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Comparative study of protective magnesium deposit behaviour obtained by continuous and pulsed currents from methylmagnesium chloride solution

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Abstract

Pulsed and continuous (or direct) currents were used for the electrodeposition of magnesium from methylmagnesium chloride solution. The analytical characterization of the magnesium coating was performed by scanning electron spectroscopy (SEM) and the X-ray diffraction (XRD). The electrochemical behaviour of the steel substrate coated by magnesium was assessed by electrochemical impedance spectroscopy and potentiodynamic polarization curves. The deposits morphology was quite different; it changed from smooth and irregular with cracks for the deposit obtained by continuous current (cc), to granulate with an average grain diameter of about 3 μm for the deposit obtained by pulsed current (pc). The electrochemical results showed that the protection of the steel substrate against corrosion was better with the magnesium deposit obtained by pulsed electrodeposition process.

Keywords: Methylmagnesium chloride; Magnesium deposit; Continuous current; Pulsed current; Corrosion; Impedance; Protection

1. Introduction

Magnesium is one of the most interesting metals for electroplating, compared with other metals used for coating. Its first advantage is its low density ($\rho = 1.74$), another consideration is that magnesium is the third most abundant structural metal in the earth's crust. This metal cannot be plated from aqueous solutions because the hydrogen ions of the water are preferentially reduced over the active metal ions. The magnesium electrodeposition is possible from solutions based on Grignard reagent RMgX where R is an alkyl grouping and X is a halide.

Reports on the electrolysis of Grignard solutions have focused on the fact that the conductivity of these solutions is moderately low and that in general, the deposit ranged in colour from white to dark grey [1].

Other researchers [2–4] have worked with ether solutions containing organomagnesium halides, magnesium borohydride and Grignard reagents. Their best deposit was a magnesium alloy (90%Mg, 10%B) from a solution of magnesium bromide and lithium borohydride.

Liebenow et al [5–7] have obtained a grey deposit of magnesium from three organomagnesium groups: organomagnsium halides, amidomagnesium halides and magnesium organoborates dissolved in tetrahydrofurane. The deposit regularity depends on the type of substrate.

Based on these results, solutions containing organomagnesium halides in ether solvents have proven to be the most effective electrolytes for the magnesium electrodeposition. However, their reactivity, their conductivity and the quality of the magnesium deposit vary considerably [2,8].

The developments of new methods such as pulsed current sought to produce better mechanical and anti-corrosion properties [9–12]. These developments that have taken place during the last three decades include the use of pulse plating in areas such as anodising,

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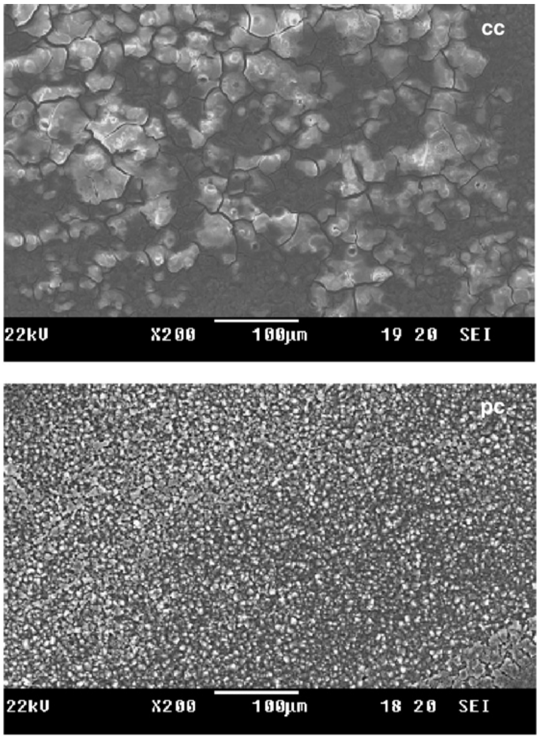

Fig. 1. SEM micrographs of magnesium deposit in continuous (cc) and pulsed (pc) currents on carbon steel substrate.

deposition of composite materials, amorphous alloy and semiconductor plating. Mass transport effects and morphological effects were studied. Pagotto et al [10] found that with pulsed current electrodeposition process, Zn–Ni films present more refined and smaller grain size and better corrosion properties with respect to films obtained by continuous current. Electrodeposition of CdTe and WSe_2 films by pulsed current [11,12] has greatly improved the composition, the optical absorption and the polycrystalline nature.

