Improvement of wear and corrosion resistance of AZ91 magnesium alloy by applying Ni–SiC nanocomposite coating via pulse electrodeposition

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Abstract: To improve the surface properties of AZ91 magnesium alloy, Ni–SiC nanocomposite coatings with various SiC contents were pulse electrodeposited in modified Watts baths containing SiC nano-particles with the concentration of 0–15 g/L. The morphology of the coatings was studied by scanning electron microscope (SEM). The SiC content of the coatings was measured by energy dispersive spectroscopy (EDS) analyzer. Microhardness measurement of the coatings showed up to 600% enhancement for the sample produced from the bath with 15 g/L SiC. The corrosion behavior of the coated AZ91 alloy was investigated by potentiodynamic polarization method. The results reveal a significant improvement in the corrosion resistance, that is, the corrosion current density decreases from 0.13 mA/cm² for uncoated specimen to 1.74×10⁻⁶ mA/cm² for the sample coated from the bath containing 15 g/L SiC and the corrosion potential increases from −1.6 V for uncoated specimen to −0.31 V for the sample coated from the bath. The wear resistance of both coated and uncoated samples was evaluated by pin-on-disc tribotester. The results show that the wear volume loss of coated sample is 8 times less than the bare alloy.

Key words: AZ91 magnesium alloy; Ni–SiC nanocomposite coating; corrosion resistance; wear resistance

1 Introduction

Owing to the high specific strength of magnesium and its alloys with the density of about 30% less than that of aluminum and aluminum alloys, a promising alternative was offered for mass sensitive structural applications in the automotive and aerospace industries [1]. However, the applications of these alloys are restricted due to their poor surface properties. Undesirable corrosion behavior of these alloys caused by high reactive nature of magnesium makes them highly susceptible to corrosion in aggressive media. In addition, low wear resistance of these alloys is another reason to hinder the use of magnesium and its alloys. Therefore, the improvement of surface properties of these alloys has turned into a serious concern, hence, this issue has subjected to lots of researches [2–6].

Corrosion can be minimized by the use of high purity alloys, the elimination of surface contamination or galvanic couples. Moreover, increasing the hardness of the alloys by the addition of proper alloying elements [7,8] or reinforcement [9] can improve the wear resistance. Also, surface grain size reduction may enhance the wear resistance as well [10,11].

One of the most effective ways to prevent magnesium alloys from being corroded or abraded is the use of protective coatings. However, due to the formation of oxide or hydroxide films, magnesium and its alloys are difficult to coat since these alloys are so reactive. It is important to achieve the flawless, dense coating with enough adhesion to the substrate. Therefore, the proper pretreatment to remove the aforementioned films is required [12].

There are a number of coatings which have been applied on magnesium substrate like pure metals such as nickel, copper and gold [13,14] or composite coatings, for example, Ni–TiO₂, Ni–P–B₄C, Al–Al₂O₃ [15–17]. Moreover, Ni–SiC nanocomposite coating has been applied on different substrates such as steel and it has shown a considerable corrosion and wear resistance improvement [18,19]. So, it can be assumed that the application of Ni–SiC nanocomposite coating on magnesium can improve both corrosion and wear behavior of these alloys.

Beside the materials for the coating, the procedure of applying is a main factor as well. It is found that appropriate selection of pulse current parameters leads to
the achievement of Ni–SiC coatings with higher incorporation and more uniform distribution of ceramic particles in the metallic matrix, which result in better properties with respect to direct current technique [20–23].

The aim of this work is to employ Ni coating reinforced by SiC nano-particle on AZ91 magnesium alloy, via pulse electrodeposition technique, to ameliorate its corrosion and wear properties.

2 Experimental

The substrate material was as-cast AZ91 magnesium alloy with dimensions of 30 mm × 30 mm × 5 mm. The chemical composition of the alloy is given in Table 1. The samples were abraded with 2000 grit SiC paper before the zinc immersion pretreatment process. In addition to the technical procedure, the used solutions with their composition and operation condition can be found in ASTM B480 [24] as well.

