Characterisation of Mg biodegradable stents produced by magnetron sputtering

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Abstract. Novel Mg-minitubes for biodegradable stent applications have been produced using PVD magnetron sputtering. The minitubes were characterised, as a function of annealing temperature, using a combination of SEM/EDS, XRD and hardness testing. The as-deposited minitubes exhibited columnar grain structures with high levels of porosity. Slight alteration to the crystal structure from columnar to equiaxed grain growth was demonstrated at elevated temperature, along with increased material densification, hardness and corrosion resistance.

1. Introduction

Biomaterials used for stents may be metallic, polymeric or composite structures. Metals, such as stainless steel, titanium alloys and super-elastic shape memory alloys such as NiTi, have received much attention due to their biocompatibility combined with their mechanical properties [1]. However, there is interest to develop biomedical implants such as coronary stents, with a temporary function, using biodegradable materials such as Magnesium-alloys rather than degradable polymeric materials with inferior mechanical properties and degradation profiles [2]. Biodegradable stents are expected to provide a temporary opening into narrowed arterial vessels and then progressively disappear once the vessel remodels. The aim is to address the clinical problems associated with in-stent restenosis and long-term thrombosis, and eliminate the need for prolonged antiplatelet therapy [2]. Mg alloys have shown sufficient cytocompatibility and the amount of Mg^{2+} ions released through degradation processes is negligible compared to the physiologic plasma concentration [3] for stent applications. Here, we report on a study to fabricate Mg narrow walled tubes (Mg minitubes), for stent applications, using magnetron sputtering and an investigation into the effect of post deposition heat treatments.

2. Materials and Methods

Highly pure (99.95%) Mg coatings were deposited using a commercial-scale, closed-field, unbalanced magnetron Physical Vapour Deposition (PVD) coating system (Teer Coatings Ltd. UK). Two diametrically opposed circular magnetrons mounted vertically on the chamber side walls were used with pure (99.95%) Mg targets of diameter 57 mm. Commercially available stainless steel spinal needles of outer diameter 1.2 mm and length ~ 80 mm (Becton Dickinson-BD) were used as substrates, covered by a very thin sacrificial layer. Substrates were mounted on supporting pins held on a twin-axis jig connected to a rotary fixture on the chamber base, thus facilitating even 360° coating of the needle substrate within the plasma fields of the two magnetrons.

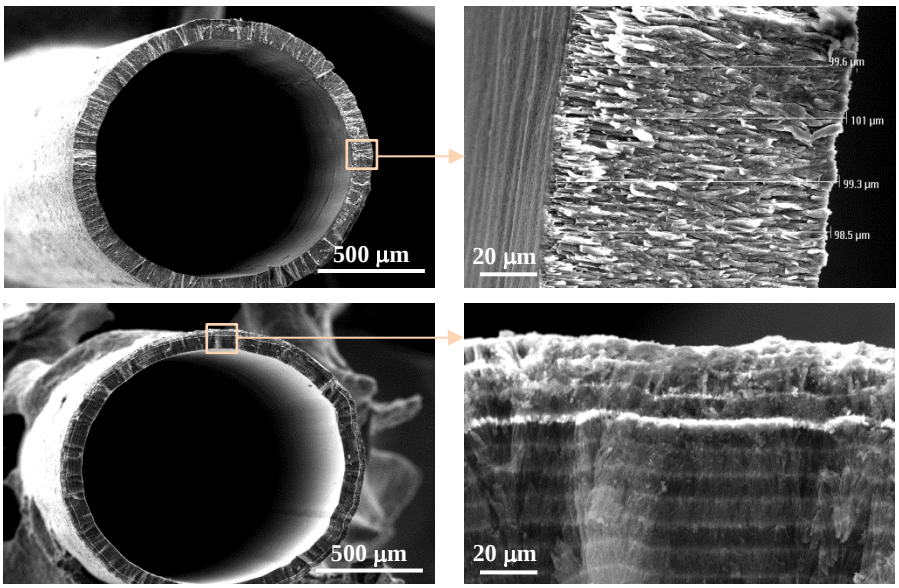

Figure 1 SE images of the fracture surfaces of (a,b) an as-deposited Mg minitube and details of the coating structure; (c,d) Mg minitube annealed at 400°C and details of the annealed coating structure.

