

# High corrosion-resistance nanocrystalline Ni coating on AZ91D magnesium alloy

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## Abstract

Nanocrystalline (nc) Ni coating was direct-current electrodeposited on the AZ91D magnesium alloy substrate aimed to improve its corrosion resistance using a direct electroless plating of nickel as the protective layer. As comparison, two electroless Ni coatings on the magnesium alloy with different thickness were also presented in the paper. The surface morphologies of the coatings were studied by SEM and FESEM. The nc Ni coating had an average grain size of about 40 nm and an evident {200} preferred texture revealed by XRD. The hardness of the nc Ni coating was about 580 VHN, which was far higher than that (about 100 VHN) of the AZ91D magnesium alloy substrate. The electrochemical measurements showed that the nc Ni coating on the magnesium alloy had the lowest corrosion current density and most positive corrosion potential among the studied coatings on the magnesium alloy. Furthermore, the nc Ni coating on the AZ91D magnesium alloy exhibited very high corrosion resistance in the rapid corrosion test illustrated in the paper. The reasons for an increase in the corrosion resistance of the nc Ni coating on the magnesium alloy should be attributable to its fine grain structure and the low porosity in the coating.

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## 1. Introduction

Magnesium is becoming increasingly significant as a lightweight metal structural material (with a density of 1.74 g/cm<sup>3</sup>) in many industries—aircraft construction, space technology, optics, and automobile manufacturing, for example. However, magnesium is intrinsically highly reactive and its alloys usually have relatively poor corrosion resistance, which restricts the application of magnesium alloys in practical environments. So, it is often desirable to alter the surface properties of a magnesium or magnesium alloy workpiece in order to improve its corrosion and wear resistance, solderability, electrical conductivity or decorative appearance. This can be accomplished by coating the parts

with a metal that has the desired properties necessary for the specific application [1].

Since magnesium is one of the most electrochemically active metals, any coatings on magnesium alloys should be as uniform, adhered and pore-free as possible. One of the most cost effective and simple techniques for introducing a metallic coating to a substrate is the plating techniques, including electroless plating and electroplating. Furthermore, magnesium is classified as a difficult substrate to plate metal due to its high reactivity. As for electroplating on the magnesium alloy, there are currently two processes used for plating on magnesium and magnesium alloys: direct electroless nickel plating and zinc immersion [2]. It can be noted that in many previous reports on the electroless plating on magnesium alloys [3–6], the nickel ions were provided by basic nickel carbonate in the plating bath. Different from the methods mentioned above, direct electroless nickel plating on the AZ91D magnesium alloy was

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recently undertaken by using a plating bath containing sulfate nickel [7].

In the recent years, there have been considerable interests in understanding the mechanical properties, the corrosion resistance and the wear resistance of nc metals produced by electrodeposition, for example [8–14]. According to them, nc materials exhibited many unusual mechanical and electrochemical properties compared with conventional polycrystalline or amorphous materials. So introducing a nc coating combined the high corrosion resistance with good wear resistance on magnesium alloy substrate would be very promising.

In the present paper, the electroless Ni plating from an acidic bath [7] was first deposited on AZ91D magnesium alloy as the protective layer for the further electroplating operation, and then a nc nickel coating was direct-current electroplated on the protective layer. The microstructures and the electrochemical properties of the coatings on the AZ91D magnesium alloy substrate were studied by SEM, FESEM, XRD and electrochemical measurement.

