(c), and filtered-FFT, Fig. 2(d), shows no indication of any local crystallinity that further verify the amorphous structure. Thus, the HR-TEM study coupled with image processing via FFT, further endorses the results of X-Ray diffraction, (Section 3.1.1), in validating the fully amorphous single-phase structure of Zr-Ti-Ni-Nb (abbreviated as ZTNN).

Apart from microstructural characterization, EDS elemental mapping is also done in STEM mode to verify compositional homogeneity in the ZTNN system in a depth-wise cross-sectional view. From Fig. 3, it is apparent that the distribution of constituent elements in the system is visually homogeneous. Mixing of individual species occurs via collisions with gas molecules in the gaseous phase and via substrate rotation that additionally ensures mixing of incoming fluxes from the two cathodes Oxygen content, as observed in the mapping, might have arisen during sputtering (O-metal-O solid solution), sample preparation via FIB and/or examination via STEM imaging.

3.2. Surface characterization

Surface chemistry of a system strongly governs its electrochemical properties. Thus, X-Ray Photoelectron Spectroscopy (XPS) analysis of ZTNN metallic glass, exposed to ambient atmosphere, is conducted for an understanding of the surface chemistry as well as compositional variations of constituent elements from surface towards bulk.

3.2.1. X-ray photoelectron spectroscopy

The XPS survey spectrum, Fig. 4(a), shows pronounced peaks of Zr 3d, Ti 2p, Ni 2p, Nb 3d, O 1s and C 1s (arising from carbon contamination). Fig. 4(b) shows the high-resolution spectra of all constituent elements deconvoluted using Gaussian-Lorentzian-Cross function. In the high-resolution spectrum of Zr 3d, a 2.4 eV spin-orbit splitting is observed between Zr 3d3/2 and Zr 3d5/2 lines. The two doublets of Zr 4+ state is identified at 183.1 and 185.5 eV binding energies, respectively [33,55]. A low-intensity peak of metallic Zr is also identified at 179.6 eV. For the spectrum of Ti 2p, Ti 4+ state is assigned to 2p3/2 and 2p1/2 at 459.4 and 465 eV, respectively [56]. In case of Ni 2p, multiplet split of Ni 2p3/2 is identified [57], along with a satellite peak, that possibly arises because of multiplet splitting of core-level peak, Ni 2p3/2 [58]. The spectrum of Nb 3d consist of both metallic states (doublet at 202.9 and 205.9 eV) and oxidized states (doublet at 208.1 and 210.8 eV, assigned to Nb5+) [59]. O 1s is decomposed into two peaks corresponding to ‘OH’ and ‘OM’ oxygen where OH denotes non-lattice oxygen, (OH– ions and bound water in the film) while OM refers to metal oxides [19]. Since the “OM” peak is comparatively intense than “OH”, it is reasonable to infer that the air-formed surface film consists of metallic oxides as principal species. All the high-resolution spectra demonstrate, metallic and/or oxidized states, with the latter being predominant, thus confirming air-formed oxides as reported for other metallic glasses [19,60].

In order to examine the compositional transition of species from surface towards bulk, XPS depth profilometry is conducted. The depth profiles, Fig. 5, demonstrate high oxygen content in the surface layer, followed by a decline towards bulk matrix. Oxygen signal in the underlying matrix may be attributed to the dissolved oxygen forming solid solution [60]. The other lines in the profilometry, Zr 3d, Ti 2p, Ni 2p and Nb 3d, are combination of all possible states, metallic and oxidized, and their trend stabilize around 600 s of etching time.

In the initial etching time (0–120 s), Fig. 5, the percent concentration of Ni 2p and Nb 3d are too low, indicative of the enrichment of the surface film with oxides of Zr and Ti. From the integrated intensities, Zr4+ and Ti4+ constitute the predominant species of the air-formed native oxide formed on the ZTNN surface. This surface enrichment of Zr4+ and Ti4+ species, upon air exposure, may be explained in terms of preferential oxidation, since both Zr and Ti possess comparatively higher negative heat of formation of oxides [19]. Additionally, Louguine-Luzgin et al. [60] have reported the migration of active Zr towards the oxide film and the diffusion of nobler copper towards oxide/metal interface in a Cu-Zr-Al bulk metallic glass, that further supports the idea of surface enrichment.

