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Electrochemical impedance spectroscopy of chitosan coated magnesium alloys in a synthetic sweat medium

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ABSTRACT

Pure magnesium and/or its alloys (AZ31E, AZ91E) are the optimum shell materials for electronic products that contact the hands of the users, and are corroded by the sweat solution (0.1% urea, 0.5% NaCl and 0.5% lactic acid). The corrosion behavior of the tested electrodes was investigated in artificial sweat solution as function of immersion time. In the electrochemical cell Mg or its alloy acts as the anode and NaCl in sweat solution is the corrosive medium. Results showed that the most corroded electrode was pure magnesium while the least corroded was AZ91E alloy. Chitosan was used as coating with different concentrations for AZ91E alloy to protect it against corrosion. The results were carried out using various electrochemical techniques such as potentiodynamic polarization, electrochemical impedance (EIS) and surface examination via scanning electron microscope (SEM). After coating AZ91E alloy with 5% chitosan the formed film was thicker than that formed on the uncoated one and its thickness increased with increasing chitosan concentration. The micrographs showed that the coated AZ91E alloy has superior corrosion resistance properties as compared to the uncoated alloy and that corrosion decreases with increasing the polymer concentration. EIS and polarization results were confirmed by SEM micrographs.

1. Introduction

Ultra light magnesium and its alloys are used in many applications including automotive and handheld products like cell phones, PC notebooks, digital cameras, etc. [1,2]. However, the poor wear resistance extensively limits their practical applications [3]. The wear mechanism of Mg alloys is complicated [4,5]. Chen et al. [6] investigated the sliding map for conventional AZ91D Mg alloy and found two wear regimes, mild wear regime and severe wear regime. The former corresponded to oxidation wear and delaminating wear, and the latter was related to severe plastic deformation induced wear and melt wear. Consequently, if corrosion and wear resistance of magnesium alloys are increased [7], their usage will become widespread. Surface modification by coatings has become an essential step to improve the surface properties such as wear, corrosion and oxidation.

Adsorption using chitosan composites is becoming a promising alternative to replace conventional adsorbents in removing dyes and heavy metal ions [8]. Highly dense HA-chitosan composite coatings were deposited on AZ31 Mg alloy to improve the corrosion resistance and biocompatibility of the alloy. Coatings which were highly adherence to the substrates were obtained, showing adhesion strengths in the range of 24.6–27.7 MPa. Corrosion resistance of AZ31 Mg alloy was remarkably enhanced by the coating of the Hydroxyapatite (HA)-chitosan composite material. Simultaneously, the biocompatibility of the alloy was improved by the HA coating and the incorporation of chitosan into the coating [9].

The inherent lightness and high stiffness to weight ratio making it an attractive choice for weight reduction in portable microelectronics, automotive industry and biomaterials [10,11]. The high reactive nature of magnesium is clearly indicated by its negative standard electrode potential ($E = -2.37$ V) which makes it and its alloys highly susceptible to corrosion in aggressive media. Many reports about corrosion research of pure magnesium and its alloys are accessible in the previous literatures [12–15]. It was previously reported that adding aluminum and increasing its content in magnesium alloys has a beneficial influence on the corrosion behavior in chloride media [16]. Aluminum is precipitated in the form of $Mg_{17}Al_{12}$ along grain boundaries as a continuous phase as well as part of a lamellar structure for AZ91 alloy [17]. Meanwhile, the distribution of β-phase ($Mg_{17}Al_{12}$) determines the corrosion resistance of Mg–Al alloys.

Electronic products that are in contact with the hands of the users may be stained by the sweat solution that consists of 0.5% NaCl, 0.5% lactic acid and 0.1% urea in mass percent [18,19] and of pH value (4.8–5.8). Sweat comes out of pores in the skin. Sweat is a mixture of three metabolic wastes: water, salts and urea. So when a sweat gets out, the body accomplishes two things: 1) cooling effect on the body, and 2) metabolic wastes are excreted [20].

This sweat leads to corrosion of several types of instruments. Zhang et al. [21] studied the corrosion behavior of magnesium alloys in artificial sweat solution and found that they suffered serious attack, thus requiring protection with suitable coatings. Hence, various methods for applying protective coatings on magnesium alloys as electrochemical

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Table 1
Chemical composition (wt.%) of tested electrodes and balance Mg.

Electrode	Al	Zn	Mn	Cu	Fe	Ni	Be	Si
Mg	0.002	–	0.005	0.002	0.029	–	–	–
AZ31E	2.8	0.96	0.28	0.0017	0.0111	0.0007	0.0001	–
AZ91E	9.0	0.7	0.13	0.03	0.006	0.004	0.0007	0.01

plating, chemical conversion coating, hydride coating, anodizing, gas phase deposition, and organic/polymer coatings have been tried [1,22–26].

Chitosan (CS) is the N-deacetylated product of chitin, where chitin is a natural polysaccharide found particularly in the shells of crustaceans such as crab and shrimp, the cuticles of insects and the cell walls of fungi. Chitosan is an attractive material because of its properties such as immunological activity, wound healing, biocompatibility, low toxicity, and biodegradability [27]. It has wide applications in medicine, cosmetics, textiles, paper, food and many other industrial branches [28].

The chitosan coating is as attractive as a biocompatible coating for Mg alloys and thus we evaluated the corrosion protective ability of chitosan coating.

