

Glass-ceramic coated Mg-Ca alloys for biomedical implant applications



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ABSTRACT

Biodegradable metals and alloys are promising candidates for biomedical bone implant applications. However, due to the high rate of their biodegradation in human body environment, they should be coated with less reactive materials, such, for example, as bioactive glasses or glass-ceramics. For this scope, RKKP composition glass-ceramic coatings have been deposited on Mg-Ca (1.4 wt%) alloy substrates by Pulsed Laser Deposition method, and their properties have been characterized by a number of techniques. The prepared coatings consist of hydroxyapatite and wollastonite phases, having composition close to that of the bulk target material used for depositions. The 100 μm thick films are characterized by dense, compact and rough morphology. They are composed of a glassy matrix with various size (from micro- to nano-) granular inclusions. The average surface roughness is about 295 ± 30 nm due to the contribution of micrometric aggregates, while the roughness of the fine-texture particulates is approximately 47 ± 4 nm. The results of the electrochemical corrosion evaluation tests evidence that the RKKP coating improves the corrosion resistance of the Mg-Ca (1.4 wt%) alloy in Simulated Body Fluid.

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1. Introduction

Recently, several research groups have investigated the idea of biodegradable metals to be used as materials for implants, helping tissue regeneration, supporting the healing process, and degrading completely and harmless [1,2]. With this regards, there is a considerable interest for magnesium (Mg) alloys application as biodegradable materials with the scope to substitute the existing metallic implants in such applications as, for example, long bone fixator having the role of a support as long as it is necessary for natural healing [3,4].

Magnesium alloys, due to various advantages they have, are very promising for surgical implants. Their good biocompatibility and the ability to decompose in the body, as well as the functional role of Mg for physiological systems, make them attractive candidates for biodegradable implants. Moreover, magnesium's outstanding physico-chemical and mechanical properties, especially strength and elasticity modulus – as well as its density, very closed to that of the natural bone, make it appealing for tissue engineering applications [5].

The biggest obstacle to use Mg as material for biomedical implants is the fact that its degradation in the human body conditions is too fast, compared to the new tissue growth rate around the implant, since its corrosion rate is high [6,7]. In addition, Mg is not homogeneous, due

to its pronounced tendency for localized corrosion. Another important issue is the release of hydrogen during corrosion, and since the gas release is too fast, it is not absorbed by the human body in time, producing the balloon effect. Another concern for the use of Mg in medical applications is the pH change in the vicinity of implanted material [8–10].

Corrosion behaviour of Mg and its alloys can be improved, in principle, in two ways: (i) by using the element alloying method to adjust the composition and the microstructure [8]. For biomedical applications, especially in orthopaedics, calcium (Ca) is known as one of the most suitable alloying elements [11]. Ca is appropriate mainly for its density of 1.55 g/cm^3 , very close to that of Mg 1.74 g/cm^3 , helping to preserve magnesium's properties [12,13]; (ii) through the use of surface treatments or protective coatings of ceramic, polymer and composite materials [2,14].

Therefore, there is a great need for new processing techniques and innovative approaches to improve the corrosion resistance, physico-chemical properties and structural characteristics of Mg alloys to be used for load-bearing applications.

Binary Mg-Ca alloys, with low Ca content (0.6–3 wt.%) have demonstrated to be promising for orthopaedic applications, but have a faster biodegradation rate than that required for trauma implants [15–17].

In a review [18], various coating techniques applied to increase the corrosion resistance of the magnesium alloys were described. Regarding the coating materials, it was confirmed that bioceramics could assure improved osseointegration and controllable biodegradability, and that organic coatings have the ability for drug delivery although

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the biodegradability is difficult to estimate in this case [19,20]. Among the different materials used to minimize the fast corrosion processes of the alloys, bioactive glasses are very promising due to their slower biodegradation rate, accompanied by the benefitting release of trace elements, involved in physiological biochemical cycles [21,22].

In this paper, we used the glass-ceramic material named RKKP (stands for A. Ravaglioli, A. Krajewski, M. Kirsch, A. Piancastelli) as coating material for Mg–Ca alloy substrates. RKKP was developed at ISTEC-CNR (Faenza, Italy) and has the following composition: SiO_2 – 43.68, $\beta\text{-Ca}_3(\text{PO}_4)_2$ – 24.00, CaO – 18.40, CaF_2 – 4.92, Na_2O – 4.53, MgO – 2.78, K_2O – 0.19, Ta_2O_5 – 1.00, La_2O_3 – 0.50 (all in wt%) [23].

The main goal of this work was the preparation and characterization of RKKP coatings on Mg–Ca alloy, in terms of composition, morphology, roughness and thickness, optimizing the deposition parameters, in order to obtain reliable films with suitable properties. The surface composition and topography will have a major impact on corrosion and biodegradability in body fluids, as well as on cells adhesion. The Pulsed Laser Deposition (PLD) technique was used for coatings preparation. In fact, PLD has successfully been used to deposit films of a large number of materials of biomedical interest [23–26]. In particular, RKKP glass-ceramic films, deposited on titanium (Ti) substrates, have shown a composition reflecting very well that of the ablated target [23]. PLD shows some important advantages with respect to other deposition techniques, such as congruent transfer of target composition to coatings, good adherence of coatings to substrate material, the possibility to control crystallinity and surface roughness, to ablate various target materials and to prepare coatings on almost any substrate material [27].