3.3. Electrochemical characterization

From the perspective of biomedical applications, the most inconvenient aspect is the corrosion-induced-degradation of metallic systems in the electrochemically aggressive physiological fluid [61], leading to release of species that can be harmful. This indicate that corrosion resistance is a vital property for metallic biomaterials to ensure biosafety. The corrosion resistance properties of ZTNN metallic glass are explored via open circuit potential measurements, potentiodynamic polarization, cyclic-anodic polarization and electrochemical impedance spectroscopy in PBS solution. SS 316L and cp-Ti are incorporated for a comparative study.

3.3.1. Open circuit potential

Open circuit potential (OCP) depends on the electrolyte composition, temperature, oxygen content of the electrolyte and the state of the metal [62]. Fig. 6 shows the OCPs of ZTNN metallic glass in comparison to SS 316L and cp-Ti. SS 316L and cp-Ti demonstrate a continued shift of OCPs towards more positive values that indicate the formation of stable passive film upon exposure to PBS solution [62]. In case of ZTNN, the OCP shifts to a positive value during initial ~1000 s, followed by a small decline (~30 mV) before achieving the stable potential of ~412 mV vs. SCE in 2 h.

As a ‘general rule of thumb’ while investigating passivity, it is maintained that any constituent of alloy having the highest affinity for
oxygen, determined from Gibbs free energy, forms the oxide layer, on a condition that the constituent is present in sufficient concentration [63]. In the stated Zr-Ti-Ni-Nb metallic glass, Zr and Ti constitute the major matrix (~75 at.%) and also exhibit the highest oxygen affinities [64,65]. That being so, the oxide layer is expected to be predominantly formed by Zr and Ti (Nb content being very less in the native oxide as demonstrated by in-situ XPS). The stability of these oxides can be justified by the Pourbaix diagrams of Zr–H₂O [66] and Ti–H₂O systems [65] indicating that both Zr and Ti passivate in a wide pH range. Thus, they are expected to form stable films in the test solution. Ni is active, however [67,68] and though its concentration is extremely low in the native air-formed oxide (XPS, Section 3.2.1), its dissolution, if any, would result in further enrichment of Zr and Ti species in the surface film [19] during exposure to PBS solution. The enrichment of oxides of Zr and Ti, and their chemical stabilities are expected to reduce the dissolution of species into the solution.

3.3.2. Potentiodynamic polarization

Potentiodynamic polarization is carried out to evaluate the corrosion behavior of ZTNN metallic glass in comparison with SS 316L and cp-Ti, as shown in Fig. 7. During cathodic polarization, the reduction of either water and/or any dissolved oxygen in PBS solution (pH 7.4) is
expected [69]. The value of corrosion potential, $E_{corr}$, in case of ZTNN is lower than the corresponding OCP, (see Fig. 6) and same holds true for SS 316L and cp-Ti, which is indicative of de-passivation phenomenon in all three systems during cathodic polarization [62]. In other words, the stability of pre-formed oxide films (air-formed and/or developed upon open-circuit immersion) is decreased during cathodic polarization and is expected to dissolve, leaving behind the more active surfaces as revealed by the relatively negative $E_{corr}$ values than their corresponding OCPs.

In the anodic polarization curve, the ZTNN represents an active-passive behaviour within 1.5 V potential region (vs OCP) with a little current nose at $\sim + 130$ mV (vs. SCE), indicative of active to passive transition. The low current density ($3.1 \mu$A/cm$^2$) of ZTNN beyond this potential, termed as the passivation current density, $I_{pass}$, attributes to relatively better barrier characteristics of the passive oxide film formed on ZTNN surface than cp-Ti. In the anodic potential range of full passivity ($-130$ to $-1088$ mV vs SCE), the ZTNN registers a small current that is independent to the applied anodic potential. This low dissolution current is ascribed to the limited dissolution rate of oxide film in PBS solution [69]. This potential-independence of the dissolution current arises due to the fact that the interfacial potential between the passive oxide developed on ZTNN surface and the PBS solution stays constant, independent of the applied anodic potential. Redox electron transfer across the film may occur via electron tunnelling, however, no ionic tunnelling is allowed (no ion transfer), therefore creating a barrier-type layer between the metallic system and electrolyte [69]. It is also noticeable that cp-Ti presents relatively higher current in both active and passive regions. However, the considerably small passive region and origin of pitting behaviour beyond $+375$ mV (vs. SCE) is shown by SS 316L, which indicate the limited stability of passive film under similar conditions.