## 2. Experimental

The substrate material used was AZ91D die cast magnesium alloy with a size of  $30 \times 40 \times 5$  mm. The alloy was mainly contained about 9.1% Al, 0.64% Zn, 0.17% Mn, 0.001% Fe and Mg balance. The samples were abraded with no.1500 SiC paper before the pretreatment processes. The technical flow chart of the electroplating on the AZ91D magnesium alloy is shown in Fig. 1. The samples were cleaned thoroughly with de-ionized water as quickly as possible between any two steps of the treatments. The direct electroless nickel plating with the thickness of about  $10 \mu\text{m}$  on AZ91D magnesium alloy [7] was used as the protective layer for further plating on the magnesium alloy. The electroplating nc Ni coating on the magnesium alloy was direct-current electroplated from a bath containing nickel sulfate, nickel chloride, boric acid and saccharin at a pH of 5.0 and a temperature of  $50^\circ\text{C}$ . During the electrodeposition process, the anode was used an electrolytic nickel plate. The operation of electroplating nc Ni coating was undertaken for about 30 min which would give the coating with the thickness of about  $15 \mu\text{m}$ . A scanning electron microscope (SEM, JEOL JSM-5310, Japan) and a field emission scanning electron microscope (FESEM, JEOL JSM-6700F, Japan) were employed for the observations of the surface of the coatings and the cross-section morphology and an EDX attachment was used for qualitative elemental chemical analysis. Crystal-line structure of the sample was studied by the X-ray diffractometer (XRD, Rigaku D/max, Japan) with a Cu target and a monochromator at 50 kV and 300 mA with the scanning rate and step being  $4^\circ/\text{min}$  and  $0.02^\circ$ , respectively. The hardness of the magnesium alloy and the coatings were evaluated using a HXD-1000 micro-

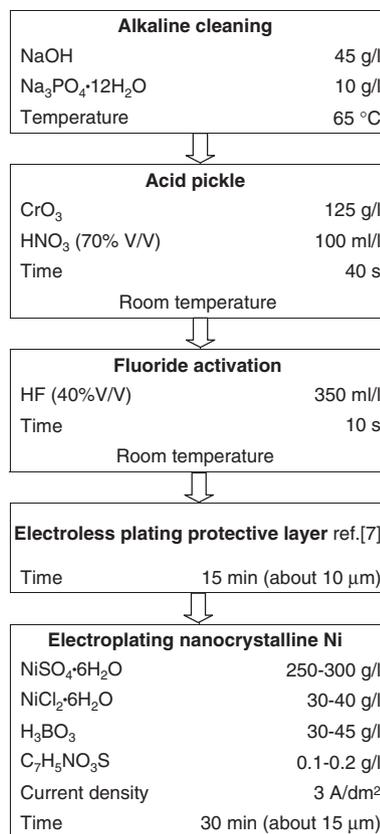


Fig. 1. The technical flow chart of the electroplating nc Ni on the AZ91D magnesium alloy.

hardness tester with Vickers indenter, at a load of 100 g and duration of 15 s.

Electrochemical measurements were performed on an Electrochemical Analyzer (CHI800, Shanghai, China), which was controlled by a computer and supported by software. Linear Sweep Voltammetry experiments were carried out in a 3 wt.% NaCl aqueous solution using a classic three-electrode cell with a platinum plate (Pt) as counter electrode and an Ag/AgCl electrode (+207 mV vs. SHE) as reference electrode. Before testing, the working electrode was cleaned in acetone agitated ultrasonically for 10 min. The exposed area for testing was obtained by doubly coating with epoxy resin (EP 651) leaving an uncovered area of approximately  $1 \text{ cm}^2$ . The reference and platinum electrodes were fixed near to the working electrode (about 0.5 mm), which could minimize the errors due to IR drop in the electrolytes. During the potentiodynamic sweep experiments, the samples were first immersed into 3 wt.% NaCl solution for about 20 min to stabilize the open-circuit potential. Potentiodynamic curves were recorded by sweeping the electrode potential from a value of about 300–400 mV lower to a value of 500–600 mV upper than the corrosion potential, respectively, at a sweeping rate of 5 mV/s. The  $\log(i) - E$  curves were measured and plotted after the above electrochemical measurements. The corrosion potential  $E_{\text{CORR}}$  and corrosion

current density  $i_{\text{corr}}$  were determined directly from these  $\log(i)-E$  curves by Tafel region extrapolation. Acid immersion test in 10% HCl solution at room temperature was undertaken to test the corrosion resistance of the nc Ni coating on the magnesium alloy. If there were micro pores in the coatings, the corrosion solution would erode the magnesium substrate through the pores. Due to the high chemical activity of the magnesium, the  $\text{H}^+$  in the corrosion solution would be reduced by the magnesium and turned into the hydrogen gas bubbles. So the time interval between the start of the test and the first hydrogen gas bubble arising from the coating surface could be used to donate the corrosion resistance of the coatings on the magnesium alloy substrate. For comparison, the electroless plating nickel coatings with different thickness (10 and 25  $\mu\text{m}$ ) were also tested in the paper.

