Evaluation of Corrosion Protection of Sol-Gel Coatings on AZ31B Magnesium Alloy

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\textbf{Abstract.} Magnesium is one of the lightest metals and magnesium alloys have good strength to weight ratio making them very attractive for many particular applications [1]. The main drawback of magnesium alloys is their high corrosion susceptibility. Improving the corrosion protection by deposition of thin hybrid films can expand the areas of applications of relatively cheap magnesium alloys. This work aims at investigation of new anticorrosion coating systems for magnesium alloy AZ31B using hybrid sol-gel films. The sol-gels were prepared by copolymerization of 3-glycidoxypropytrimethoxysilane (GPTMS), titanium alcoxides and special additives which provide corrosion protection of magnesium alloy. Different compositions of sol-gel systems show enhanced long-term corrosion protection of magnesium alloy. The sol-gel coatings exhibit excellent adhesion to the substrate and protect against the corrosion attack. Corrosion behavior of AZ31B substrates pre-treated with sol–gel derived hybrid coatings was tested by Electrochemical Impedance Spectroscopy (EIS). The morphology and the structure of sol-gel films under study were characterized with SEM/EDS techniques.

\textbf{Introduction}

The Mg-3Al-1Zn alloy (AZ31B) is of industrial interest because of relatively high strength, room-temperature ductility and homogeneous microstructure. However, magnesium is too reactive and because of the low corrosion resistance the use of magnesium alloys in the industry is limited to some components in mild service environments. [1-3] Therefore, improving the corrosion resistance of magnesium alloy will significantly increase their service life raising the areas of applications.

The deposition of thin inorganic or hybrid films on metallic surfaces has been suggested as a pre-treatment for different metallic substrates to provide an additional barrier against the corrosion species and mainly to improve adhesion between the metal and polymer coating system. The films are usually deposited by the plasma polymerization technique or the sol-gel route. Sol-gel-derived thin films that contain either inorganic (phosphates, vanadates, borates, cerium and molybdenum) or organic (phenyl phosphoric acid, mercaptobenzothiazole, mercaptobenzoimidazole, triazole) inhibitors are investigated as substitutes for chromates [4] and also improve the corrosion resistance of metallic substrate.

The sol-gel process seems promising for preparation of adherent, chemically inert metal oxide coatings at the low temperatures (< 200 °C) required for magnesium alloys as already an all shown on steel substrates.[5, 6] The process is economic, environmentally friendly and coatings can be easily deposited on all types of surfaces. A significant advantage is that irregular shapes and larger integral structures can also be coated. However, sol-gel coatings tend to fail if the film thickness
exceeds 5 microns because the shrinkage strains during drying and densification of the as-deposited film. [6]

In the present work, a novel hybrid sol-gel process is suggested for enhancing the corrosion resistance of AZ31B magnesium alloy. The AZ31B alloy was coated by zirconia-containing hybrid organic-inorganic sol-gel coatings cured at different temperatures. The structure of the films was characterized by Scanning Electron Microscopy (SEM). The Electrochemical Impedance Spectroscopy (EIS) was used here to estimate the corrosion protection of the systems under study.

Materials and Methods

The AZ31B alloy samples without surface finishing were cleaned by acid solution (H₃PO₄, HNO₃, CH₃COOH and water with volume ratio 3:2:4:1) during 3 s and then dried in air.

Final solution used for films application was prepared by sol-gel route mixing two different sols. First sol was obtained from zirconium propoxide solution 70% in propanol (CAS 23519-77-9, FLUKA) and ethylacetoacetate (CAS 141-97-9, FLUKA) with volume ratio 1:1, acidified with water (pH~0.5) and ultrasonically agitated with continuous magnetic stirring by 60 minutes. The second sol was prepared hydrolyzing (3-Glycidloxypropyl) trimethoxysilane (CAS 2530-83-8, ALDRICH) and 2-Propanol (CAS 67-63-0, Riedel-de Haën) with 1:1 volume ratio, by acidified water (pH~0.5) under magnetic stirring for 60 min. The final sol was synthesized mixing initial two solutions and ultrasonically and magnetically stirred for 60 min. The sol-gel films were then applied on magnesium alloy samples by dip coating of with 18 cm/min withdrawal rate.

The samples were cured in an oven at two different temperatures, 130°C and 140°C, during 1 hour. The bare AZ31B alloy was used as a reference to compare corrosion resistance.

The Electrochemical Impedance Spectroscopy method (GAMRY FAS2 potentiostat) was used as a main technique to study corrosion resistance of the samples during immersion in 0.005 M sodium chloride solution. The frequency range was from 100 kHz to 10 mHz taking 7 points per decade.

Scanning Electron Microscopy (SEM/EDS) was employed to study the structure and composition of hybrid films. SEM images were taken with a Hitachi S-4100 system; beam energy was 25.0 keV.

