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INFLUENCE OF Na_2SiF_6 ON THE SURFACE MORPHOLOGY AND CORROSION RESISTANCE OF AN AM60 MAGNESIUM ALLOY COATED BY MICRO ARC OXIDATION

VPLIV Na_2SiF_6 NA MORFOLOGIJO POVRŠINE IN KOROZIJSKO ODPORNOST MAGNEZIJEVE ZLITINE AM60, PREKRITE Z MIKROOBLOČNO OKSIDACIJO

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Oxide coatings were formed by micro arc oxidation (MAO) on an AM60 magnesium alloy substrate. The effects of Na_2SiF_6 in an electrolytic solution on the micro arc oxidation process and the structure and mechanical properties of the oxide coatings were investigated. The results showed that the MAO coating produced in the electrolyte with Na_2SiF_6 was thicker and more uniform than that produced in the electrolyte without Na_2SiF_6. The pore diameter of the MAO coatings was reduced by the addition of Na_2SiF_6, while the coating density and surface roughness were increased. The coating formed in the electrolytic solution with or without the Na_2SiF_6 had a higher surface hardness than the AM60 alloy and the results of the corrosion behavior for including Na_2SiF_6 showed better resistance than that formed in the solution without Na_2SiF_6.

Keywords: magnesium alloy, micro arc oxidation (MAO), Na_2SiF_6, corrosion

Oksidne prevleke nastajajo pri oksidaciji v mikroobloku (MAO) podlage iz magnezijeve zlitine AM60. Preiskovan je bil vpliv Na_2SiF_6 v elektrolitni raztopini na proces oksidacije v mikroobloku in na mehanske lastnosti oksidne prevleke. Rezultati so pokazali, da je oksidna prevleka MAO, izdelana v elektrolitu z Na_2SiF_6, debelejša in bolj enakomerna, kot če je izdelana v elektrolitu brez Na_2SiF_6. Premer por v MAO prevleki se je zmanjšal z dodatkom Na_2SiF_6, medtem ko sta gostota prevleke in hrapavost površine narasli. Prevleka, nastala v elektrolitski raztopini, z ali brez Na_2SiF_6, ima večjo trdoto površine kot AM60 zlitina. Rezultati obnašanja pri koroziji, vključno z Na_2SiF_6, kažejo na boljšo odpornost kot pri prevleki, nastali v raztopini brez Na_2SiF_6.

Ključne besede: magnezijeva zlitina, oksidacija v mikro obloku (MAO), Na_2SiF_6, korozija

1 INTRODUCTION

Magnesium (Mg) alloys have been used in many industrial applications due to their high specific strength, low density and excellent mechanical properties. In recent years, Mg alloys are widely used in automotive production, with their low density, good castability and stiffness.[1–6] However, the poor corrosion resistance of Mg alloys is restricting their applications. That is why it is essential for magnesium alloy products to be protected with a surface treatment.[1,4,7] There are many techniques to improve the corrosion resistance of Mg alloys, such as electroless plating, conversion films, laser surface melting and organic coatings. Micro arc oxidation (MAO) is another efficient method to improve the properties of Mg alloys by producing ceramic films on their surface.[1,4,8] The MAO coatings have a strong adhesion to the Mg substrate, controllable thickness and other excellent properties, such as corrosion resistance, thermal shock resistance. However, the properties of MAO coatings are affected by the processing parameters, such as the composition of the electrolyte, voltage, current density, time, etc.[1,9] In this work, micro arc oxidation films have been coated on a Mg alloy with and without the Na_2SiF_6 in an electrolytic solution and the structure and corrosion resistance of the oxide coatings were investigated. The properties of the coatings were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD). The results were compared and correlated to understand the influence of the Na_2SiF_6 in the electrolytic solution on the coating-formation process, properties and corrosion behavior.

2 EXPERIMENTAL PART

2.1 Material and coating process

AM60 magnesium alloy was used as the substrate material in this study. The chemical composition of AM60 is given in **Table 1**.