A base pressure of 2.0 x 10^{-5} torr was establish prior to deposition and a controlled flow (50 sccm) of Ar (BOC Pureshield, 99.998%) was admitted into the chamber with deposition pressure maintained at ~ 1×10^{-3} torr. Sample rotation was set at 2 rpm, and a DC current of 0.3 A was applied to both Mg targets. Samples were rotated within the deposition plasma for a period of 8 h, which added ~ 9-10 µm of Mg layer thickness. Upon completion of each deposition phase, following a 30 minute cool down period, the chamber was vented, the twin-axis sample stage removed and fresh Mg targets were mounted on both magnetrons; the sample stage was re-admitted to the chamber and pump-down recommenced prior to continued layer deposition. A total of 10 such Mg depositions were conducted in order to build a tube with layer thickness ~ 100 µm. Tubes were coated with a final layer of hydroxyapatite (HA) of ~ 100 nm thickness from a similar sized target of HA by radio frequency magnetron sputtering. The minitubes were heat treated, post-deposition, at temperatures of 300°C, 400°C and 450°C under mixed He/H_2 conditions to eliminate oxidation effects during crystal regrowth. Tubes were also heat treated up to 600°C under Ar to encourage more strongly grain regrowth. Samples were allowed to cool slowly to room temperature under flowing Ar.

The Mg-minitubes were imaged using SEM (FEI XL30, 15 kV, spot size 4, working distance 10 mm), whilst EDS was used to appraise minitube chemistry. Complementary XRD (Bruker AXS D8 Advance, Cu K_α (λ= 1.54060 Å), 40 kV, 35 mA) was used to appraise the microstructure of the as-deposited and heat treated minitubes, whilst mechanical properties were appraised using Vickers microhardness indentation in cross-section. A potentiostat (VoltaLab PGZ 100, UK) was used to investigate the corrosion behaviour of the as-deposited and heat treated Mg-minitubes. Corrosion tests were performed using a jacketed three-electrode corrosion cell, with the tested metal cross-section being the working electrode; a $0.5\times10\times10$ mm Pt sheet the counter electrode; and saturated calomel (Hg_2Cl_2) the reference electrode (Thermo-scientific, UK). Phosphate buffer solution (PBS, 125 mL, pH 7.2 ± 0.06) was used as the test solution and a controlled-temperature water bath was used to establish a body temperature of 37±1°C. Prior to sample immersion, the O_2 level in the PBS was reduced by bubbling N_2 at a rate of 2 sccm for 30 min. A 1 h settlement was used to establish the open circuit potential (OCP, E_{oc}). A potential scan rate of 5 mV min^{-1} was applied, from -200 mV to +500 mV with respect to E_{oc}.

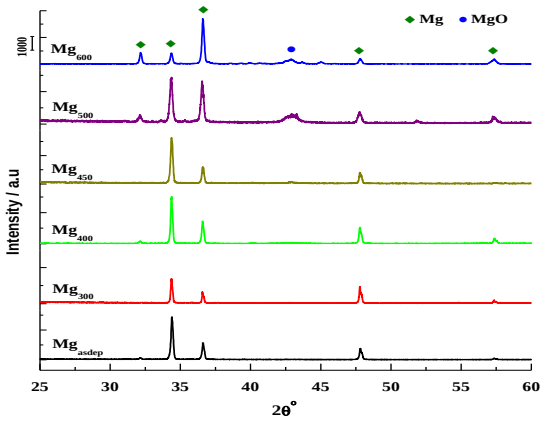

Figure 2. XRD patterns for the as-deposited and annealed Mg-minitubes

Sample	Hv	Corrosion behaviour	
		E_{cor} (V)	CR (mm/yr)
$Mg_{as\text{-}dep}$	38.7 ± 3.5	-1.66	270.1
Mg_{300}	40.0 ± 6.1	-1.55	45.2
Mg_{400}	51.6 ± 4.1	-1.57	67.1
Mg_{450}	31.9 ± 6.5	-1.55	17.3
Mg_{500}	52.1 ± 9.6	-1.57	4.6
Mg_{600}	32.6 ± 7.3	-1.37	16.0

Table 1. Hardness values and corrosion parameters for the as-deposited and annealed Mg minitubes

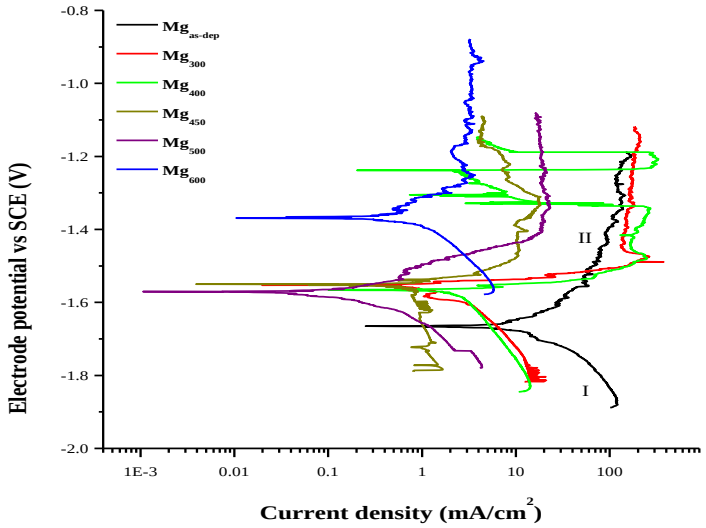

Figure 3. Potentiodynamic polarization curves for as-deposited & annealed Mg-minitubes in PBS at 37°C

