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THE APPLICABILITY OF SOL-GEL OXIDE FILMS AND THEIR CHARACTERISATION ON A MAGNESIUM ALLOY

UPORABNOST SOL-GEL OKSIDNIH TANKIH PLASTI IN NJIHOVA KARAKTERIZACIJA NA MAGNEZIJEVI ZLITINI

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Magnesium and its alloys are widely used in many industrial applications because of their high specific strength (strength/density) ratio. However, these applications are still restricted by the relatively poor surface resistance of these materials. To overcome the inherent drawbacks a useful solution is to deposit a protective coating on the magnesium alloys. The sol-gel process is an effective method for fabricating oxide films on a magnesium alloy in order to produce a higher corrosion resistance. The objective of this study is to comparatively investigate the process and properties of repeated sol–gel oxide (ZrO_2, Al_2O_3) coatings. The coatings were characterized by SEM, XRD, ellipsometry and the effects of the process on their properties were comparatively analysed.

Keywords: sol-gel, oxide films, magnesium alloy

Magnezij in njegove zlitine se uporabljajo v vrsti industrij zaradi visoke specifične trdnosti (razmerje trdnost – gostota). Vendar pa je industrijska uporaba omejena zaradi njihove slabe odpornosti površine. Da bi to pomanjkljivost odpravili, je uporabna rešitev varovalni nanos na površini magnezijevih zlitin. Sol-gel postopek je učinkovita metoda za izdelavo oksidnih tankih plasti na magnezijevi zlitini za povečanje njihove korozijske obstojnosti. Namen te študije je primerjava postopka in ugotavljanje lastnosti ponavljajočih se sol-gel nanosov ZrO_2 in Al_2O_3. Nanosi so bili ovrednoteni s SEM, XRD in elipsometrijo, izvršena pa je bila tudi primerjava vpliva procesa na njihove lastnosti.

Ključne besede: sol-gel, oksidni nanosi, magnezijeva zlitina

1 INTRODUCTION

Magnesium and its alloys have a high specific strength, excellent mechanical properties, a good damping capacity and a high electromagnetic shielding capability. They can be used for a variety electronic and many automotive parts.[1,2] However, corrosion protection is one of the main obstacles to the application of magnesium alloys in real environments. Conversion coating, anodizing, plating, laser surface alloying and plasma electrolyte oxidation have been applied on magnesium alloys. Material designers attempted to improve the corrosion resistance of the surface.[3–5] However, with these technologies the protection of magnesium alloys it is hard to achieve a good cost-to-benefit ratio or there is a higher energy consumption or environmentally adverse effects. The sol–gel thin-film deposition method is described as a practical, environmentally friendly and cost-effective way to produce magnesium alloy surfaces. It is well known that Al_2O_3 thin films have been extensively used as an isolator, oxidation barrier, for anti-corrosion and for anti-wear.[6–8] However, sol–gel ZrO_2 thin films, owing to their chemical stability, have important applications as corrosion-resistant coatings on metal surfaces.[9] Thin (0.2–10 μm), dense, sol–gel oxide coatings exhibited significant advantages in overcoming metallic surface-corrosion problems. From the point of view of synthesis, the sol–gel route offers versatile ways to synthesize effective coatings with specific properties. Surface functionality can be optimized by varying experimental parameters such as the chemical structure, the composition and the ratio of precursors and complexing agents, the rate and conditions of hydrolysis, the synthesis media, the aging and curing conditions, and the deposition procedure.[10–14] The objective of this study is to comparatively investigate the process and properties of repeated sol-gel ZrO_2 and Al_2O_3 coatings. The coatings were characterized and the effects of the process on their properties were analysed.[15–17]

2 EXPERIMENTAL

AM60 magnesium alloy plates were used as the substrates. The specimens were cut into pieces of 20 mm × 20 mm × 2 mm and their surfaces were ground and degreased ultrasonically in acetone and then dried with hot air. The deposition steps were as follows: sol preparation, gelation and heat treatment (**Figure 1**). Initially, deionized water was heated in a glass beaker until it reached 80 °C. Aluminium sec-butoxide (ASB) was added to the water with continuous mixing. The molar