Corrosion behavior of pure Mg and its alloys is a major issue. Since chitosan coating is as attractive as a biocompatible coating, it was deemed interesting to investigate the corrosion behavior of Mg and its alloys coated with chitosan in sweat solution. Evaluation of the corrosion protection of chitosan using various electrochemical techniques is an attempt in this work.

2. Experimental

2.1. Alloy composition and preparation

Three samples of pure magnesium (99.96%), and extruded magnesium aluminum alloys (AZ31E, AZ91E), are given in Table 1, were donated from Department of Mining, Metallurgy and Materials Engineering, Laval University, Canada and tested in this work. The electrode surface area for any electrode was 0.196 cm^2. The surface of the test electrode was mechanically abraded using emery paper with 400 up to 1000 grit to ensure the same surface roughness, degreased in acetone, rinsed with ethanol and dried in air.

2.2. Cell composition

The cell used was a typical three-electrode one fitted with a large platinum sheet of size 15 × 20 × 2 mm as a counter electrode (CE), saturated calomel (SCE) as a reference electrode (RE) and the alloy as the working electrode (WE).

2.3. Sweat solution preparation

The artificial sweat solution consisted of 0.1% urea, 0.5% NaCl and 0.5% lactic acid [18,19] in triply distilled water at 298 K (25 °C).

2.4. Preparation of chitosan coating

The coated AZ91E electrode was prepared by dipping it for 3 h in each concentration in 5, 10 and/or 15% chitosan solution (in 1% acetic acid) then removed and dried. The coating films thus obtained were dried at 353 K (80 °C) for 2 h before characterization.

2.5. Instrumentation

Polarization and EIS measurements were carried out using the electrochemical workstation IM6e Zahner-elektrik GmbH, Germany. The impedance diagrams were recorded at the free immersion potential (open circuit potential) by applying a 10 mV sinusoidal potential through a frequency domain from 100 kHz down to 100 mHz. Polarization behavior of the tested electrodes was measured by scanning from −2.0 to −1.0 V vs. SCE after 10 h of immersion in test solution using

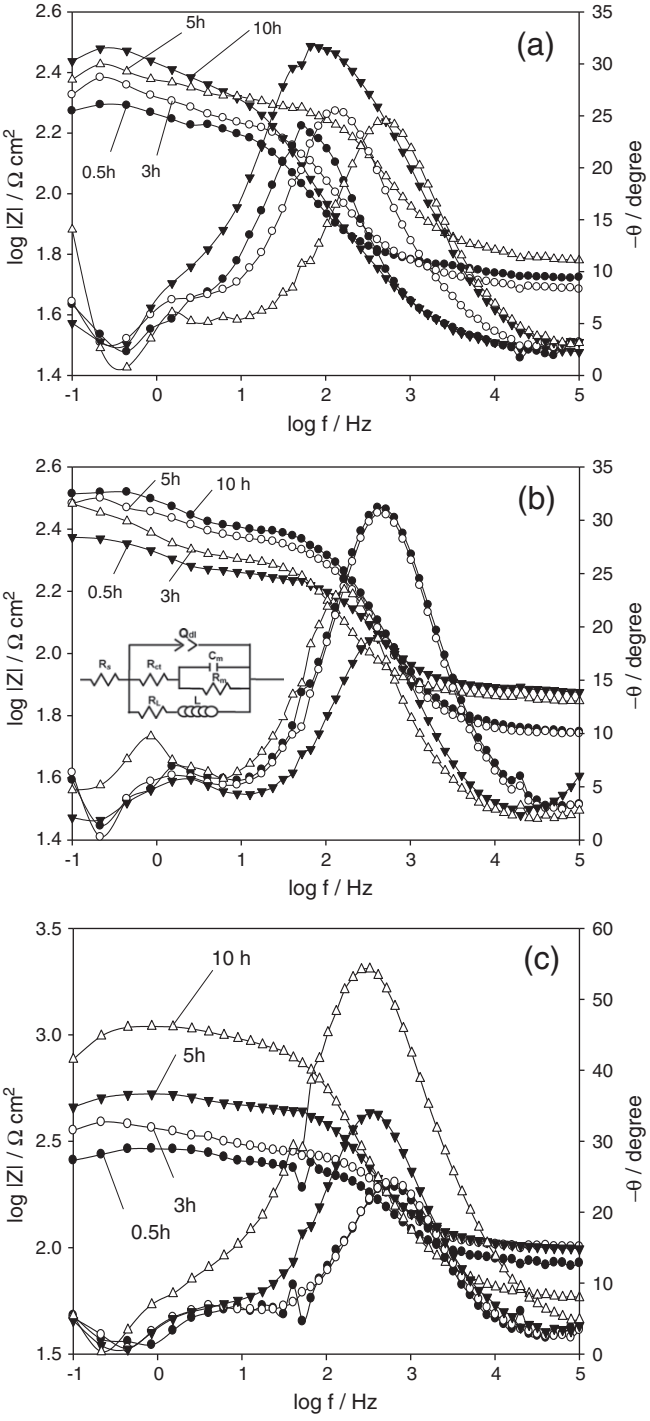

Fig. 1. Bode plots of (a) pure magnesium; (b) AZ31E and (c) AZ91E electrode in artificial sweat solution with time.

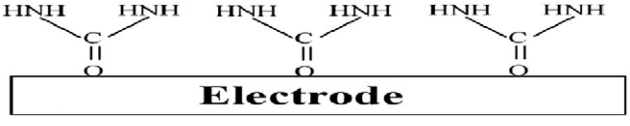

Fig. 2. Adsorption model of urea on electrode surface [23].