The quantitative values of electrochemical parameters is determined from the potentiodynamic polarization scans and are presented in Table 2. Owing to the presence of highly active species in ZTNN metallic glass, the more negative $E_{corr}$ ($-480$ mV vs SCE) than cp-Ti ($-326$ mV) and SS 316L ($-285$ mV) is expected after removal of oxide film (during preceding cathodic polarization scanning). However, approximately two orders of magnitude lower $I_{corr}$ of ZTNN (17 nA/cm$^2$) than SS 316L (1.1 $\mu$A/cm$^2$) is an interesting feature of the ZTNN which demonstrates its very slow dissolution in the PBS solution. Very similar results of $I_{pass}$ (in the order of 1 $\mu$A/cm$^2$) and $I_{corr}$ (in the order of 10 nA/cm$^2$) are also reported for Zr Ti alloys when exposed to Ringer’s solution [70]. Thus, from potentiodynamic polarization scans, the ZTNN metallic glass demonstrates relatively better corrosion resistance properties than SS 316L and cp-Ti in PBS solution.

### 3.3.3. Cyclic-anodic polarization

Zr-based metallic glasses are commonly known to possess superior corrosion resistance properties, however, they are reported to be susceptible to pitting corrosion, particularly in chloride-containing solutions [71–74]. Cyclic polarization offers a qualitative view of the pitting corrosion mechanism and can be used to determine the pitting tendency of a system under applied conditions [75]. Therefore, to investigate the pitting resistance and stability of the passive film, cyclic-anodic polarization scan of ZTNN metallic glass is obtained in PBS solution, in comparison with SS 316L and cp-Ti, as shown in Fig. 8. The scans are registered by polarizing the samples away from their respective OCPs towards more positive (anodic) potentials, to avoid the dissociation of pre-existing oxide films due to cathodic polarization [9], as observed in case of potentiodynamic scans (Section 3.3.2).

It is interesting to note that upon reversing the scan either from anodic to passive potential (1.5 V vs OCP) or apex current density (25 mA/cm$^2$), the ZTNN and cp-Ti display negative hysteresis loop (anti-clockwise upon potential reversal) indicative of invulnerability to pitting corrosion [76,77]. In contrast, in case of SS 316L, the origin of transpassive region (large anodic current during forward scan) is followed by relatively larger current during reverse scan (positive hysteresis) which is indicative of its tendency towards pitting corrosion in PBS solution. However, the considerably small current response by ZTNN and cp-Ti manifests that once the passive oxide film is formed on these materials during anodic polarization, it will remain intact and would protect the underlying material from localized attack in PBS solution.

### 3.3.4. Electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is conducted on ZTNN metallic glass, SS 316L and cp-Ti, represented by Bode and Nyquist plots, as shown in Fig. 9. It is expected that uniform oxide film can form on the surface of these materials as predicted from the polarization studies (described above) but at OCP, the kinetic processes at the electrode/electrolyte interface strongly depend on the type of material in PBS solution. The Bode-impedance plots are shown in Fig. 9(a) which represent the area normalized total impedance, $Z_{norm}$ vs frequency, $f$, within 100 kHz to 0.01 Hz range. At the lowest frequency (0.01 Hz), the considerably higher $Z_{norm}$ of ZTNN (0.728 MΩ·cm$^2$) compared to SS 316L (0.187 MΩ·cm$^2$) and cp-Ti (0.178 MΩ·cm$^2$) demonstrates the barrier-type characteristics of the oxide film formed on ZTNN metallic glass. Similarly, the phase angle variation at different frequencies and Nyquist plots are provided for comparison in Fig. 9(b) & (c), respectively. From the Nyquist plots, Fig. 9(c), the diameter of the semicircle (intercepts on $Z_{real}$ axis at $f \to 0$), depicting the charge transfer resistance, is also comparatively larger for ZTNN. From these
spectra, the quantitative information of the electrochemical processes is obtained by simulating the experimental EIS spectra with equivalent electrical circuit (EEC) models.