In order to characterize the deposited coatings, in this work, various techniques were applied, such as Micro-Raman, Angular Dispersive (ADXRD) and Energy Dispersive X-ray Diffraction (EDXRD), Scanning Electron Microscopy (SEM-EDS) and Atomic Force Microscopy (AFM).

2. Materials and methods

2.1. Mg–Ca alloy preparation

In order to obtain Mg–Ca alloy, raw materials, such as compact magnesium (99.7% purity) and granules of calcium (99.8% purity), were used. A rocker crucible furnace with sulphur hexafluoride (SF_6) to protect against oxidation was applied. Calcium granules were added to the magnesium melt at the temperature of 680 °C, and after mixing, the load was poured into a metal plaster pre-heated up to 250 °C. The ingots were obtained by casting the melt, after holding and stirring, into a permanent mold using a mild steel crucible. After solidification and cooling the cast, bar were trimmed and cleaned. A CT-AL-1.1 electric crucible furnace with a graphite crucible DIAMANT type – capacity of 1.1 l, with KANTAL resistors, automatic temperature control (± 5 °C) and instant thermocouple were applied. Casting was performed in a cast iron multiple mold for rods. The casting temperature was 750 °C.

The prepared bulk Mg–Ca alloy was cut into square shaped pieces, $1 \times 1 \text{ cm}^2$, of 3 mm thickness, for the subsequent use as substrates for glass-ceramic coatings. The surface of Mg–Ca alloy samples was just polished and cleaned using metallographic techniques for magnesium alloys, described previously [8,17], without any special surface's pre-treatment, because usually PLD technique provides coatings with good adhesion.

Table 1
SEM-EDS analysis results for Mg–Ca alloy.

Spectrum	Mg	Ca	Total
Spectrum 1	98.7	1.3	100.0
Spectrum 2	98.1	1.9	100.0
Spectrum 3	99.1	0.9	100.0
Mean	98.6	1.4	100.0
Std. deviation	0.5	0.5	

All results in weight%.

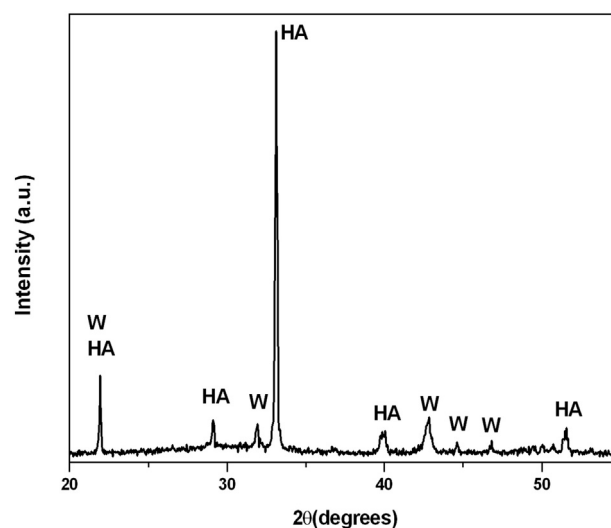


Fig. 1. ADXRD pattern of RKKP target.

2.2. Melt-processing synthesis of RKKP glass-ceramic material

In this synthesis procedure, described in details elsewhere [28], the following powders (SiO_2 – 43.68, $\text{Ca}_3(\text{PO}_4)_2$ – 24.00, CaO – 18.40, CaF_2 – 4.92, Na_2O – 4.53, MgO – 2.78, K_2O – 0.19, Ta_2O_5 – 1.00, La_2O_3 – 0.50, all in wt%) were melted in a Pt crucible in a laboratory kiln at 1450 °C for 60 min and poured into a graphite die. Afterwards, the final sample was cooled down to the room temperature. The RKKP material, developed at ISTEC-CNR (Faenza, Italy), was obtained adding to the AP40 composition of a small amount of Ta_2O_5 and La_2O_3 oxides. The $\text{La}^{3+}/\text{Ta}^{5+}$ ion couple was found to be crucial in supplying biomaterial surface with a suitable Z potential, regulating the adherence of some proteins [28,29].

2.3. Pulsed laser deposition of films

The film deposition was carried out by laser ablation of the RKKP target in a stainless steel vacuum chamber, operating at a pressure of 4×10^{-4} Pa. The ablation source was the second harmonic (532 nm) of an Nd:YAG laser (Handy YAG- Quanta System), operating at 10 Hz repetition rate and with a pulse length of 7 ns. The laser beam, focused on the target surface by a lens system, was oriented with an inclination of 45° with respect to the target [30]. During deposition experiments,

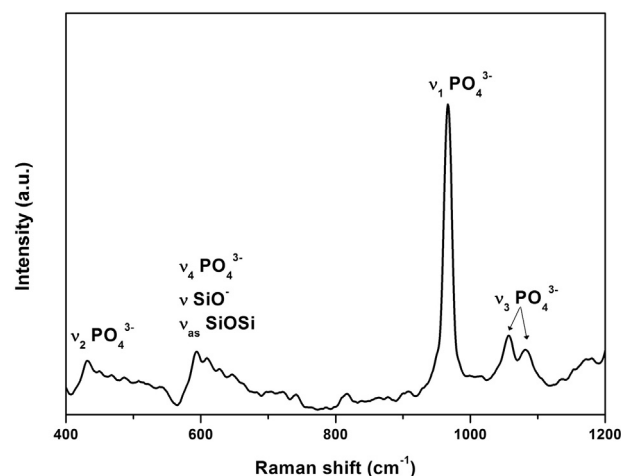


Fig. 2. Raman spectrum of RKKP target.

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