### 3. Results and discussions

#### 3.1. Microstructures and hardness of the coatings

Fig. 2(a) showed the pattern of XRD of the AZ91D magnesium alloy, which indicated that the substrate alloy consisted of primary  $\alpha$  (Mg) grains surrounded by an eutectic mixture of  $\alpha$  and  $\beta$  ( $\text{Mg}_{17}\text{Al}_{12}$ ) [15]. It also can be seen from the XRD pattern of Fig. 2 (b) and the morphology of Fig. 3 that after electroless Ni plating for about 15 min, the AZ91D magnesium alloy was fully covered by the electroless nickel deposition. The phosphorus content in the electroless deposition was very low, because Ni was first deposited on the surface of magnesium alloy according to the deposition mechanism of electroless plating on the magnesium alloy [7]. The XRD analysis results of the as-deposited electroplating nc Ni coating was shown in Fig. 2

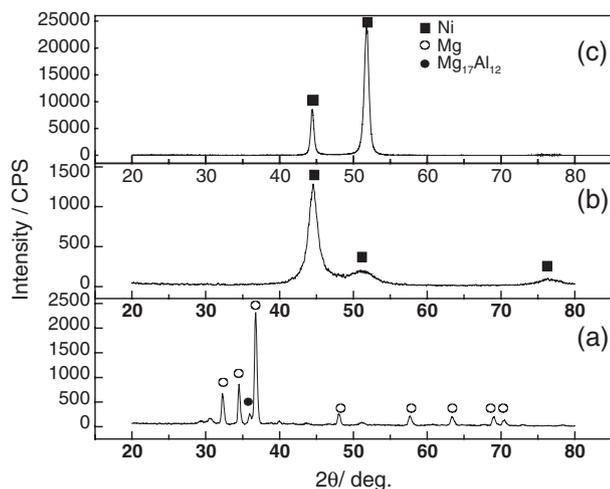


Fig. 2. The XRD patterns of the electroplating Ni on the AZ91D magnesium alloy at different intervals, (a) AZ91D magnesium alloy substrate, (b) electroless plating on the substrate for 10 min, (c) the electroplating nc Ni coating.

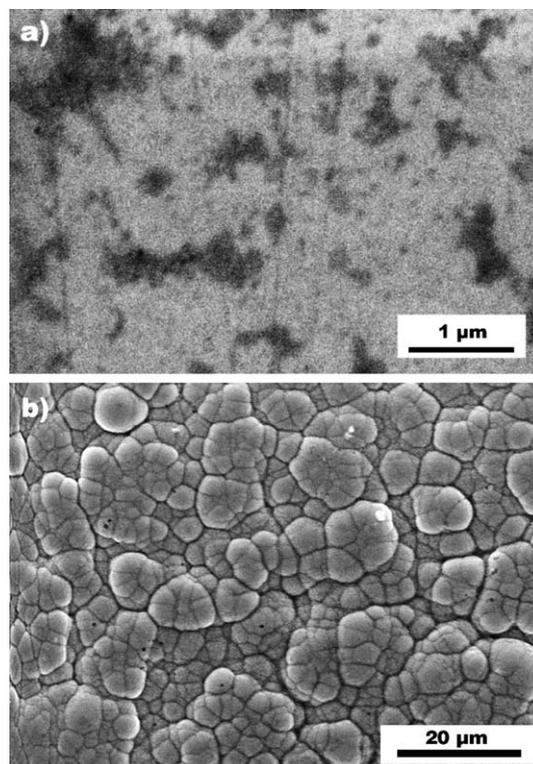


Fig. 3. The surface morphology of a) the nc Ni coating and b) the electroless nickel plating on the AZ91D magnesium alloy for about 10 min.

(c). The grain size  $d$  of nc Ni can be determined from the (200) peak via the Scherrer equation [16]:

$$d_{\text{XRD}} = \frac{k\lambda}{\beta(\theta)\cos\theta} \quad (1)$$

Where  $\lambda$  is the X-ray wavelength,  $\beta$  the FWHM (full width of half maximum) of the (200) diffraction peak,  $\theta$  the diffraction angle and the constant  $k \approx 1$ . From Eq. (1) the average grain size of this nc Ni was about 40 nm. In addition, the XRD results also showed that the nc Ni coating had an evident {200} preferred texture. In fact, Ni electrodeposits are known for giving numerous, well-defined preferred orientations depending on electrodeposition conditions, i.e. electrolyte composition, temperature, pH, current density, stirring and organic additions [17,18]. The {200} preferred texture of the nc Ni in this study may be attributable to the given electrodeposition conditions which may lead to higher electrode overpotential and reduced concentration of  $\text{Ni}^{2+}$  at the electrode surface [18].

