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Thin films of binary amorphous Zn-Zr alloys developed by magnetron co-sputtering for the production of degradable coronary stents: A preliminary study

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1. Introduction

Vascular stents are endo-prostheses that allow the restoration of blood flow in case of obstruction of a vessel. A stent usually consists of a corrosion-resistant metal such as Nitinol, 316L steel or a CoCr alloy [1]. Many studies have been undertaken for the production of polymer degradable stents [2,3] or metallic stents [4,5] and, among these, devices made of pure zinc or crystallized alloy based on zinc obtained by molding and extrusion are promising in terms of biodegradability, biocompatibility and mechanical properties [6], but also concerning the degradation rate of the stent which should to be effective until arterial remodeling and tissue healing are complete [5]. The objective of this preliminary study is the comparison of the degradation in simulated biological medium and the endothelial cytotoxicity of amorphous and crystallized thin ZnZr films according to their composition and structure. In this work, the thin layers were deposited on silicon substrates by magnetron co-sputtering. This technology is already used to make metal stents [7,8].

2. Materials and methods

The thin layers are made in the 4-source magnetron sputtering frame on silicon substrates. Two pure metal targets (Zinc and Zirconium) with a diameter of 2 inches and a thickness of 6 mm were used. A Schematic of the magnetron RF co-sputtering system and ZnZr plasma deposition are presented in Fig. 1.

2.1. Preparation of thin layers

ZnZr binary thin film metallic glasses with different compositions were prepared on silicon substrate by RF magnetron co-sputtering technique using Zn and Zr pure metal targets. The operating conditions were set at a base pressure lower than 10^{-5} Pa, a working pressure of 0.5 Pa and an Ar flow rate of 40 sccm. The sputtering time was varied with a sputtering power in 25–100 W and 25–200 W range for Zn and Zr targets respectively. The atomic content of Zn in the films increases with increasing the power ratio (P_{Zn}/P_{Zr}) applied to the two targets Zn and Zr. Deposition conditions and chemical composition are presented in Table 1.

2.2. Characterization of thin layers

The chemical composition of the thin layers after deposition was determined by energy dispersive X-ray spectroscopy (EDX) using a SEM-EDX LEICA S440. The acquisition was performed for a voltage of 15 kV and a probe current of 1000 pA. The thickness of the thin layers after deposition as well as their morphology after deposition and after degradation were obtained following the respective observation of their cross section and their surface under a scanning electron microscope with a field emission gun (SEM-FEG) ZEISS Supra 40VP. A voltage of 5 kV is used. The crystalline structure

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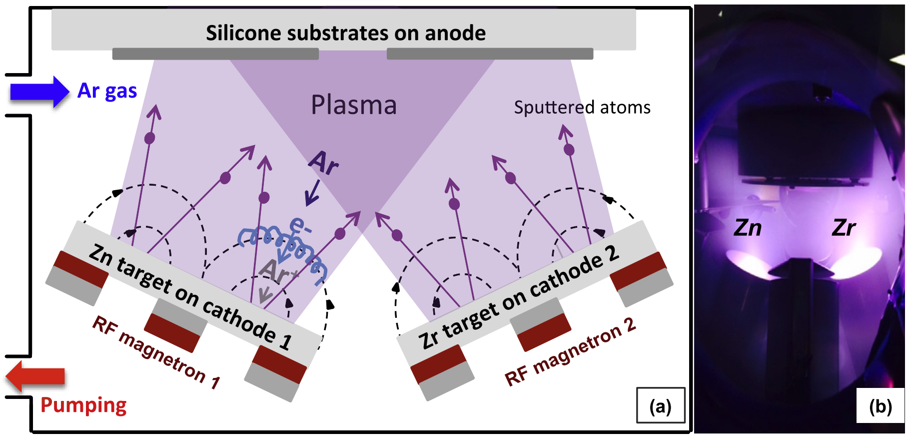

Fig. 1. (a) Schematic of the magnetron RF co-sputtering system and (b) image of ZnZr plasma deposition.

Table 1
Deposition parameters, film thickness, and chemical composition of the ZnZr thin films deposited by RF magnetron co-sputtering.