In order to fit the experimental EIS spectra of ZTNN, SS 316L and cp-Ti with appropriate EEC model, several modelling circuits are discussed. Fig. 10 summarizes the various EEC models used to represent the impedance behavior of systems developing oxide layers under open-circuit immersion conditions. The EEC circuit elements, comprised of resistors (R) and constant phase elements (CPE, representing non-ideal capacitor) are plotted corresponding to the physical nature of the system, Fig. 10.

Model-A represents a duplex oxide structure consisting of relatively porous outer layer and a barrier-type compact inner layer [70,78]. $R_{ct}$ and $CPE_{dl}$ represent the electrochemical process at the oxide/solution interface, determining the impedance behavior at high frequency range of the spectrum. Model-B, widely employed for Ti-based systems [79–81], is a bi-layered oxide consisting of an outer porous and inner barrier layers with parallel implementation of time constants. Model-C

Fig. 4. (a) XPS survey spectrum of ZTNN metallic glass showing the individual spectral lines of all constituents. (b) The high-resolution deconvoluted spectra for individual states. The superscripts ‘m’ and ‘ox’ denote metallic and oxidized states, respectively.
demonstrates a porous passive film formed on a system during immersion in electrolyte (open-circuit), with ions migrating through the film from the surface of the working electrode, and the film acting as a barrier layer \[68,82\]. In this model, the total corrosion resistance is comprised of the passive film resistance and the charge transfer resistance at metal/oxide interface. Depending on the properties of the passive film, either of the contributions can dominate the overall impedance response. Model-D is the simple one-time-constant model used to represent the impedance of the electrode/solution interface. However, the $R_x$ and $CPE_x$ elements are given different explanations. For instance, $R_x$ and $CPE_x$ are reported to represent charge-transfer resistance and double layer capacitance at oxide/solution interface \[62\], charge-transfer resistance and double layer capacitance at metal/oxide interface \[83\], or the barrier resistance and capacitance of oxide layer, respectively \[70\].

Based on the aforementioned models, Model-C may explain the ZTNN metallic glass, having a surface oxide layer (not fully sealed) formed during open-circuit immersion in PBS solution. However, given that the phase angle plot demonstrates the involvement of a one relaxation time constant, Fig. 9b, the implementation of model C (as well as Model-A & B for the same reason) is disregarded. Based on the kinetic information retrieved from polarization trends, the significant variation in the phase angle at medium and low frequency regime, it is suggested that parallel combination of charge transfer resistance ($R_{ct}$) and double layer capacitance ($CPE_{dl}$) can demonstrate the electrochemical activity at the electrode/electrolyte interface. The parallel combination of these parameters corresponds to the faradaic and non-faradaic processes at the electrode/electrolyte interface, respectively. Thus, Model-D, representing the electrode/electrolyte interface, is used as an EEC model to fit the EIS spectra of ZTNN metallic glass. The constant phase element (CPE) is used to consider the surficial distribution of charge within the double layer owing to the surface roughness and its impedance response is governed quantitatively by $Z_{CPE} = \left[\frac{Q}{\omega^n}\right]^{-1}$, where $n = 1$ represents the phase shift by an ideal capacitor. The Bode-phase angle plots of SS316L and cp-Ti also show one relaxation time constant, and therefore, their EIS spectra are also fitted with the same EEC model. The best fitting of experimental spectra with the EEC model is evaluated from the very small (~$10^{-4}$) chi-squared values.