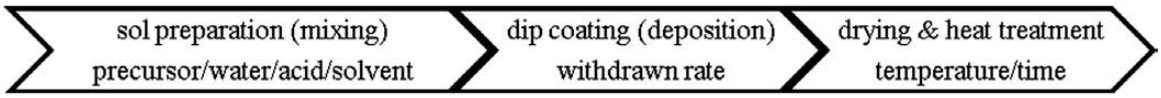

Figure 1: Flow chart for the preparation of coatings
Slika 1: Postopek priprave nanosa

ratio of ASB to water was 1 : 25. As hydrolysis took place, the temperature of the solution rose to 90 °C, at which it was maintained for 3 min. Then, acetoacetate (AcAc) was added to the mixture. The molar ratio of AcAc to water was fixed at 1 : 25. After stirring for 2 min, nitric acid was added to the solution stepwise, with stirring until it was transformed into a transparent solution. The pH value of the as-synthesized sol was about 3. The Al_2O_3 sol–gel film was deposited onto the magnesium substrate via the dip-coating method and withdrawing at a constant rate of 2 cm/min. The coated substrate was dried in a clean cabinet at 130 °C for 10 min to produce the alumina gel film. Then, the supported gel films were subjected to a thermal treatment at 500 °C for 1 h in an oxygen atmosphere. Zirconium n-propoxide (ZrNP) was diluted in n-propanol as the source of zirconia, and then acetylacetone AcAc and deionized water (diluted with n-PrOH) were added. The molar ratio of $Zr(n\text{-}OPr)_4$: AcAc : H_2O : n-PrOH was 1 : 2 : 2 : 60. After stirring for 3 h at room temperature, a clear precursor solution was obtained.[16] The ZrO_2 coatings were deposited by dipping the substrate into the sol and withdrawing it at a constant rate of 5 cm/min. Thin layers were prepared by repeating the dip coating and after every deposition there was a heat treatment of the sample at 500 °C for 1 h in an air atmosphere. The thicker films were produced by repeating the dipping process four times, followed by a thermal treatment.

The deposited films were studied by using scanning electron microscopy (SEM), while the film thicknesses and the refractive indices were measured using the ellipsometry method (Jobin Yvon, UVISEL HR 460). The structures of the resulting films were examined by grazing-incidence X-ray diffraction (XRD) with Cu K_α radiation using a thin-film apparatus. The electrochemical measurements were performed on a EG&G 273A-type potentiostat, using Pt as an auxiliary electrode, a saturated calomel electrode (SCE) as a reference electrode and 3.5 % NaCl solution as an aggressive medium. The potential was scanned from –1.8 V to 0.7 V (vs. SCE) at a scanning rate of 0.5 mV/s.

3 RESULTS AND DISCUSSION

3.1 Morphology and Thickness

Different viscosities of sols were created by the addition of the required amounts of nitric acid to the synthesis mixture of aluminium sec-butoxide and AcAC in n-propanal, which allowed us to control the rate of the condensation reactions. Uniform, mesoporous alumina coatings were obtained for the solvent-withdrawal rates below 10 cm/min. The limiting withdrawal rate increases as the solvent evaporation rate increases and it decreases as the sol viscosity increases. The cross-sectional morphologies indicate a mean thickness of approximately 1.6 μm and 2.3 μm for the repeated sol-gel coating for