	Zn power (W)	Zr power (W)	P_{Zn}/P_{Zr} Power ratio	Deposition temp. (°C)	Annealing temp. (°C)	Film thickness (nm)[a]	Chemical Composition (EDX)[b]	
							Zn (% at.)	Zr (% at.)
ZnZr1	25	200	0.125	RT	–	330	16.1	83.9
ZnZr2	50	200	0.25	RT	–	334	29.8	70.2
ZnZr3	100	200	0.5	RT	–	291	37.3	62.7
ZnZr4	100	100	1	RT	–	275	55.8	44.2
ZnZr4-200	100	100	1	200	–	nd	53.1	46.9
ZnZr4-A300	100	100	1	–	300	275	55.3	44.7
ZnZr5	100	25	4	RT	–	276	91.7	8.3
ZnZr5-200	100	25	4	200	–	209	80.5	19.5
ZnZr5-A300	100	25	4	–	300	276	89.0	11.0

[a] ±10 nm.
[b] ±SD = 3–5%.

of the films was determined by the analysis of X-ray diffraction (XRD) spectra obtained using an Inel EQUINOX 1000 diffractometer in the Ω-2θ configuration equipped with a curved detector and an anticathode of Cobalt. The measurements were made for an angle of incidence of 2° and the line Kα1 of Cobalt (λ = 1.789010 Å). JCPDS data sets have been used for Zr hexagonal phases (JCPDS: 04-004-5064 and 04-006-2822) and Zn hexagonal phase (JCPDS: 04-008-6027). ZnZr thin layers were ex-situ investigated by X-Ray Photoelectrons Spectroscopy (XPS) performed with a Kratos Ultra Axis spectrometer using Al Kα radiation (photon energy 1486.6 eV) and 20 eV analyzer pass energy. The chemical composition of ZnZr films could be determined by the integration of Zr3d and Zn3p core level peaks, for Zr and Zn respectively.

2.3. Degradability of thin layers and corrosion test

The samples (0.7 cm 2) are each placed in 5 ml of simulated body fluid (SBF) [9] at 37 °C under gentle shaking. After 1 week or 2 weeks the samples are rinsed with distilled water and dried in an oven at 40 °C and their surface is observed under a scanning electron microscope. For corrosion study, electrochemical experiments were conducted in a standard three electrodes cell with 0.8 cm^2 of exposed area in the working electrode, having a platinum mesh as counter electrode and Ag/AgCl electrode as reference. The working electrolyte of simulated body fluid (SBF) was introduced in Teflon® cell at 20 °C. The corrosion test was evaluated by DC polarization curves. The immersion time of each sample was 1 h to investigate the corrosion current density (I_{corr}) and corrosion potential (E_{corr}). The voltage was scanned between −1 V and 0 V with a scan rate of 0.05 V/s. The corrosion current density (I_{corr}) was obtained using Tafel extrapolation technique at ± 50 mv around open circuit potential. DC test was carried by Autolab PGSTAT. For each sample, two replications were performed. An anodization of the two samples ZnZr4 and ZnZr5 made at RT were conducted at 1 V during 1 h in SBF.

2.4. Cytotoxicity test

Human umbilical cord vein endothelial cells (HUVEC-Cs, ATCC) were seeded on the samples at a density of 2×10^4 cells/cm^2 in DMEM containing 10% FBS and 1% Antibiotic-Antimycotic. Cell viability was analyzed after 72 h using a resazurin based metabolic activity assay (In vitro Toxicology Assay Kit, Sigma Aldrich®) following the manufacturer's instructions. Experiments were carried out according to the ISO 10993-5: 2009 standard applicable to the MTT and resazurin tests. The fluorescence intensity, proportional to the cell number, was normalized to control cells seeded in multi-well plate. Experiments were performed in triplicate with n = 8. Statistics were performed using One-way Anova and a Tukey post test.

3. Results and discussion

According to the model of Egami and Waseda [10] and the work of Braic and co-workers [11] we have established that amorphous ZnZr alloys could be synthesized for zirconium concentrations between 23% at. and 70% at. Table 1 gathers the experimental conditions, composition and thickness of ZnZr films for zinc