Table 3 presents the quantitative information after fitting the spectra with EEC model. Clearly, the considerably higher $R_{ct}$ of ZTNN metallic glass (6.9 MΩ·cm$^2$) compared to SS316L (0.52 MΩ·cm$^2$) and cp-Ti (0.3 MΩ·cm$^2$) is evident which corresponds to the improved barrier characteristics of the passive oxide film on ZTNN. On the other hand, the relatively smaller $Q$ for the CPE and larger $R_x$ at the oxide film/electrolyte interface are related with the resistive nature of passive oxide film which is most likely stable in the PBS solution. The presence of active Zr and Ti enriched species on the surface of ZTNN (as determined from XPS analysis) may react with the PBS solution to form compact passive oxide film. However, in case of SS316L and cp-Ti, the relatively lower $R_x$ is related with the nature of the oxide film when these interact with the ionic species. In other words, it is considered that the composition of oxide film equilibrated with PBS solution may change due to adsorption/desorption of ionic species. In case of cp-Ti, the semiconductive Ti$_6$O oxide film containing defects (oxygen deficient sites) may form which may interact with the ionic species in the electrolyte and its composition may change \[84\]. Therefore, one can expect the relatively lower $R_x$ and dominant charge distribution at the surface as represented by larger $CPE_{dl}$ values in case of SS316L and cp-Ti. In summary, the trend of $R_x$ varies in the decreasing order of ZTNN > SS316L > cp-Ti. ZTNN exhibits a roughly one order higher $R_{ct}$ in comparison to SS316L and cp-Ti, signifying its relatively higher corrosion resistance. Thus, the EIS results also corroborate the aforementioned electrochemical polarization techniques.
3.4. Mechanical characterisation

The mechanical properties of ZTNN metallic glass are assessed via nanoindentation, carried out both in quasi-static and dynamic mode to determine the contact stiffness, elastic modulus and hardness.

3.4.1. Quasi-static nanoindentation

Fig. 11 shows the typical load-displacement curves obtained from the quasi-static nanoindentation of ZTNN. The serrations or pop-in events in the loading segment (expanded view, Fig. 11) is generally ascribed to the coalescence of free volume, a well-known phenomenon observed during nanoindentation of metallic glasses [85,86]. Elastic modulus can be calculated from the initial unloading segment, using contact mechanics.

\[ E_2 = (1 - \nu^2) \left[ \frac{E_r E_i}{E_r - E_i (1 - \nu^2)} \right] \]  

where \( E \) and \( \nu \) represent elastic modulus and Poisson's ratio, respectively. Subscripts \( r \), \( i \) and \( r \) refer to 'sample', 'indenter material' and 'reduced', respectively.

The reduced modulus, \( E_r \), in Eq. (1) can be found from the load-unload curve, Fig. 11, using the following equation:

\[ E_r = \frac{1}{F} \left( \frac{dp}{dh} \right) \sqrt{A} \]  

A represents the contact area at initial unloading, while \( \left( \frac{dp}{dh} \right) \) is the slope of the load 'p' versus displacement 'h' curve at the start of the unloading portion, that can be measured by fitting a power law relation to the initial unloading section of p-h curve, as per Oliver and Pharr method [87].

Quasi-static test might reveal the general deformation behavior, however, for the accurate assessment of elastic modulus and hardness in case of a film-substrate system, analysis as a function of contact depth is essential. Thus, dynamic nanoindentation is considered necessary to assess these properties as a function of contact depth.

3.4.2. Dynamic nanoindentation (continuous stiffness mode)

In order to study the depth-dependence variations in mechanical properties, dynamic nanoindentation is conducted in continuous stiffness mode (CSM) to study the contact stiffness, elastic modulus and hardness of ZTNN metallic glass. In this mode a harmonic force is added on top of the quasi-static increasing force, \( p \), on the indenter. The displacement response of the indenter at the excitation frequency and the phase angle between the two are measured in a continuous fashion as a function of contact depth. By solving the in-phase and out-of-phase portions of the response, contact stiffness as a function of depth is determined, thus allowing continuous measurement of mechanical properties [88]. Contact stiffness, \( S \), is given by:

\[ S = \left[ \frac{1}{\text{F}_{(0)}} \cos \phi - (K_r - m \omega^2)^2 - K_y \right]^{-1} \]  

where \( P_{osc} \), the magnitude of oscillation force; \( h(\omega) \), the magnitude of displacement; \( \omega \), the frequency of oscillation; \( \phi \), the phase angle between the force and displacement signals; \( K_r \), the spring constant; \( m \), mass of the indenter; and \( K_y \) the stiffness of indenter frame.