<p>| Table 1 Chemical composition of AZ91 magnesium alloy |
|-----------------|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>w(Al)/%</th>
<th>w(Zn)/%</th>
<th>w(Mn)/10^-6</th>
<th>w(Fe)/10^-6</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1</td>
<td>0.17</td>
<td>0.01</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Ni–SiC coatings were electrodeposited from a modified Watts bath containing different amounts of SiC powders with average particle size of 40 nm. First, SiC powder and SDS surfactant were added to distilled water. The mixture was stirred for 6 h. Then the Watts solution was added to the suspension and the volume of the bath was raised to 300 mL. The prepared suspension was again stirred for 12 h and exposed to the ultrasonic waves for 1 h in an ultrasonic bath with 160 W power before performing the coating procedure. The bath composition and operating conditions are shown in Tables 2 and 3. To adjust the pH value of the solution, NaOH and H₂SO₄ were used, respectively.

| Table 2 Chemical composition of bath (g/L) |
|----------------|----------------|----------------|----------------|----------------|
| NiSO₄·7H₂O      | NiCl₂·6H₂O     | H₃BO₃          | Saccharin      | SDS            |
| 300            | 45             | 45             | 1              | 1              |
|                |                |                |                | 0, 5, 10, 15   |

| SDS: Sodium dodecyl sulfate |

| Table 3 Operating conditions of electroplating |
|----------------|----------------|-----------------|-----------------|-----------------|
| pH             | Temperature/ °C | Frequency/ Hz   | Duty cycle%     | Current density/ (mA·cm⁻²) |
| 4.5            | 50             | 10              | 30              | 50              |

Electrodeposition of Ni–SiC composite coatings was performed by square pulse current in which the duty cycle is defined as t_on/(t_on+t_off), where t_on and t_off are the on-time and the off-time period of the imposed pulse, respectively. After 150 min electroplating, the thickness of the coatings was measured as (35±5) µm.

A scanning electron microscope (SEM) was employed for observation of the surface and the cross-section morphology of the coatings while a thin layer of gold was deposited on the samples. The mass fraction of SiC particles in the coatings was determined using an EDS analyzer, and the average value of three independent measurements was presented as final results.

The potentiodynamic polarization tests were performed by suspending the samples in 3.5% NaCl solution. The counter and reference electrodes were platinum and saturated calomel electrode (SCE), respectively. After about 1 h stabilization at rest potential, polarization test was commenced at a scan rate of 1 mV/s using an EG&G273 instrument. The corrosion current density and corrosion potential were determined by varying ±20 mV around the E_OCP.

Vickers microhardness of substrate and the coatings was evaluated using a microhardness tester with Vickers indenter, at a load of 1.96 N and duration of 30 s. For each specimen, the average hardness was taken from at least 3 tests.

The adhesion strength of the Ni–SiC coating pulse electroplated on AZ91 substrate was measured by a pull-off adhesion testing with the loading rate of 0.01 mm/s. Wear tests were carried out under dry sliding condition at room temperature, using a pin-on-disc tribotester with round head AISI 52100 steel pins. The tests were performed under 3 N of normal load for 100 m sliding distance. The sliding and the angular velocity were 0.15 m/s and 380 r/min, respectively. The wear testing machine recorded continuously the friction coefficient of the coating. The specimens were weighed before and after the tests with balance accuracy 0.0001 g to measure the mass loss. Then, the volume loss was assessed by use of the density of nickel (8.9 g/cm³) for coated samples and the density of magnesium (1.73 g/cm³) for uncoated specimens.

3 Results and discussion

3.1 Microstructure

The morphologies of coatings are presented in Fig. 1 in two magnifications. It can be observed that the coatings covered the whole surface of the substrate with sufficient compaction and uniformity. There are no macro or micro cracks or pores, so, good properties can be expected. The numerous of submicron and nano size particles are discerned. However, some agglomerated
Fig. 1 SEM images of surface morphology of coatings electrodeposited from bath with 0 g/L (a,b), 5 g/L (c,d), 10 g/L (e,f), 15 g/L (g,h) SiC.
particles larger than 1 μm are seen. But, uniform distribution of these agglomerates throughout the Ni matrix could decrease their negative effects. For further investigations of SiC nano-particles distribution, the typical X-ray map analysis of the sample coated from the bath with 15 g/L SiC is depicted in Fig. 2. The fine distribution of the SiC particles is noticeable.

The typical SEM image of the cross section of the sample coated from the bath containing 15 g/L SiC with X-ray map analysis is shown in Fig. 3 after etching with 65% nitric acid (volume fraction). In AZ91 substrate, the magnesium and Al-rich phases are distinctive, the nickel and the copper layers are distinguishable. The presence of Si element in the coating can be the evidence of SiC nano particles with fine distribution in the cross section of the coatings. The interface of the coatings and the substrate shows no cracks or abortion. Hence, the desirable adhesion between the coating and the substrate is expected.

