Nanostructured Zr-Pd Metallic Glass Thin Film for Biochemical Applications

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Zr-Pd metallic glassy thin films with a hierarchical nano-scale structure, produced by magnetron sputtering of the Zr and Pd powder mixture, demonstrate a unique combination of physical and biochemical properties. Thermal stability of the nano-structured glassy samples, their resistance to oxidation in dry air and phase transformation behavior are discussed in the present work. These binary alloy samples also show exceptionally high corrosion resistance and spontaneous passivation in a simulated body fluid. Experiments on the catalytic activity and biocompatibility of this nanostructured metallic glass indicate that this is a very suitable material for biochemical applications. Compared to the multicomponent alloys studied earlier this binary alloy has much simpler chemical composition, which makes preparation of the sample with defined stoichiometry easier, especially when the elements have different sputtering rates.

A s a rule metallic alloy samples have a polycrystalline structure after solidification. Casting of commercial alloys even into a thin mould (with a cavity thickness of about 1 mm) produces a crystalline structure which is typical for metallic materials. Following the earlier works on rapidly solidified metallic glasses, a large number of metallic glassy alloys in the different alloy systems, including bulk glassy samples, have been produced in the past two decades by using various casting processes1–5. Physical vapor deposition methods are widely used to produce metallic glassy thin films. However, even by these methods, which have one of the highest available cooling rates, thin films with amorphous structure only of the certain chemical composition can be obtained6.

Both Zr- and Pd-based alloys (Pd alloys being flux treated) are the best metallic glass-formers known up to date7–9. Zr-Pd system alloys were used to produce thin metallic glassy ribbon samples (∼20 μm thick) by melt spinning. The formation of a primary nanoquasicrystalline phase was observed in Zr-rich area on heating10,11. It was shown that local atomic structure of the Zr65Pd35 glassy alloy is well described by taking into account the icosahedral atomic configuration12. It was also found that ZrxPd1-x (x = 0.59, 0.63, 0.67, and 0.70) amorphous alloys exhibit negative temperature coefficient of the resistivity between 10 and 300 K. These amorphous alloys also exhibit a transition to superconductive state at low temperatures13.

Nanostructured metallic glasses or nanoglasses, consisting of irregularly placed spheroid glassy nanoparticles, represent a new and unique group of metallic materials with novel physical and chemical properties owing to their large surface area14. Metallic nano-glasses were first discovered several decades ago. Prof. Gleiter and his research group members fabricated nanoglasses by compaction of the spheroid nanoparticles produced by the inert gas condensation method15. Similar materials also can be produced by phase separation16,17. At certain conditions, individual metallic glassy particles of alloys18 and even pure metals were also obtained19. Recently, nanostructured metallic glasses were also produced by magnetron sputtering20. It was found that Au-based20 and Ti-based21 nanoglasses have good catalytic activity and biocompatibility, respectively. Also Fe80Sc10 nanoglassy samples, unlike ribbon samples with a homogeneous glassy structure of the same chemical composition, exhibit ferromagnetism at room temperature22.

Both Zr and Pd are suitable constituent elements for biomaterials and Pd is also a good catalyst for certain chemical reactions. In the present paper we investigated the Zr-Pd amorphous thin films with nano-grained structure, prepared by magnetron sputtering technique. We also present their functional properties: resistance to corrosion and oxidation as well as their catalytic activity and biocompatibility.
Results

High catalytic activity of Pd in crystalline state is well known. Therefore, a glassy sample with high catalytic activity is presumed to contain as much Pd as possible. In present work, concentration of Zr in the sputtered films was varied from 10 to 46 at.%. X-ray diffraction patterns of the films with different Zr concentration are presented in Figure 1. As one can notice, only at 46 at.% of Zr (and above) the sputtered thin film becomes fully amorphous. However, further experiments on biocompatibility in the cell culturing solution revealed that, owing to the weak adhesion to the substrate, pieces of the nanoglass detached from the sample destroying osteoblasts. Therefore, in further experiments the compositions with lower palladium content were used. Also, according to the Pd-Zr phase diagram, higher Zr concentration leads to deeper eutectics and more stable glasses. Finally, the nominal composition of 60 at.% Zr – 40 at. % Pd was chosen. Its X-ray diffraction pattern is shown in Figure 2.

According to the results of Gaussian fitting of the first diffraction maximum ranged from 35 to 46 degrees of 2θ in the X-ray diffraction pattern of the sputtered film (Figure 2) the center mass of the peak is located at 40.31 ± 0.05°. This value is not far from 37° of 2θ value obtained earlier for Zr70Pd30 glassy alloy prepared by melt spinning. The difference is owing to somewhat higher Pd content in the sputtered alloy. This element, being smaller than Zr in size (Goldschmidt atomic radius of Zr is 160 pm while Pd has a size of 138 pm) causes a shift in the peak position. High-resolution transmission electron microscopy and selected-area electron diffraction patterns also confirm amorphous nature of the sputtered films (Figure 2a, b).