Contact stiffness varies linearly with contact depth in case of a uniform material having a constant elastic modulus [88]. However, for a non-uniform material (such as film-substrate system), the linearity does not exist as demonstrated [88]. This is also verified by the film-substrate system in case of ZTNN, Fig. 12(a). The linear relationship between contact stiffness and depth nearly holds up till 60 nm (approx. 10% of film thickness) and decreases with increasing contact depth, depicting that substrate influence is becoming prominent.

Fig. 12(b) shows the trend of hardness and elastic modulus as a function of contact depth. The hardness values at the very beginning may have come from the contribution of both surface oxides [89] and underlying non-oxidized metallic system. However, as the contact depth increases, the hardness continues to rise which can be ascribed to the substrate effect coming into action [90,91]. Likewise, the elastic modulus follows the same trend. Thus, to avoid this interference and determine the 'film-only' properties, a widely adopted rule of thumb is to limit the indentation depth below 10% of the film thickness [90,91]. Based on this criterion, the values for hardness and elastic modulus are averaged in the range of 30–60 nm (∼5–10% of the film thickness of ZTNN system).

The CSM nanoindentation test reveal high hardness of ZTNN (7.1 ± 0.12 GPa), which is comparable to other Zr-based metallic glasses [26,85,92]. The elastic modulus of ZTNN (121.7 ± 2.81 GPa) is comparable to the values of Ti (128 GPa) [93] calculated via nanoindentation methods, but is significantly lower than SS 316L (200 GPa). Nevertheless, further studies need to be conducted to decrease the elastic modulus sufficient to avoid stress-shielding effect.

4. Discussion

Why metallic glasses generally exhibit better corrosion resistance properties have been ascribed to multitude of factors, for instance, the
role of chemical composition, the role of structural and compositional homogeneity, as well as the role of intrinsic amorphous structure.

Role of chemical composition in governing the corrosion properties of metallic glasses is a familiar viewpoint [19,94,95] though it is challenging to separate this approach from the role of amorphous structure. Wang et al. have reported that corrosion behavior of Ni-Zr-Ti-Si-Sn metallic glass is more sensitive to chemical composition rather than structural homogeneity [94] which suggests the dominant role of chemical composition. The role of chemical composition is also endorsed by systems where corrosion behavior improves with certain alloying addition [95,96] implying that alloy composition plays a significant role in influencing electrochemical properties of metallic glasses.

Role of homogeneity (compositional and structural) is also critical in explaining why metallic glasses generally outperform their crystalline counterparts in terms of corrosion resistance properties. In case of polycrystalline and/or multi-phase materials, the corrosion phenomenon is governed by chemical and structural heterogeneities, for instance, precipitates, preferred crystal orientation, dislocations, and grain boundaries, that are vulnerable to localized attack leading to locally varying corrosion kinetics. The absence of these defects, along with the absence of galvanic effects (associated with multi-phase materials), is expected to result in higher corrosion resistance in metallic glasses [95]. However, this factor all alone is insufficient in explaining the better anticorrosion properties displayed by metallic glasses. For example, taking the homogeneity perspective into consideration, a Zr-Ni metallic glass and its single-crystal counterpart (both homogeneous in terms of composition and structure), should offer roughly similar corrosion resistance (if the intrinsic structural role is ignored). However, this is not the case, in a work reported by Wang et al. [45]. In this study, the authors have done a comparative electrochemical study of the metallic glass and its single-crystal counterpart and the better corrosion resistance of the former is ascribed to the role of amorphous structure influencing the composition and compactability of passive films (and not to the structural/chemical heterogeneities or grain boundaries).