Figure 4 illustrates the variation of SiC content in the coatings vs the concentration of SiC in the bath. As can be seen in Fig. 4, with increasing the concentration of SiC in the bath, the content of SiC particles in the coating increases as well. During the off-time period, when the current is disconnected, the ceramic particles can reach the cathode surface due to the bath agitation and be loosely adsorbed on it. By increasing the concentration of ceramic particles in the electrolyte, more particles can reach the cathode surface during off-time period. These loosely adsorbed particles can be hardly adsorbed during the subsequent on-time period. So, an increase in the amount of ceramic particles suspended in the electrolyte increases the SiC content in the coating.

### 3.2 Corrosion

Figure 5 represents the polarization curves for the substrate, pure Ni coated sample and Ni−SiC coated specimens. The $I_{corr}$ and $\phi_{corr}$ of specimens are collected in Table 4. The corrosion current density and potential of the substrate are 0.13 mA/cm$^2$ and −1.6 V, respectively, which indicate the poor corrosion properties of the substrate. The application of the Ni coating improves the corrosion behavior, namely, the corrosion occurs at a higher potential (−1.28 V) and a lower current density ($9.07 \times 10^{-2}$ mA/cm$^2$). The Ni coating acts as a barrier against the corrosive media and protects the substrate from being corroded. The incorporation of the SiC nano particles into the coating enhances the corrosion resistance even more, and with increasing the SiC concentration in the bath the corrosion current density and potential shift become lower and higher, respectively. Somehow, the sample coated from the bath with 15 g/L SiC displays the highest corrosion resistance ($I_{corr}=1.74 \times 10^{-6}$ mA/cm$^2$, $\phi_{corr}=-0.31$ V). The corrosion improvability of SiC particles can be attributed to the following reasons.

1) Ceramic particles such as SiC, WC and Al$_2$O$_3$ have good corrosion properties, and the presence of these particles in the coating enhances the corrosion resistance. When these particles are distributed in the coating, the area of the coating in contact with corrosive media reduces. Thus, the codeposition of SiC particles in the coating improves its corrosion resistance [25].

2) SiC particles distributed in the nickel matrix act as the barriers which can change the corrosion path and even prevent its progress [19].
3) Codeposition of SiC particles in the nickel coating can change its morphology from a columnar morphology to a coaxial one. In a columnar morphology, there are straight paths that through them corrosion can take place readily and fast. But in a coaxial morphology, the straight and long paths are substituted with short and meandrous ones which lead to a decline in corrosion rate [26].
Table 4 Polarization data calculated from Fig. 5

<table>
<thead>
<tr>
<th>Coating</th>
<th>$J_{corr}$/mA·cm$^{-2}$</th>
<th>$\phi_{corr}$ (vs SCE)/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91</td>
<td>0.13</td>
<td>−1.6</td>
</tr>
<tr>
<td>Pure Ni</td>
<td>$9.07 \times 10^{-2}$</td>
<td>−1.28</td>
</tr>
<tr>
<td>Ni−5SiC</td>
<td>$7.72 \times 10^{-3}$</td>
<td>−1.23</td>
</tr>
<tr>
<td>Ni−10SiC</td>
<td>$1.70 \times 10^{-3}$</td>
<td>−0.42</td>
</tr>
<tr>
<td>Ni−15SiC</td>
<td>$1.74 \times 10^{-6}$</td>
<td>−0.31</td>
</tr>
</tbody>
</table>

4) The presence of SiC nano-particles reduces the submicron defects of the coating and restricts the access passages of corrosive media to the coating surface [27].

3.3 Microhardness

Figure 6 presents the variation of microhardness of bare and coated substrate. It can be observed that the application of Ni−SiC leads to a meaningful increase in the hardness of the substrate. With SiC codeposition in the coating the hardness becomes higher, and the more addition of SiC nano particles into the bath results in increase of the hardness of the coated samples.