Table 1: Chemical composition of AZ91D magnesium alloy (in mass fractions, *w*/%)

Tabela 1: Kemijska sestava magnezijeve zlitine AZ91D (v masnih deležih, *w*/%)

Al	Mn	Si	Fe	Mg
5.93	0.18	0.02 (max.)	0.013	Balance

Table 2: Concentration of the electrolyte solution
Tabela 2: Koncentracija elektrolitske raztopine

Sample code	Na_2SiO_3 (g/L)	NaOH (g/L)	Na_2SiF_6 (g/L)	Conductivity (mS/cm)	Roughness (μm)	Average thickness (μm)
AM60-%0	15	5	–	14.6	2.986	31.2±5
AM60-%1	15	5	1	15.1	3.532	32.6±5
AM60-%2	15	5	2	15.3	3.565	46.63±5
AM60-%4	15	5	4	17.4	3.920	47.63±5

The samples for all the tests were cut into cylinders with dimensions of 30 mm × 10 mm × 10 mm and mechanically polished with 600- and 1200-grit emery papers, rinsed with distilled water and dried in warm air. The MAO process of the sample was coated in alkali silicate electrolyte solution, which consisted of Na_2SiO_3 in distilled water with NaOH. After that 1%, 2%, and 4% Na_2SiF_6 was added to the electrolytic solution. The effects of the Na_2SiF_6 in the electrolytic solution on the MAO process and the structure and mechanical properties of the oxide coatings were investigated. The electrolyte composition is given in **Table 2**. The surface roughness (*R*a) of the MAO coatings was detected using a Mahr, Perthometer M1 surface roughmeter. The thicknesses of the coatings were measured using an SEM and the values of the conductivity for the electrolytes prepared with the base electrolyte and different concentrations of Na_2SiF_6 were measured and are shown in **Table 2**.

The oxide coatings were produced at a constant anodic voltage of 370 V for 30 min. The temperature of the electrolyte was kept at approximately 30 °C using a stirring and cooling system and the current density was varied in the range of 0.6–2 A cm^{-2}. The samples were rinsed in water and dried in hot air after the MAO process was finished.

2.2 Microstructure

The surface morphologies of the AM60 samples coated by MAO were characterized with scanning electron microscopy (SEM). The phase components of the coated samples were analyzed with X-ray diffraction (XRD) using Cu-K_α radiation.

2.3 Hardness test

The hardnesses of the AM60 and coated samples were measured using an FUTURE TECH-CORP.FM-700 microhardness tester at a load of 100 g for loading time of 10 s. The average of three measurements was reported.

2.4 Corrosion test

The immersion corrosion test was carried out in 10 % of mass fractions of NaOH solution for 10 d in an open system, the corrosion products were cleaned in distilled water with an ultrasonic cleaner, all the samples were weighed with a JA5003N electronic balance (accuracy: 1 mg) before and after the immersion test, and the corrosion rate was calculated from the weight-loss data. The PH of the solution was around 12±0.5.

3 RESULTS AND DISCUSSION

The SEM microstructures of the AM60 alloy after the MAO treatment for different electrolyte compositions are shown in **Figure 1**. It is clear that an increase in Na_2SiF_6 in the electrolytic solution changed the surface morphologies of the MAO coatings. The MAO coating processed for AM60-% 0, as shown in **Figures 1a** and **1b**, exhibits a relatively uniform surface appearance with large pores. **Figures 1c** to **1f** show the morphologies of the MAO coatings when adding 1 % and 4 % Na_2SiF_6, respectively, and the coatings are much rougher when compared with **Figure 1b**. Na_2SiF_6 can change the solution's properties, such as the solution conductivity, which