The role of amorphous structure is also very influential, as the growth mechanism of passive film is sensitive to amorphous structure [45]. To further clarify the role of intrinsic amorphous structure and answer the fundamental question of why metallic glasses passivate spontaneously or lead to the formation of a less-defective passive oxide, a new explanation may be presented in terms of ‘atomic mobility’ [82]. According to this perspective, metallic glasses, unlike crystalline materials (that stay in lower energy wells corresponding to an equilibrium state), are thermodynamically in a metastable state having higher energy, and therefore, higher atomic mobility. Thus, the atoms in metallic glasses, as opposed to crystalline systems, are considered electrochemically more active [82] resulting in relatively faster passivation. In a study conducted by Tang et al. [82], a decrease in atomic mobility upon annealing of a Zr-Nb-Cu-Ni-Al metallic glass resulted in a decrease in passivating ability of the system due to a weakened migration ability of passivating elements [82]. However, it is important to mention that this approach works only in the case of passivating metallic glass systems and predict active corrosion in case of non-passivating systems (metallic glasses with high content of non-passivating elements). Apart from atomic mobility, the role of intrinsic amorphous structure upon corrosion behavior of metallic glasses, can also be explained in terms of bond length. Higher metal-metal bond strength may result in reducing the dissolution rate by raising the activation energy barrier for the disruption of metal-metal bonds [97]. This perspective is validated by
Tailleart et al. [98], in a comparative study of Al-Co-Ce as-quenched amorphous, thermally relaxed amorphous and devitrified systems. In this comparative study, the authors attribute the highest corrosion resistance of the thermally relaxed amorphous system to the shorter bond length, that decrease the corrosion kinetics from the perspective of bond cleavage energy. Nonetheless, the role of structure in governing the corrosion resistance properties of metallic glasses, akin to others, is also disputed as competing studies exist reporting the relatively higher corrosion resistance [72,99], relatively lower corrosion resistance [100] and approximately similar corrosion resistance [45,101] of

<table>
<thead>
<tr>
<th>MODEL ID</th>
<th>EQUIVALENT ELECTRICAL CIRCUIT</th>
<th>$R_{\text{TOTAL}}$</th>
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<tr>
<td>MODEL-A</td>
<td>![MODEL-A Diagram]</td>
<td>$R_{\text{ic}} + R_{\text{ct}}$</td>
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<tr>
<td>MODEL-B</td>
<td>![MODEL-B Diagram]</td>
<td>$R_{\text{ic}} + R_{\text{op}}$</td>
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<tr>
<td>MODEL-C</td>
<td>![MODEL-C Diagram]</td>
<td>$R_{\text{ct}} + R_{\text{por}}$</td>
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<tr>
<td>MODEL-D</td>
<td>![MODEL-D Diagram]</td>
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Fig. 10. Different EEC models widely reported for Zr-, Ti-based metallic glasses, titanium-based alloys and biomedical stainless steel. Model A and B represent a bi-layer oxide model, while C represents a single-layer oxide model. Model D has received diverse interpretations. $R_{\text{TOTAL}}$ represents the combined resistance.

M/O: metal-oxide; O/S: Oxide-solution; M/S: Metal-solution. Subscripts, ic: Inner compact oxide; op: Outer porous oxide; ct: Charge transfer; dl: Double layer; por: Porous oxide; s: Solution.
amorphous systems in comparison to their crystalline counterparts. This suggests that amorphous structure alone may not always justify the relatively higher corrosion resistance of metallic glasses in comparison to their crystalline counterparts.

Given these diverse explanations and competing reports, instead of relying on either compositional role, homogeneity role, or structural role, a composite effect, taking into consideration all the factors, may be used in explaining the higher corrosion resistance properties of ZTNN metallic glass.

Role of chemical composition in governing the electrochemical properties of ZTNN metallic glass is ascribed to the predominant matrix forming species (Zr & Ti, 75 at.%) possessing very high oxide forming tendencies as well as higher thermodynamic stabilities of their respective oxides in aqueous solution, as per their respective Pourbaix diagrams \[65,66\]. The compositional role in case of ZTNN can be further strengthened in view of a study conducted by Qin et al., where the high corrosion resistance of Ti-Zr-Pd-Cu-Sn is attributed to the Ti- and Zr-enriched protective surface film \[19\].