3. Results

The Mg minitubes were successfully produced by magnetron sputtering. The total tube wall thickness was ~ 100 µm, as expected. In general, the minitube internal surfaces exhibited wrinkles and folds due to the influence of the sacrificial substrate, whilst the outer surface exhibited rough surfaces with voids and cracks. Figure 1a illustrates the fracture surface of an as-deposited Mg minitube, whilst figure 1b indicates brittle fracture and the presence of a columnar grain structure. Figure 1c illustrates an Mg minitube following annealing at 400°C, whilst figure 1d illustrates details of a layered structure, indicative of oxidation at the interfaces between the sequential Mg deposits, whilst also suggesting a less brittle fracture mechanism. EDS investigations revealed the presence of some Si within the minitubes, originating from the sacrificial layer.

Complementary XRD data (figure 2) confirmed that the as-deposited minitubes were single phase, polycrystalline, columnar-structured Mg, with an intense 002-reflection suggesting preferred growth along the c-axis, which is typical for magnetron sputtered Mg coatings. The as-deposited HA capping layer was found to be amorphous (~100 nm thick). Evidence for MgO formation was detected in samples annealed above 400°C. The average hardness of the as-deposited samples was 38.7±3.5 Hv (Table 1), which is in the lower range for bulk cast Mg, whilst hardness values were variable but increased to a maximum of 52.0 Hv upon annealing at 500°C, suggesting possibly an increase in densification.

Figure 3 present typical potentiodynamic polarization curves for the as-deposited and annealed Mg minitubes, immersed in aerated PBS at 37°C. Table 1 also summarises technical values for the onset and rate of corrosion extracted from these curves. The as-deposited minitube showed normal hydrogen evolution in the cathodic region with the development of a typical Tafel region (I). Fast passivation acted to slow down the generation of Mg^{+} ions during rapid anodic passivation (II). The annealed Mg-minitubes showed generally increased noble behaviour, as compared with the as-deposited sample, demonstrating increased resistance to the onset of corrosion, with the minitube annealed at 600°C showing the most resistance at -1.37 V. A general reduction in the rate of corrosion was also measured as a function of annealing, with best performance shown for the hardest sample annealed at 500°C.

3. Discussion

It is evident that using this novel PVD technique to build up Mg structures, layer by layer, can be an appropriate method for the production of thin, narrow-walled biodegradable stents. However, the as-deposited minitubes exhibited weak mechanical properties, *i.e.* low ductility and flexibility, and a highly brittle nature, whilst increased densification and improved corrosion resistance was demonstrated with annealing.

The developed tube microstructures were compared with the models proposed by Thornton for growing PVD thin films, as a function of temperature and working gas pressure [4]. The Mg minitubes exhibited similar features with zones of tapered grains separated by voids. More dense structures preserving initial nuclei orientations were formed at higher temperatures. However, all of the tubes exhibited high levels of porosity. Preferred orientation along the c-axis is recognised as a strain relief mechanism. Full re-crystallisation of the Mg-minitubes at elevated temperature was not achieved, although some alteration from anisotropic to isotropic grain growth was indicated from XRD, suggesting a process of limited recrystallization at voids and open grain boundaries, consistent with the slight increase in hardness.

The Mg-minitube behaviour varied dramatically when exposed to corrosive environments, with the as-deposited minitube being highly reactive within PBS, limiting its practical use within the biological environment. However, the corrosion resistance of the Mg minitubes improved significantly after heat treatment. The combination of partial grain regrowth, increased densification and oxide layer formation at the Mg layer interfaces, and possible oxide formation around the Mg grains, after annealing at ~ 500 – 600°C, is suggested as the reason for the reduced rate and delayed onset of corrosion.

4. Summary

Mg minitubes, being a candidate system for a biodegradable stent, have been produced using PVD. They exhibited columnar growth structures with open grain boundaries. Slight alteration to the crystal structure of the as-deposited minitubes from columnar to equiaxed grain growth was demonstrated at elevated temperature, with slight increase in material hardness, accompanied by improved corrosion resistance in PBS.

Acknowledgements

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References

[1] Hanawa T 2009 *The Japanese Society for Artificial Organs* **12** 73
[2] Hermawan H, Dubé D and Mantovani D 2010 *Acta Biomaterialia* **6** 1693
[3] Brown D, Lee E, Loh C & Kee S 2009 *Journal of Vascular and Interventional Radiology* **20** 315
[4] Thornton J 1977*Annual Review of Materials Science* **7** 239