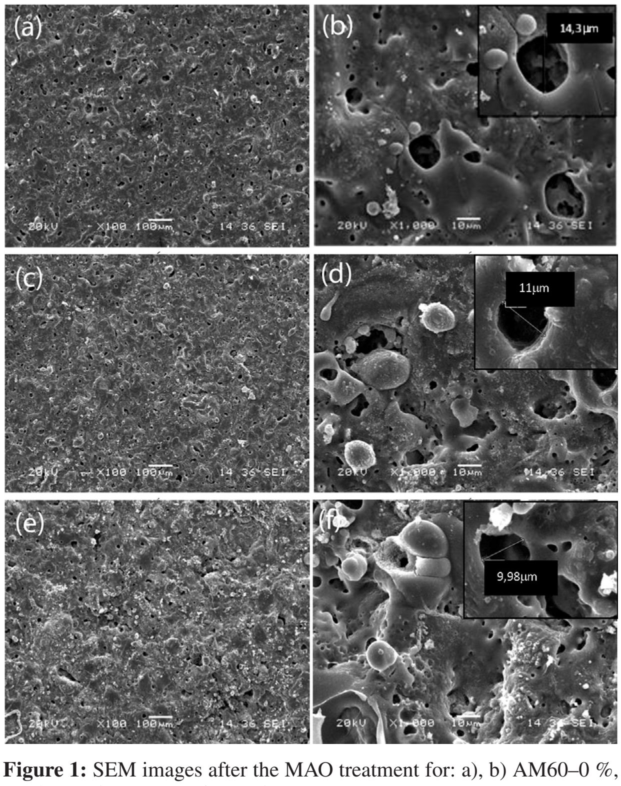

Figure 1: SEM images after the MAO treatment for: a), b) AM60–0 %, c), d) AM60–1 %, e), f) AM60–4 %
Slika 1: SEM-posnetki po MAO-obdelavi: a), b) AM60–0 %, c), d) AM60–1 %, e), f) AM60– 4 %

