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Anodic film growth and silver enrichment during anodizing of an Mg-0.6 at.% Ag alloy in fluoride-containing organic electrolytes

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ABSTRACT

Binary Mg-Ag alloys are of interest as antibacterial biodegradable materials. In the present work, the behaviour of silver during galvanostatic anodizing of a sputtering-deposited Mg-0.6 at.% Ag alloy in a fluoride/glycerol electrolyte containing 5 or 60 vol.% water was investigated. Similar alloy compositions have been shown to have potential as biomaterials in in-vitro tests. The resultant barrier-type anodic films were examined using scanning and transmission electron microscopies, glow discharge optical emission spectroscopy and Rutherford backscattering spectroscopy. The films were shown to be nanocrystalline and to contain oxide and fluoride species, with O:F atomic ratios dependent on the amount of water in the electrolyte. Silver species were incorporated into the films, accompanied by loss of silver species to the electrolyte. Notably, silver was enriched in a ≤6 nm thick alloy layer, to concentration of at least 12 at.%.

1. Introduction

Silver is an alloying element in commercial magnesium alloys that improves the age-hardening response and strength properties [1–3]. These alloys are used in applications such as aerospace gearbox and engine casings where high-temperature strength is required. In addition to such applications, binary Mg-Ag alloys have attracted recent interest as biodegradable materials with a potential for providing a high level of antibacterial activity [4]. Cast alloys containing 2 to 6 wt.% silver revealed increasing tensile and compressive strength with increasing silver content [4]. Electrochemical testing in Dulbecco's modified eagle medium revealed general and pitting corrosion [4], with the rates dependent on the silver content of the alloy and the influence of cathodic Mg_3Ag second phase. MgO, $Mg(OH)_2$ and $MgCO_3$ were identified in the corrosion product by x-ray photoelectron spectroscopy, with silver detected as AgCl and also as metal. A subsequent study demonstrated that the corrosion resistance of the cast Mg-Ag alloys can be substantially improved by either solutions heat treatment or by a combined solution heat treatment and age hardening treatment [5]. The solution heat treatment substantially reduced the amount of silver-rich dendrites and β phase, identified by x-ray diffraction as Mg_4Ag, which led to lower corrosion rates. Although the greatest antibacterial activity occurred for the Al-6 wt.% Ag alloy, the solution treated Mg-2 wt% Ag and Mg-4 wt.% alloys showed better property combinations for applications as antibacterial biodegradable materials.

A wide range of surface treatments have been considered to control the corrosion rate, the surface chemistry and morphology of biodegradable coatings on magnesium alloys for biomedical applications, including anodic conversion processes, ion implantation, physical vapour deposition, electrodeposition and sol-gel, among others [6,7]. Plasma electrolytic oxidation (PEO) is the most commonly investigated method of anodic processing [8–12] and has been used to incorporate silver nanoparticles into coatings [13]. Coatings have also been prepared by conventional anodizing in a $KOH/KF/Na_3PO_4$ aqueous electrolyte and post-treated with cell culturing medium to improve the coating stability [14]. The thicknesses of these anodic films were about 1 μm and consisted of MgO. Subsequent in-vitro tests revealed improved cell attachment and

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differentiation compared with untreated magnesium.

In the present study, the effect of anodizing on Mg-0.6 at.% Ag alloy (0.22 wt.% Ag) is examined. The alloy composition is close to that recommended as an antibacterial biodegradable material [4,5]. An anodic surface treatment has a potential to control and modify surface composition as well as the alloy properties. The alloy used in the present study was prepared by magnetron sputtering, which results in a metastable solid solution of silver. The anodizing behaviour is expected to be similar to that of the matrix region of a cast and solution-treated bulk alloy. The selected anodizing electrolyte contains ammonium fluoride with glycerol and water as solvents, which results in barrier-type films containing fluoride and oxide species.

2. Experimental

High purity (99.94%) aluminium foil of 0.3 mm thickness was cut to provide substrates of dimensions 50 × 20 mm. In order to create flat surfaces for deposition of the Mg-0.6 at.% Ag alloy, the substrates were electropolished for 3 min at 20 V in 60 vol.% perchloric acid/ethanol solution (20:80 by vol.) at 278 K followed by several rinses in ethanol and deionized water and drying in a stream of cool air.

An ATOM TECH magnetron sputtering system with two separate high purity sputtering targets of 99.99% magnesium and 99.95% silver, of 50 mm diameter, was used to deposit the Mg-Ag alloy layers on the electropolished aluminium substrates. The sputtering chamber was evacuated to 7×10^{-5} Pa; sputtering was then carried out for 45 min in 99.999% argon at 0.5 Pa. The alloy composition was controlled by the currents on the magnesium (495 ± 3 mA) and silver (38 ± 1 mA) targets.