In the pulsed electrodeposition process, the average current density (i_m) is equivalent to the current density applied in the continuous electrodeposition process [9–14] and is defined as:

$$i_m = i_c t_{\text{on}} / (t_{\text{on}} + t_{\text{off}}) \tag{1}$$

Where i_c is the cathodic current density, t_{on} is the time of cathodic pulse (on-time) and t_{off} is the time between pulses (off-time).

This work is aimed at a comparative study of magnesium deposit morphology and composition electroplated by continuous and pulsed currents obtained from the organic solution methyl magnesium chloride in tetrahydrofuran (THF) on a carbon steel substrate. This paper also investigates the corrosion behaviour of both deposits in 0.03% sodium chloride solution by electrochemical and impedance measurements.

2. Experimental

2.1. The electrolyte

The Grignard reagent methylmagnesium chloride was obtained from Sigma-Aldrich as 3M solution in tetrahydrofuran (THF). All experiments undertaken with the organomagnesium electrolyte were carried out at 25 °C under a controlled gas atmosphere of nitrogen in a glove compartment so as to avoid all reaction of the organomagnesium with the air.

2.2. The electrochemical cell

The magnesium electrodeposition with continuous current was realised by imposing a current density of about −1 mA cm^{-2}. After several preliminary tests of electrodeposition with pulsed current, the pulsed parameters were optimised and are:

$$t_{\text{on}} = 0.2\ ms; t_{\text{off}} = 19.8\ \text{ms and } i_c = -100\ \text{mA cm}^{-2}.$$

The deposition time was 45 min for both currents. The electrochemical cell was an Mg reference electrode, platinum as counter electrode and the steel working electrode [5–7]. Magnesium rod was obtained from 99.9% pure Mg as Goodfellow product. For the corrosion test in 0.03% sodium chloride solution, the electrochemical cell was a saturated calomel electrode (SCE) as reference, platinum as counter electrode and carbon steel as working electrode. The surface of the carbon steel samples was polished with SiC paper, washed with anhydrous acetone and dried. The working area was 0.29 cm^2.

2.3. Electrochemical and analytical techniques

The polarization curves were obtained by means of a potentiostat–galvanostat Radiometer Copenhagen PGZ 402 model, piloted by software Voltlab4. The polarization curves

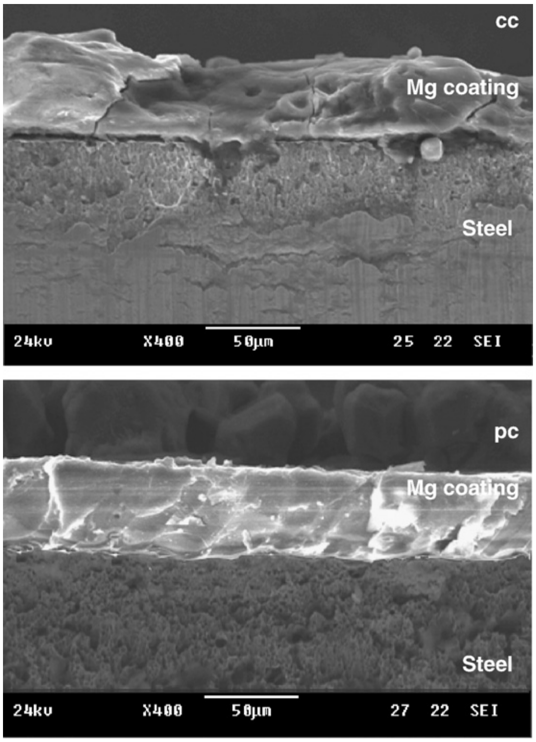

Fig. 2. Cross-section micrographs of magnesium deposit in continuous (cc) and pulsed (pc) currents on carbon steel substrate.