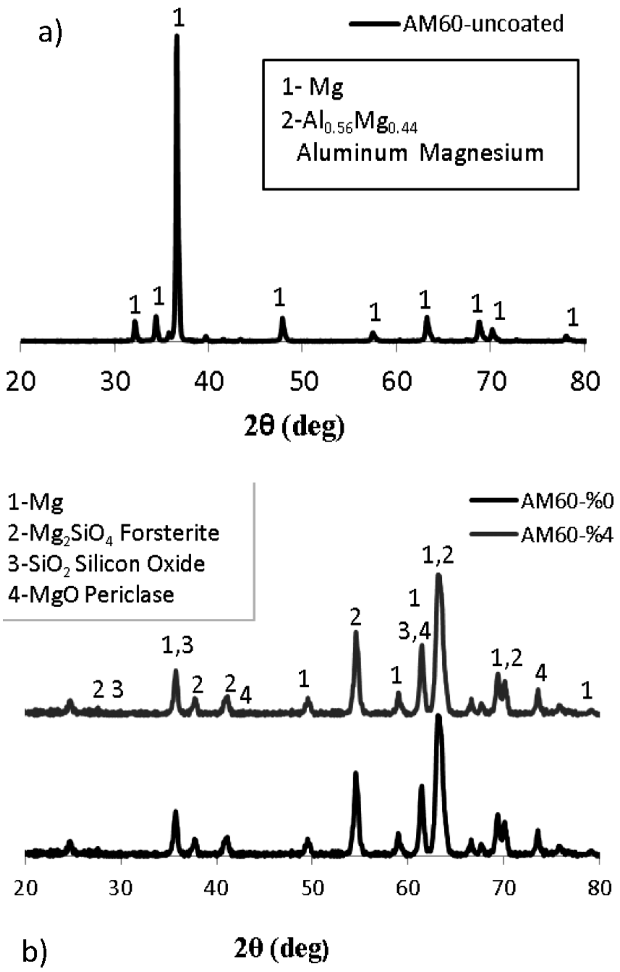

Figure 2: XRD patterns for: a) uncoated AM60, b) AM60-%0 and AM60-%4

Slika 2: Rentgenogram za: a) AM60 brez prevleke, b) AM60 0 % in AM60 4 %

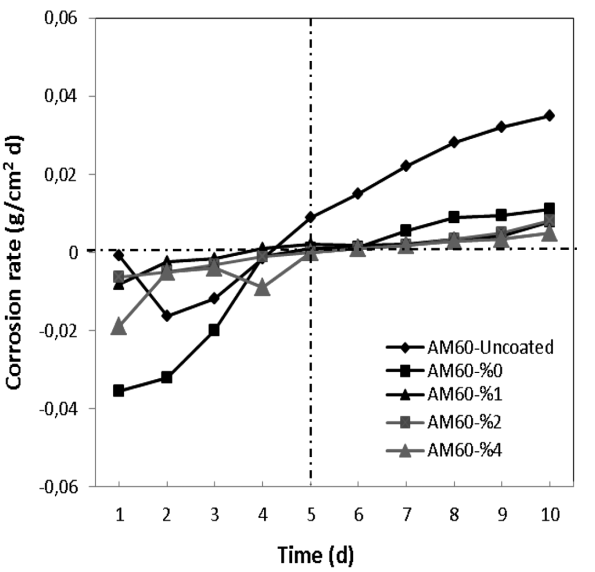

Figure 3: Variation of corrosion rate with immersion time in 10 % of mass fractions of NaOH

Slika 3: Spreminjanje hitrosti korozije s časom potapljanja v 10 % masnem deležu raztopine NAOH

plays an important role in determining the morphology and thickness. The sizes of certain pores decrease obviously with an increase of the Na_2SiF_6 solution, which is considered to be related to the increasing electrolyte conductivity.[10] According to **Table 2**, the electrolyte conductivity increased an increase in the concentration of Na_2SiF_6.

Table 2 reveals the roughness and average thickness of the MAO coatings on the AM60 alloy. It can be seen that the thickness and roughness increase with the concentration of the Na_2SiF_6, especially after 2%. The coating properties such as thickness and porosity are influenced by the final voltage, which is closely related to the solution conductivity. The electrical conductivity of the electrolytes increases with an increase of the Na_2SiF_6 concentration. The higher Na_2SiF_6 concentration corresponds to a higher current and thus a more intensive micro-arc discharge will occur on the surface.[11,12]

Before the coating, the average micro-hardness value is about 60±5 $HV_{0.1}$ for the AM60 alloy. After the MAO coating, the surface hardness increases with increasing Na_2SiF_6 concentration, and nearly all the coated samples have a hardness of approximately 479±5 $HV_{0.1}$ (AM60-%1). The surface hardness increases eight times when compared with the uncoated sample

The phases identified through the analysis of the XRD patterns for the uncoated AM60 alloy, AM60-%0 and AM60-%4 samples are presented in **Figure 2**. It is clear that the bulk material is formed of Mg and $Al_{0.56}Mg_{0.44}$ phases. However, the MAO coatings formed of Mg, Mg_2SiO_4 (Forsterite), SiO_2 (Silicon Oxide) and MgO (Periclase) phases. In addition, it can be seen from **Figure 2b** that the Mg_2SiO_4 (Fosterite) is the minor common phase that is present in all the coatings. This phase is formed due to the composition of Si in the Na_2SiO_3 (present as a constituent of the electrolyte) in the coating in the form of Mg_2SiO_4. Different phases were not seen on AM60-%4 sample surface when adding Na_2SiF_6.

Figure 3 shows the corrosion rate variation with the immersion time of the MAO coatings in 10 % mass fractions of NaOH solution. It is clear that three characteristics behaviors occur in the corrosion test, as can be seen from the curves. First of all, the corrosion rate values of the samples were negative at the initial periods. The mass gain phenomenon can result from the re-oxidation and attachment of the corrosion products. Then, the mass loss happened after immersion for about 5 d. After a long immersion period the coating layer and corrosion products began to exfoliate from the samples' surfaces. Thirdly, the corrosion rates of the MAO-coated samples were lower than the as-cast sample (AM60) for the whole immersion test. This indicates that the samples having the MAO coating with Na_2SiF_6 a have higher corrosion resistance.

4 CONCLUSIONS

Oxide coatings were produced on the AM60 alloy by micro arc oxidation in different solutions with and without Na_2SiF_6. The coatings produced with Na_2SiF_6 were thicker than the ones produced without Na_2SiF_6 for the same parameters. The pores on the surface decrease with an increasing Na_2SiF_6 concentration and the surface becomes rougher. The hardness improves nearly eight times when compared with uncoated sample. The corrosion resistance of the samples coated in the Na_2SiF_6 electrolyte solution can be attributed to the more uniform and compact structure of this coating, which acts as a barrier to the transfer of corrosive ion from the aggressive solution into the coating. The AM60-%4 sample shows the best corrosion resistance in 10 % mass fractions of NaOH solution.

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