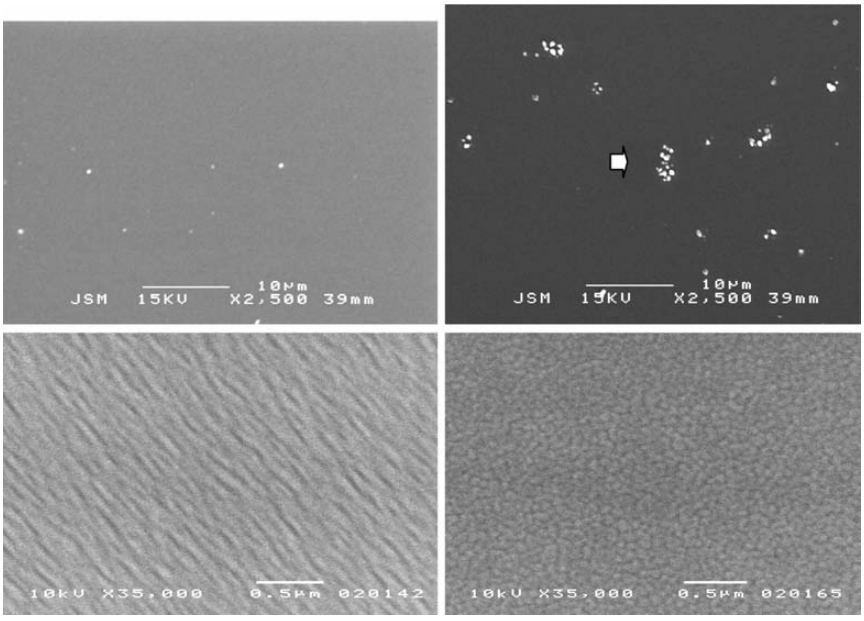

Figure 2: Surface morphology of sol-gel coatings using the dip-coating method (SEM micrographs)
Slika 2: Morfologija površine sol-gel nanosa s potapljanjem (SEM)

ZrO_2 and Al_2O_3, respectively (**Table 1**). The deposition efficiency is higher in the Al_2O_3 than in the ZrO_2 sol-gel coating. The porosity level of the alumina coating is lower than the zirconia coating.

Table 1: Thicknesses of the coatings
Tabela 1: Debeline nanosov

Composition	Average bilayer thicknesses (nm) for 9 measurement		
	Min	Average	Max
ZrO_2	63.42	65.2 ± 5	68.72
Al_2O_3	82.33	87.2 ± 4	90.14

It is clear from **Figure 2** that both films were smooth, compact and crack-free, and the thicknesses were between 60 nm and 95 nm. In addition, a lot of bumps and small pores were observed in this film.

3.2 Crystal Structure

Figure 3 illustrates the structure of the coatings formed on the AM60 alloy substrate. Both of the coatings have an amorphous structure. A small quantity of crystallite structures were observed, depending on the heat-treatment temperature and the time. However, the crystallisation growth was inadequate for both coatings. At higher temperatures than 600 °C for 1 h the crystallites started to produce strong peaks in the XRD pattern for the Al_2O_3 film. The characteristic peaks of γ-Al_2O_3 and δ-Al_2O_3 that were observed imply the existence of crystallized γ-Al_2O_3 and δ-Al_2O_3, which were transferred from the alumina sol annealed at 500 °C in the amorphous coating. The repeated sol-gel coating, which indicates a more crystallized α-Al_2O_3 phase, is due to the direct introduction of Al_2O_3 particles. These results are similar to those in Wang's study.[18] The zirconia coatings are made up of m-ZrO_2 (monoclinic crystal structure) and t-ZrO_2 (tetragonal crystal structure) after a heat treatment at 600 °C for 4 h (**Figure 3**). Partial spinodal decomposition was observed in the ZrO_2 coating.

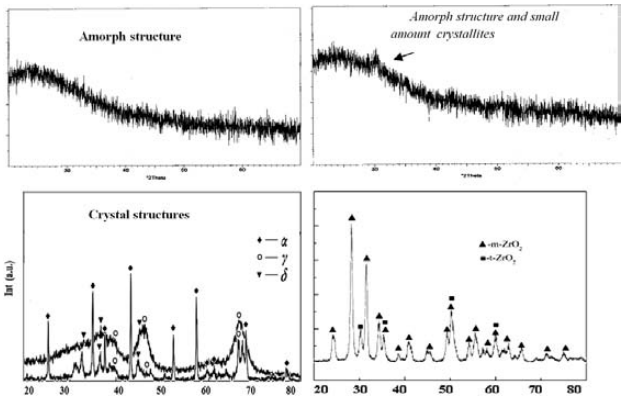

Figure 3: XRD patterns of the sol–gel coatings
Slika 3: XRD-posnetki sol-gel nanosov

3.3 Optical Properties

Figure 4 shows the reflective spectra of a glass substrate, alumina bi-layer coatings with 1.5 and 1.625 refractive indices in the region 300–800 nm. The refractive index is changing between 1.9 and 2.2 for the zirconia coating. The magnitude of the refractive index decreases with the heat-treatment temperature and the refractive indices of the Al_2O_3 and ZrO_2 thin films decrease with the increasing coating thickness. With an increase in the crystallinity there is a decrease in the refractive index of the thin films. The refractive index of the films depends strongly on their morphology. Up to the heat-treatment temperature, limiting the amorphous and crystallized phase, it increases steadily, probably in relation to an increasing densification of the layer. The lowering of the refractive index for the crystallized films is probably related to a lower densification of the films. The decrease of light intensity is strongly lowered for amorphous layers.