The scanning electron microscopy (SEM) images obtained at different magnifications illustrate the granular morphology of the films (Figure 2c, d). The resulted composition measured by x-ray energy-dispersive analysis (EDX) installed in SEM over a large area of about 10μm² was 62.5 ± 0.2 at.% Zr and 37.5 ± 0.2 at.% Pd. The average composition and confidence interval values were obtained as a result of five independent measurements. The difference with the intended composition could be due to the inhomogeneous distribution of the powder particles on the target surface and the difference in the sputtering yields of each component.

X-ray photoelectron spectroscopy (XPS) analysis of the as sputtered films surface revealed that the surface oxide film mostly consists of Zr atoms in 4+ oxidation state (Zr⁴⁺ peaks are very weak in Figure 3a). It is interesting to note that Pd²⁺ is also present in the surface oxide (Figure 3b) which indicates that Pd on the surface is also partially oxidized.

Thermal stability and oxidation behavior of the sputtered films were investigated. Isothermal annealing of the samples was carried out in the sputtering chamber, filled with dry air, right after the films preparation (temperature range: 100–500°C (373–773 K) for 1 hr (3.6 ks)). Analysis of the X-ray diffractometry (XRD) results (Figure 3c) revealed that annealing of the film in the temperature range of 100–300°C (373–573 K) does not lead to the formation of thick surface oxide and the surface retained its metallic color. Sharp peaks appeared in the XRD pattern only after annealing at 400°C (673 K). They were found to belong to the crystalline ZrO₂ (cubic symmetry, Pearson symbol cF12). The annealing at 500°C (773 K) caused formation of monoclinic mP12 ZrO₂ and tP4 PdO. Early crystallization stage of the metallic glassy matrix in dry air starts with the formation of the weak diffraction peak at 2θ = 40.2° which may belong to the FCC Pd. Also, after annealing at 400°C (673 K) the color of the films surface changed from metallic to violet due to the oxidation, which is in agreement with the XRD results. One can also note that the XRD peaks, which belong to the ZrO₂ formed at 773 K, are significantly broader compared to those of the ZrO₂ formed at 673 K, which implies nanocrystallization of the surface oxide at 773 K. It should be noted here, that before in-situ annealing in the sputtering chamber for each annealing temperature an independent sample was prepared.

Corrosion behavior and chemical stability of the samples were studied in a simulated body fluid (Hank’s solution, a water solution...
Figure 2 | X-ray diffraction pattern of the sputtered film with 60 at.% of Zr. The inserts (a) high-resolution transmission electron microscopy, (b) selected-area electron diffraction pattern and (c and d) SEM images obtained in secondary electrons at different magnification and (e) particles size distribution calculated from the SEM images (c) and three fits using Lognormal (full range and up to 12 nm size) and Gaussian (up to 12 nm size) function.

Discussion

Physical vapor deposition methods including the magnetron sputtering technique, having high cooling rates (higher than 10⁶ K/s), are powerful tools to produce amorphous metallic thin films. However, even these methods do not always ensure formation of amorphous film. It may be partly connected with a relatively low deposition rate (about 110 pm/s) which allows surface diffusion to take place during deposition. In the present work, fully amorphous films were obtained only at high enough Zr content. In general, the obtained results correlate with the empirical rules introduced by Inoue. In Pd-rich side the eutectic point is located at 40.1 at. % Zr, but only the films containing 46 at.% Zr or more were in amorphous state. The deeper eutectic point at 25 at.% Pd content allowed to produce even more stable glassy film.

Thin films with an extremely fine glassy nano-granular structure (Figure 2c), as well as smooth thin films can be obtained via magnetron sputtering. Here we consider not individual glassy particles, but a material consisting of spheroid glassy particles connected by the glassy interfaces of the similar to the particle chemical composition. Fitting of the glassy particle size distribution (Figure 2e) with Lognormal distribution function (Lognormal Fit 1) gives the average size of about 6.5 nm (coefficient of determination R² = 0.929). If one removes the small fraction of the largest particles the (Lognormal Fit 2) the distribution becomes less well described (R² = 0.887), while the Gaussian fit produces the best fit (R² = 0.998) with the average particles size of 6 nm. These results indicate that real distribution is rather neither normal nor lognormal (right side part of the distribution is more steep compared to lognormal one), though both allowed to estimate the average particles size at 6–7 nm. Nevertheless, the absolute majority of the particles (99%) have a size ranging from 2 to 12 nm. At the same time, one can see that the sample
has a hierarchical structure, where small particles below 12 nm in size are clustered, forming larger quasi-particles or columns which are roughly about 50 nm in size (see Figure 2c,d). Such a hierarchical (fractal-type) structure is known to be suitable for biomaterials. Ti-Zr-Cu-Pd nano-structured metallic glass, having a similar structure, was recently tested as a coating for biomaterials, and found to be suitable for living cells attachment.