Results and Discussions

The dipping of magnesium alloy substrate into the synthesized sol leads to formation of dense intact hybrid film with thickness about 2 micron as shown in Figure 1. The EDS profile taken across the cross-section confirms that brighter zone in the middle of micrograph is composed by the sol-gel film.

Figure 1 EDS profile and SEM images of cross section of AZ31 coated with hybrid film cured at 130 °C after 14 days of immersion in 5mM NaCl.
The magnesium alloy samples coated with sol-gel films cured at different temperatures were immersed in 0.005 M NaCl electrolyte to accelerate the corrosion processes and to assess the corrosion protection ability of different films. The bare alloy surface seems to be heavily corroded after 2 weeks of immersion in the solutions (Figure 2a). The many large white-deposits are formed being composed by the corrosion products precipitated on the surface. The careful SEM analysis of a defect shows that a deep pitting is formed in middle of white deposit confirming strong localised attack. The surface of AZ31 coated by the hybrid sol-gel film cured at 130°C seems completely different (Figure 2b). No points of corrosion attack of metal can be revealed at this stage. Only some defects are formed in sol-gel film demonstrating the hydrolytical degradation of the coating. The coating cured at 140°C demonstrates even better appearance Figure 2c. Lower number of defects can be observed on the surface with no signs of pitting corrosion. The results presented above demonstrate drastic improvement of the corrosion resistance of AZ31 when hybrid sol-gel is applied on its surface. It also seems that increase of the curing temperature tends to increase of the hybrid sol-gel stability.

![Figure 2](image)

**Figure 2** Photographs of surfaces of bare AZ31 (a) and alloy coated with hybrid films cured at samples 130 °C (b) and 140°C (c) after 14 days of immersion in 5mM NaCl. SEM images demonstrate typical defects on the surface.

The Electrochemical Impedance Spectroscopy was employed in this work to estimate corrosion resistance of sol-gel coating in more quantitative way. The frequency dependence of the complex impedance of the coated substrate permits effective evaluation of the different components of the system such as capacitance and resistance of the protective layers, polarization resistance and double layer capacitance. Representation of these parameters as a function of immersion time allows assessment of the corrosion protection performance of the coated system.

![Figure 3](image)

**Figure 3** Typical Bode plots of bare alloy (red) and AZ31B coated with sol-gel films cured at different temperatures (130°C-green and 140°C-yellow-) after 12 days of immersion in 5mM NaCl solution.
Figure 3 presents typical Bode plots taken after the 12 days of immersion of AZ31 alloy. Both samples treated with sol-gel films demonstrate sufficiently higher impedance during immersion when compared to the bare alloy. The impedance at lowest frequency is more than one order of magnitude higher than for untreated magnesium. Higher impedance in low frequency range confirms superior corrosion resistance of coated samples.

The spectrum of bare alloy is constituted by two time constants. The very weakly defined one at high frequencies is related to the response from the passive oxide film formed on the surface. The second time-dependent process appears at intermediate frequencies due to corrosion processes going in active pittings of the alloy. The sol-gel coated samples show different spectra. The high frequency part contains well-defined relaxation process originated from the sol-gel film instead of the oxide film in the case of bare alloy. The second low frequency time constant has a similar nature to that of bare alloy. However the values of the impedance module are sufficiently higher showing the higher polarization resistance and in turn the lower rate of the corrosion processes.

The equivalent circuit depicted in Figure 4a was used to fit the experimental impedance plots allowing estimation of the sol-gel film evolution during corrosion tests. The equivalent circuit is constituted by two time constants related to the sol-gel film and corrosion processes as described above. The parameters of the sol-gel film were then calculated and plotted against the immersion time.

Both sol-gel films demonstrate very stable values of coating capacitance proving their high hydrolytical stability (Figure 4b). The lower capacitance of the sol-gel film cured at higher temperature can be probably caused by the lower content of the water remaining in the film after the heat treatment.

Figure 4c presents the evolution of the sol-gel film pore resistance during corrosion tests. The pore resistance of the film is directly related to the barrier properties of the coating. Both films provide reasonable barrier. What is also very important that the pore resistance remains stable during immersion showing low rate of the coating degradation. The hybrid film cured at 140°C demonstrates higher resistances in comparison to resistance of film treated at lower temperature. This fact is in a good agreement with visual observations of the sol-gel film appearance demonstrated above (Figure 2). The higher pore resistance and the lower capacitance of the sol-gel film cured at higher temperature are most probably related to the higher shrinkage degree when curing temperature is raised.

(a) \( R_{\text{Sol-gel}} (\Omega \cdot \text{cm}^{-2}) \)
(b) \( C_{\text{Sol-gel Real}} (\text{F.cm}^{-2}) \)

**Figure 4** The equivalent circuit for fitting the experimental impedance spectra. (a) Evolution of sol-gel film capacitance (b) and resistance (c) with immersion time.
Conclusions

• The application of novel hybrid sol-gel film confers the effective corrosion protection to the AZ31B magnesium alloy.
• Increase of the curing temperature leads to better shrinkage of the sol-gel film.

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