3.4 Corrosion Properties

In both cases, the polarization curves of the sol-gel-coated substrates were appreciably different from that of the bare substrates. The corrosion test showed a smooth surface with no appreciable delamination or cracking of the coating on the magnesium alloy substrates. The open-circuit potential, E_{oc}, of the sol-gel-coated substrates was significantly lower than that of the bare surfaces

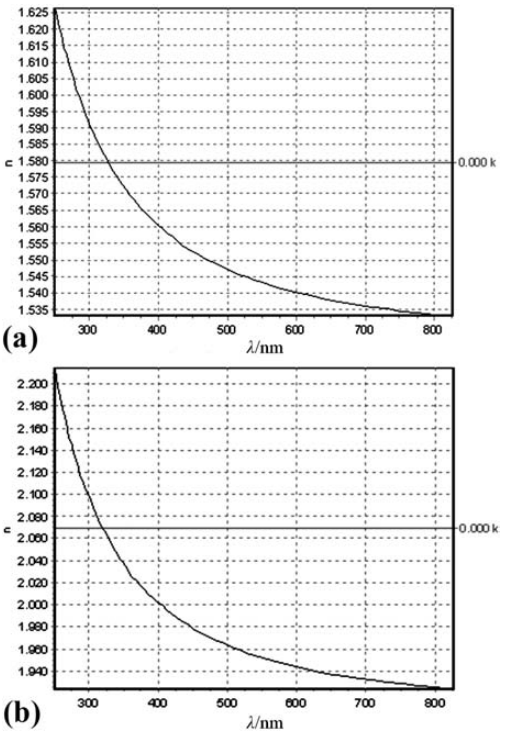

Figure 4: Refractive index (n) versus the wavelength λ/nm change for the coatings
Slika 4: Spremembe lomnega količnika (n) v odvisnosti od valovne dolžine λ/nm pri nanosih

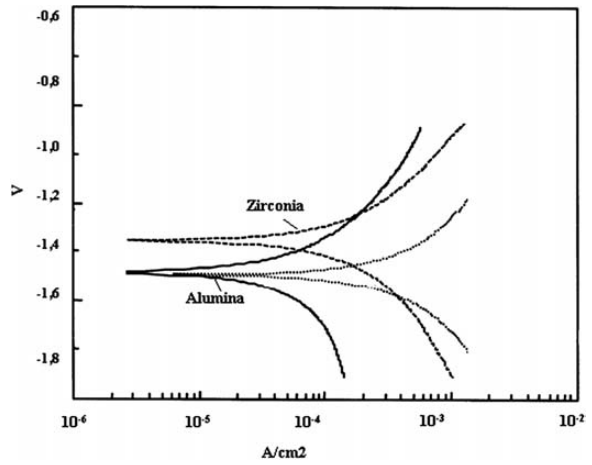

Figure 5: Polarization curves for the thin oxide films: ZrO_2 and Al_2O_3
Slika 5: Polarizacijski krivulji za tanek oksidni nanos ZrO_2 in Al_2O_3

(**Figure 5**). In addition, a distinct passivation region was present for the coated substrates. The corrosion-protection properties of the sol–gel-derived coatings are strongly dependent on the processing conditions. As evident from **Figure 5**, the alumina (Al_2O_3) film corrosion protection is better than the zirconia (ZrO_2) films.