High corrosion resistance of the Zr-Pd samples with extremely low current density of about 3.5 mA/m² (at 0.6 V) in a simulated body fluid provides compelling evidence that this nanostructured material can be applicable as a protective coating for biomaterials. Spontaneous passivation is achieved and low current density below 6 mA/m² maintains up to a very high potential of 1 V. This potential value is very high for metallic glasses and up to 1.1 V current density rise is very small (only about two times) while many other Zr-based metallic glasses studied earlier, exhibit a steep increase in the corrosion current after 0.5–0.6 V. Obtained average current density value of about 3.5 mA/m² in the passivation region is very low for metallic alloys. Actual value per area should be even lower considering a non-smooth surface of the sample on the nanoscale (Figure 2c,d). The average current density value is lower than those values obtained for Ti-based, Zr-based, and Fe-based glassy alloys as well as for crystalline alloys.

Zr as well as Ti forms a passive oxide layer. In addition, Zr ions show lower cell cytotoxicity than Ti. Moreover, the corrosion current density for pure Zr from its potentiodynamic polarization curve in Hank’s solution at 0.3 V is about 15.3 μA/cm² which corresponds to 153 mA/m² and is significantly higher than that of the present nanostructured glassy alloy.

It was previously found that the addition of Pd to crystalline Zr decreases the passive current density. This indicates the stability of the passive film and decrease the amount of released metal ion at passive state. Among the six pure metals investigated for in vitro
cytotoxicity together with palladium alloys, Au, Pd and Ti were found to be the least cytotoxic, followed by Ag, then Ni, and finally Cu37.Pd42.5Cu30Ni7.5P20 bulk metallic glassy samples in Hank's solution exhibited passive current densities of the order of 10^{-2}–10^{-1} \text{A/m}^2 (10–100 \text{mA/m}^2) in the anodic polarization curves, which are higher than those observed in the present Zr-Pd alloy.

Moreover, the investigation of the thermal stability and oxidation process of the nano-structured glassy samples showed that the present samples are steady against oxidation in a dry air up to 673 K while thermal crystallization of the glassy matrix is detected after annealing for 1 h at 773 K. This is consistent with the differential scanning calorimetry studies of the crystallization process in Zr70Pd30 and Zr65Pd35 glassy alloys studied earlier, which exhibited crystallization temperature of 727 and 771 K, respectively, at a heating rate of 0.67 K/s. Following the observed tendency, the present Zr62.5Pd37.5 nano-structured glassy alloy should have even higher crystallization temperature (Tc) at such a heating rate (Tc is the heating rate dependent). Moreover, an increase in the crystallization temperature of the nanoglassy samples was reported recently. At 673 K only Zr severely oxidizes forming cubic form of ZrO2, while at 773 K Zr forms the monoclinic form of ZrO2, and even Pd starts to oxidize forming PdO (Figure 3c). This result is in consistence with oxidation of pure Pd performed at 823 K.

It was shown that melt-spun Zr70Pd30 monolithic glassy alloy samples underwent fast oxidation at 653 K in 30 min forming simultaneously two polymorphs of ZrO2: tetragonal and monoclinic with underlying crystalline Pd41. Fast "catastrophic" oxidation of glassy Zr70Pd30 and Zr65Pd35 was also observed and reported in Ref. 42. It was correlated with the formation of a lamellar structured scale consisting of the two phases, i.e. monoclinic and tetragonal ZrO2, thus allowing fast oxygen diffusion. In addition, elements like Pd or Au found to accelerate the oxygen diffusivity in ZrO2. Present results, however, indicate that nanostructured glassy films are quite stable up to 573 K.

XRD analysis of the annealed films revealed the existence of an untransformed metallic glassy phase underneath ZrO2, even after annealing for 1 h at 673 K in dry air. Only at 773 K a minor fraction of a crystalline phase starts to form in the metallic glassy matrix. This finding allows us to anticipate that the nanostructured metallic glass is more stable against crystallization than the homogeneous one, produced by the melt spinning technique.

After electrolytic polishing of the native surface oxide the sample exhibited a moderate catalytic activity in Suzuki-coupling reaction owing to the presence of a catalyst - Pd and nanostructured surface morphology of the sample with relatively large surface area. Earlier, such a behavior was also observed in de-alloyed nanoporous Pd-Ni-P metallic glassy sample. Pd-Si metallic glasses were also applied such a behavior was also observed in de-alloyed nanoporous Pd-Ni-P metallic glassy sample. Pd-Si metallic glasses were also applied.
Figure 7 | Alkaline phosphatase activity (a), calcium secretion (b), proliferation (c) and live/dead staining of cells (d) cultured on Ti and metallic glass (MG) for 7 days.
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Author contributions
S.V.K. and D.V.L.-I. wrote and corrected the manuscript text and figures, X.T. Sh. and H.W. prepared fig. 6 and wrote the biocompatibility part, G.X. and R.K. prepared fig. 3 and wrote XPS measurement part, A. Yu. Ch., A.I.B. and N. Ch. prepared fig. 4 and wrote corrosion testing part, Y.I. and N.A. prepared fig. 5 and wrote catalytic activity part. All authors reviewed the manuscript.

Additional information
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