

Microelectrochemical Characterization of Corrosion Behavior of Mg Alloys: Microstructural, Aging and Inhibiting aspects

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Magnesium alloy production shows a sustainable growth (> 20% pro year for the past couple of years) for applications in the transportation industry, for example, and new promising production processes such as the New Rheocasting Method (NRC) are being developed (1). Although relatively resistant in standard atmospheric conditions, these alloys are among the most corrosion susceptible metallic components used in industrial applications when small amount of aggressive ions are present in solution (2). The structure of the Mg hydroxide film formed on the surface is known to be complex and microstructure also plays a key role in the case of corrosion of magnesium. The limited solubility range of alloying elements used induces the formation of multiple microscopic phases in the alloys resulting in very detrimental galvanic coupling during exposure to aggressive solutions. In this study, the influence of alloying elements and its distribution at a micrometer level is investigated.

Corrosion behavior of different type of Mg alloys (AZ, AM series) is investigated with a microcapillary cell characterization technique developed at the Institute of Materials Chemistry and Corrosion (IBWK) at the ETHZ as well as with other standard electrochemical techniques. Solutions with small amount of Cl⁻ are tested as Mg alloys are obviously not foreseen to be used in concentrated salt solutions. Figure 1a presents the microelectrochemical potentiodynamic polarization curves for the Mg α phase and the eutectic phase of the AZ91 NRC alloy in 0.1M NaCl. The polarization curves clearly indicate that the Mg α phase is the more active phase with a corrosion potential approximately 200 mV lower than the eutectic phase. The pitting potential of most grains of the Mg α phase is lower than the corrosion potential of the eutectic phase. Severe localized corrosion of this phase occurs upon immersion in 0.1M NaCl. Optical images taken after 1 day of immersion confirmed that the Mg α phase is corroded leaving holes approximately 80-100 μ m deep.

Investigation of the Mg₁₇Al₁₂ and Al₈Mn₅ intermetallic phases are carried out with smaller capillaries than the one used for the measurements showed in this abstract. However, optical microscopy investigation in concentrated NaCl solutions indicates that coupling between eutectic (+intermetallic phases) and Mg α phase is the problem and that the influence of the intermetallic phases Mg₁₇Al₁₂ and Al₈Mn₅ seem limited to the fact that they contribute to the cathodic reaction together with the eutectic phase.

Figure 1b shows polarization curves in more dilute 0.01M NaCl. The pitting potential of the Mg α phase is raised by a few hundred mV over the corrosion potential of the eutectic phase. Corrosion of the alloy at open circuit potential proceeds by rapid uniform dissolution of the Mg α phase. The extent and morphology of the attack drastically changed, the depth of the attack being only 3-4 μ m after 1 day. Although the alloy is not pitting at OCP,

the intersection of the cathodic polarization curve of the eutectic phase and the anodic dissolution of the Mg α phase occur at a current density of 20-50 μ A/cm² which can still induce significant damage on the surface. For this NaCl solution, the pitting potential of both phases show significant scattering; this can be explained by the presence of a relatively thick hydroxide film that has a limited stability when the environment is not too aggressive. However, the position of the pitting potential is less relevant to this particular corrosion process.

Changes in microstructure can influence the corrosion behavior Mg alloys at the boundary of the stability range of the Mg hydroxide (pH range 11 to 13) (3). However, in neutral NaCl solution, protection of the Mg alloys is best achieved by a protective coating. The first step is to test the influence of addition of inhibitors (4). Polarization curves were performed for samples exposed to 0.01M NaCl + 10⁻⁴M Na₂CrO₄ (5). This small concentration of chromate is chosen because it typically represents the amount that is leaching out from standard protective coatings (6). The microelectrochemical potentiodynamic polarization curves show a similar general behavior as in absence of chromate. Important differences are that the anodic current is significantly decreased on the Mg α phase as well as the cathodic current on the eutectic phase. This indicates a double inhibiting effect of chromate. Results obtained with other type of possible inhibitors will be discussed, also in combination with anodization of the surface. These conditions have been tested to replace chromate in oxide stabilization process. Although relatively efficient, this carcinogenic agent should be avoided.

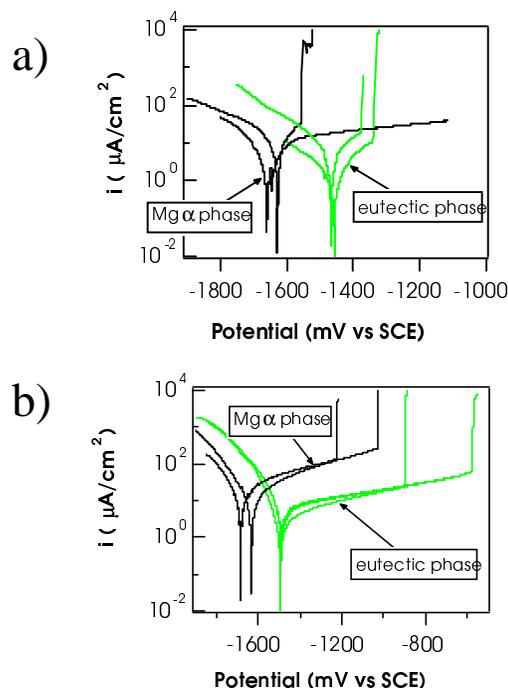


Fig. 1: Micro-electrochemical polarization curves obtained on the different phases of the AZ91 NRC alloy: a) in 0.1 M NaCl, b) in 0.01 M NaCl

References

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