Fig. 6 Variation of microhardness of coatings as function of SiC concentration in bath

It has been reported [28,29] that in microcrystalline Ni−SiC composites, the enhanced hardness is originated from the presence of ceramic particles. The claimed mechanism is Orowan type, namely, the incorporation of ceramic particles in nickel matrix, could restrain the growth of nickel grains and the plastic deformation of the matrix under loading, by way of grain fining and dispersion hardening effects. The grain fining and dispersion hardening effects become stronger with increasing SiC nanoparticulate content, thus the microhardness of Ni−SiC nanocomposite coatings increases with increasing SiC nanoparticulate content. However, in nanocrystalline matrixes, this mechanism is unlikely to operate since the particle size is larger than the grain size of the matrix. So, if the dispersion hardening is not operative and no grain refining hardening occurs at high concentrations of SiC particles, why does the microhardness of the deposits increase continuously? The suggested deformation mechanism for nanocrystalline materials called as “stress-assisted activation of GB (grain boundary) atoms” [30,31] is the key reason. This mechanism includes GB sliding, atom displacement in GB, nucleation and emission of partial dislocation at a very small loop at a GB facet crack tip or triple point. It has been proposed [32] that the SiC particles are responsible for the commencement of stress-assisted activation of GB atoms. It can relax the local stress concentration and hence, improves the plasticity. Another result of stress-assisted activation of GB atoms is that the SiC particles suppress the formation of nano-cracks. These effects cause the specimens sustain larger loads. Therefore, with increasing embedded SiC in matrix, the microhardness increases.

3.4 Wear

Before the wear test, the adhesion strength of the coating was evaluated and the data showed that the coatings can tolerate 11 MPa at the point of separation. This value is in good agreement with the other results [33] and can be considered appropriate for bearing the wear forces. The wear rates of bare substrate and coated specimens are exhibited in Fig. 7. The data clearly demonstrate a significant reduction in wear rate of coated samples. This can be confirmed by comparing the wear tracks on the worn surfaces of coated and uncoated samples in Fig. 8.

Fig. 7 Wear rate of bare substrate and coated samples prepared from baths with different SiC concentrations

The Ni−SiC nanocomposite coating improves the wear resistance of the AZ91 by the hardness enhancement. According to ARCHARD’s law [34] as the hardness of the samples shifts towards higher values the ware rates decline as well. The other effect can be the
Fig. 8 SEM images of worn surfaces of bare substrate (a), coated samples prepared from baths with SiC concentrations of 5 g/L (b), 10 g/L (c) and 15 g/L (d)

formation of tribological films. The EDS analysis indicates that these films are probably the iron oxides created during the contact between the coated samples and the steel pin.

The cross section of worn surface is displayed in Fig. 9. There are no cracks or abortions along the interface of the coating and the substrate. This is the evidence of the suitable adhesion required for improving the wear resistance of AZ91 magnesium alloy.

4 Conclusions

1) The corrosion potential increases from −1.6 V for AZ91 alloy to −0.31 V for the coating applied from the bath containing 15 g/L SiC.

2) The corrosion current density of the coated AZ91 magnesium alloy reduces from 0.13 mA/cm² to 1.74×10⁻⁶ mA/cm², namely, a significant improvement in corrosion resistance is achieved.

3) The microhardness of bare AZ91 alloy is HV 74, and increases to HV 523 for the coating applied from the bath containing 15 g/L SiC.

4) The wear resistance of AZ91 magnesium alloy enhances substantially, that is, the reduction of the wear volume loss from 0.005 mm³/m for bare substrate to 0.0006 mm³/m for the coated samples obtained from the bath with 15 g/L SiC.

Fig. 9 SEM image of cross section of worn surface of specimen coated from bath containing 15 g/L SiC
References


AZ91 镁合金脉冲电沉积 Ni–SiC 纳米复合涂层的磨损与腐蚀性能

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摘 要: 为了改善 AZ91 镁合金的表面性能，在含 0~15 g/L SiC 纳米颗粒的改进的瓦特槽中，采用脉冲电沉积得到不同 SiC 含量的 Ni–SiC 纳米复合涂层。采用扫描电子显微镜(SEM)研究涂层的形貌，采用能谱仪(EDS)测试涂层的 SiC 含量。从 15 g/L SiC 槽中电沉积得到的样品，其涂层的显微硬度提高了 600%。采用动电位极化法研究包覆 AZ91 镁合金的腐蚀行为。结果表明，样品的耐腐蚀性能明显提高，即腐蚀电流密度从未包覆样品的 0.13 mA/cm²降低到槽中含 15 g/L SiC 电沉积包覆样品的 1.74×10⁻⁶ mA/cm²，腐蚀电位从未包覆样品的−1.6 V 增加到槽中电沉积包覆样品的−0.31 V。使用盘销摩擦测试仪评估了包覆和未包覆样品的耐磨性能，包覆样品的磨损量比未包覆的小 8 倍。

关键词: AZ91 镁合金；Ni–SiC 纳米复合涂层；耐蚀性；耐磨性

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