After deposition of the alloy, the substrates were cut to provide specimens of dimensions 20 × 20 mm. The specimens were then anodized individually at 5 mA cm^{-2} in 0.35 mol dm^{-3} ammonium fluoride (NH_4F) in a glycerol-water mixture, containing either 5 or 60 vol.% of deionized water, at room temperature (~20 °C). Previous work has shown that in electrolytes containing at least up to 40 vol.% water, the films grow at high efficiency [15]. The specimens were anodized to 189 V in the electrolyte containing 60 vol.% of water and to 385 V in the electrolyte containing 5 vol.% of water. The voltages were close to the dielectric breakdown voltage in the respective electrolytes. A further specimen was anodized to 189 V in the latter electrolyte. The anodizing voltages cited are those developed across the anodic films i.e. after removal of the voltage surge due to the electrolyte resistance.

Each specimen was clamped against the port of a three-electrode Perspex cell, where an O-ring provided a seal with the specimen surface. The working area of the specimen, which was defined by the diameter of the O-ring, was 1.54 cm^2. The cathode was a titanium disc; a platinum wire was used as a pseudo-reference electrode. The constant current was supplied by a DC constant current power supply (Metronix Model 6912). The cell voltage during anodizing was recorded using software developed in-house based on Labview. The specimen was removed from the cell after anodizing, rinsed with de-ionized water and dried in a flow of cool air.

Scanning electron microscopy (SEM) was used for investigation of the surfaces of the alloy and anodic films, employing a Zeiss Ultra 55 instrument operated at either 1 or 6 kV. An FEI Quanta 3D FEG SEM was employed to prepare cross-section of the magnetron sputtering-deposited layer by focused ion beam milling (FIB). An FEI Magellan 400 FEG SEM was used for imaging of the section at 30° stage tilt. Cross-sections of anodized specimens were prepared for transmission electron microscopy (TEM) using a TESCAN Lyra 3 XMU scanning electron microscope equipped with a focused ion beam (FIB) milling facility. Specimens were coated with platinum to prevent radiation damage during section preparation. The FIB was operated at an accelerating voltage of 30 kV, with currents of 4 and 1 nA for rough milling and rough pre-thinning, respectively. An ion current of 200 pA was used for final thinning to an electron-transparent thickness. At the end of the preparation procedure, all TEM sections were cleaned by a gallium ion beam, using an accelerating voltage of 2 kV and a current of 150 pA, in order to minimize the radiation damage. This procedure has been described in detail elsewhere [16]. TEM investigations were performed using a JEOL 2100F instrument operated at 200 kV and equipped with an Oxford instruments X-max energy-dispersive X-ray (EDX) analysis facility. Elemental distributions in sections were measured in the STEM mode with Aztec software.

Elemental depth profiling of the specimen was investigated by glow discharge optical emission spectroscopy (GDOES), using a GD-Profiler 2 instrument (Horiba Jobin Yvon). The argon pressure was 635 Pa during sputtering at a power of 35 W. Wavelengths of 396.15, 383.83, 338.29, 130.22 and 156.14 nm were employed to detect Al, Mg, Ag, O and C respectively. The data were recorded at a sampling interval of 0.05 s. Due to the use of argon for sputtering, optical emission from fluorine could not be excited.

The elemental compositions of the anodized specimens were investigated by Rutherford backscattering spectroscopy (RBS) employing 2.0 MeV $^4He^+$ ions supplied by the Van de Graff generator at the University of Paris. The incident ion beam was normal to the specimen surface, with scattered ions detected at 165° to the direction of the incident beam. The data were interpreted using RUMP software [17].

3. Results and discussion

3.1. Morphology of as-deposited alloy

A scanning electron micrograph of the surface of the as-

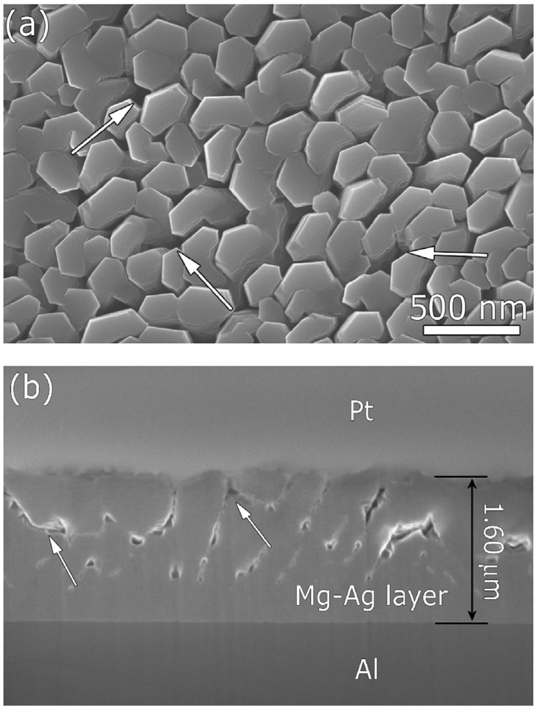

Fig. 1. Scanning electron micrographs (secondary electrons) of the (a) surface and (b) FIB milled cross-section of the magnetron sputtering-deposited Mg-0.6 at.% Ag alloy.