4 CONCLUSIONS

The sol-gel-deposited oxide films formed with these compounds had good adhesion, reflectivity or UV protection. After the appropriate deposition and heat treatment the oxide films were formed with very favourable properties, such as high adhesion, homogeneity and density. The sol-gel alumina coatings developed on the magnesium alloy surface provide superior corrosion protection. After the heat treatments the XRD patterns revealed crystalline structures. With a controlled heat treatment a slight increase in the corrosion resistance was observed. However, both of the alumina- and zirconia-based coatings can be used for optical applications with suitable heat-treatment conditions. The refractive index of the alumina film was lower than that of the zirconia films. This depends on the crystallite structure and the surface morphology, such as bubbles and the porosity effect.

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5 REFERENCES

[1] E. F. Emley, Principle of magnesium technology, Pergamon Press, London 1966, 297
[2] M. M. Avedsian, H. S. Baker, Magnesium and magnesium alloys, ASM International, New York 1999, 138
[3] J. E. Gray, B. Luan, Protective coating on magnesium and its alloys, A critical review, Journal of Alloys and Compounds, 336 (**2002**) 1–2, 88–113
[4] R. Arrabal, E. Matykina, F. Viejo, P. Skeldon, G. E. Thompson, Corrosion resistance of WE43 and AZ91D magnesium alloys with phosphate PEO coatings, Corrosion Sci., 50 (**2008**) 6, 1744–1752
[5] Z. M. Liu, W. Gao, Electroless nickel plating on AZ91 Mg alloy substrate, Surface and Coatings Technology, 200 (**2006**) 16–17, 5087–5093
[6] Y. Tamar, D. Mandler, Corrosion inhibition of magnesium by combined zirconia silica sol-gel films, Electrochim Acta, 53 (**2008**), 5118–5127
[7] Y. Kobayashi, T. Ishizaka, Y. Kurokawa, Preparation of alumina films by the sol-gel method, J Mater Sci., 40 (**2005**), 263–283
[8] X. K. Zhong, Q. Li, B. Chen, J. P. Wang, J. Y. Hu, W. Hu, Effect of sintering temperature on corrosion properties of sol-gel based Al_2O_3 coatings on pre-treated AZ91D magnesium alloy, Corrosion Sci., 51 (**2009**), 2950–2958
[9] Q. Li, B. Chen, S. Xu, H. Gao, L. Zhang, C. Liu, Structural and electrochemical behavior of sol–gel ZrO_2 ceramic film on chemically pre-treated AZ91D magnesium alloy, Journal of Alloys and Compounds, 478 (**2009**), 544–549
[10] M. L. Zheludkevich, I. M. Miranda Salvado, M. G. S. Ferreira, Sol-Gel Coatings for Corrosion Protection of Metals, J. of Materials Chemistry, 15 (**2005**), 5099–5111
[11] A. Atkinson, D. L. Segal, Some recent developments in aqueous sol-gel processing, J. Sol–Gel Sci. Technol., 13 (**1998**), 133–139
[12] D. Niznansky, J. L. Rehspringer, Infrared study of SiO_2 sol to gel evolution and gel aging, J. Sol–Gel Sci. Technol., 180 (**1995**), 191–196
[13] L. Nicole, C. Boissiere, D. Grosso, A. Quach, C. Sanchez, Meso structured hybrid organic-inorganic thin films, J. Mater. Chem., 15 (**2005**), 3598–3627
[14] F. Mammeri, E. Le Bourhis, L. Rosez, C. Sanchez, Mechanical properties of hybrid organic-inorganic materials, J. Mater. Chem., 15 (**2005**), 3787–3811
[15] E. Altuncu, Practicability of a ceramic thin film formation technique in order to improve the surface properties of magnesium and its alloys, Kocaeli University, Metallurgical and Materials Engineering, Master Thesis, 2004
[16] H. Li, K. Liang, L. Mei, S. Gu, S. Wang, Oxidation protection of mild steel by zirconia sol–gel coatings, Materials Letters, 51 (**2001**), 320–324
[17] C. Jing, X. Zhao, Y. Zhang, Sol–gel fabrication of compact, crack-free alumina film, Materials Research Bulletin, 42 (**2007**), 600–608
[18] Z. L. Wang, R. C. Zeng, Comparison in characterization of composite and sol-gel coating on AZ31 magnesium alloy, Trans. Nonferrous Met. Soc. China, 20 (**2010**), 665–669