Role of structural and compositional homogeneity in case of ZTNN can be explained in terms of the very low I_cor in potentiodynamic scan (Section 3.3.2) prior to the formation of a complete barrier layer, and the highest R_n from EIS conducted at OCP (Section 3.3.4) suggesting that the homogeneity might be influencing the corrosion properties before the formation of a barrier oxide layer. However, it is worth mentioning that this role of homogeneity would have been clearer in case of a non-passivating system where surface oxidation would not blur the intrinsic role of structural and chemical homogeneity. Additionally, to substantiate the homogeneity perspective, a direct comparison of ZTNN metallic glass with its crystalline counterpart may be helpful in revealing if the structural/chemical heterogeneities in the crystalline system are deteriorating the corrosion properties via micro/nanoscale galvanic corrosion.

Intrinsic role of amorphous structure in case of ZTNN may be ascribed to the earlier passivation registered in potentiodynamic scan that may be ensured by the higher electrochemical activity of Zr & Ti in the amorphous matrix, leading to rapid surface enrichment of their respective oxides as demonstrated in XPS, Section 3.2.1. Furthermore, the formation of a barrier-type oxide layer as manifested by the very low I_cor(3.1 μA·cm⁻², Section 3.3.2) and the higher stability of the barrier layer at very high anodic potentials (even exceeding 1 V) may offer an explanation in justifying the role of amorphous structure. A likely explanation of such excellent stability can be linked to a less-defective compact oxide formed on the surface of ZTNN as reported elsewhere \[45\]. However, validating the role of amorphous structure may also require a direct comparison with crystalline counterpart. Therefore, further investigations may be done.

Implantable medical devices are commonplace today to treat cardiac dysfunction, orthopaedic conditions and many others necessitating surgical intervention. The materials used for such devices must possess very high resistance to corrosion and wear in human’s physiological environment to prevent adverse biological responses after implantation. Additionally, the materials should have sufficient strength capable of deforming or bending in response to the pressure or movements of the patient’s body or organs where they are implanted. Owing to metallic glasses’ superior electrochemical \[102\], mechanical and biocompatibility properties, they are gaining ground as ideal candidates for implantable medical devices including pacemaker \[103,104\], cardiovascular stents \[105,106\], knee-replacement devices \[104\], hybrid scaffolds \[107\], minimally invasive devices \[108,109\], high-

### Table 3

| System | R_n (MΩ·cm²) | CPE_n | | 2 | 3 | 4 |
|--------|--------------|-------| | 2 | 3 | 4 |
| SS 316L | 0.52 | 53.5 | 0.88 | 1.87 | 3.13 |
| cp-Ti  | 0.30 | 53.6 | 0.92 | 1.78 | 3.12 |
| ZTNN   | 6.9  | 19.9 | 0.97 | 7.28 | 1.05 |

![Fig. 11. Quasi-static load-unload curves using nanoindentation. The slope of the unloading section at the beginning of unloading portion is used to determine elastic modulus.](image1)

![Fig. 12. (a) Contact stiffness as a function of contact depth showing a nearly linear trend up till a certain point (patterned region), followed by non-linearity. (b) The trend of elastic modulus and hardness as a function of contact depth, both properties being influenced by substrate effect. The patterned region (~5–10% of film thickness) is taken to calculate the average hardness and elastic modulus of ZTNN.](image2)
performance biosensors [110], and dental implants [111] etc. Other exciting areas where metallic glasses may be considered ideal, include the development of implantable medical devices with complex geometries. Metallic Glasses are among the strongest artificially engineered materials, yet they allow to be molded like polymers. This polymer-like formability allows complex geometries and thus may allow the fabrication of miniaturized micro-/nano-architected medical devices with high complexity and precision, for diverse biomedical applications. The ZTNN metallic glass with high corrosion resistance, high hardness, and moderate elastic modulus, may thus find applications in the area of implantable medical devices, specifically in micro−/nanoarchitectured metallic glasses with high strength and compressive plasticity, Adv. Eng. Mater. 8 (10) (2006) 953–957.


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