Fig. 3 (a) showed the typical surface morphology of the as-deposited nc Ni coating. It can be seen that the as-deposited surface of the nc Ni coating was very compact and no colony structures, which was totally different from the “cauliflower-like” (in micrometer size) surface morphology of the electroless nickel deposition (see Fig. 3 (b)). Moreover, the as-deposited surface of the nc Ni coating exhibited a flat and mirror-like appearance and the grain size of the deposits could not be resolved by conventional SEM observations. In order to make a clear

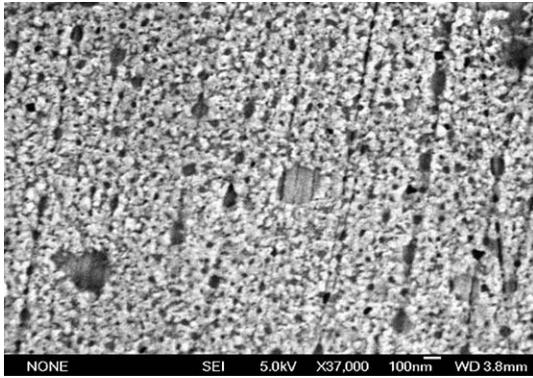
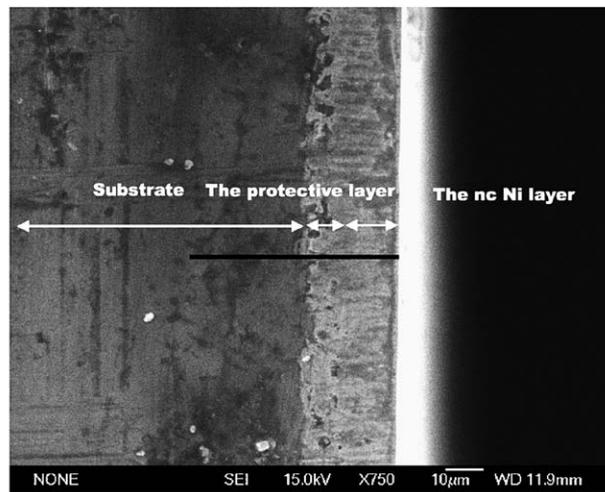


Fig. 4. The surface morphology of the electroplated nc Ni coating after polishing and corroded by dilute nitrate/ethanol solution.

observation of the fine grain structure, specimen of this nc Ni was polished and corroded by dilute nitrate/ethanol solution before the SEM observation. The surface morphology of the nc Ni after above pretreatments was shown in Fig. 4. The very uniform nc grain structures can be seen on the surface of nc Ni after slightly corroded. Fig. 5 (a) showed the cross-section morphology of the nc Ni coating

on the AZ91D magnesium alloy. To indicate the substrate and two types of the Ni layers on the cross-section of the coating, the substrate, the protective layer and the nc Ni layer were marked by the line with two arrows, respectively, in the Fig. 5 (a). From this figure, it can be seen that the acid pickle pretreatment prior to electroless plating protective layer for the magnesium alloy provides surface pits to act as sites for mechanical interlocking to improve adhesion [7]. Moreover, there were no obvious boundaries between the protective layer and the nc Ni layer, which indicated that the nc Ni layer was tightly attached to the protective layer. In addition, the nc Ni layer showed very compact and no pores from its cross-section observation. Fig. 5 (b) gave the qualitative element analysis of the nc Ni coating on the AZ91D magnesium alloy by EDX analysis. For the lower phosphorous content in the protective layer previous deposited on the AZ91D magnesium alloy substrate, the distribution of element of phosphorous was not detected by EDX. From the elements distributing from the substrate to the coating surface along the line labeled in Fig. 5 (a), it can be seen that the coating was connected closely to the magnesium alloy substrate.

a)



b)

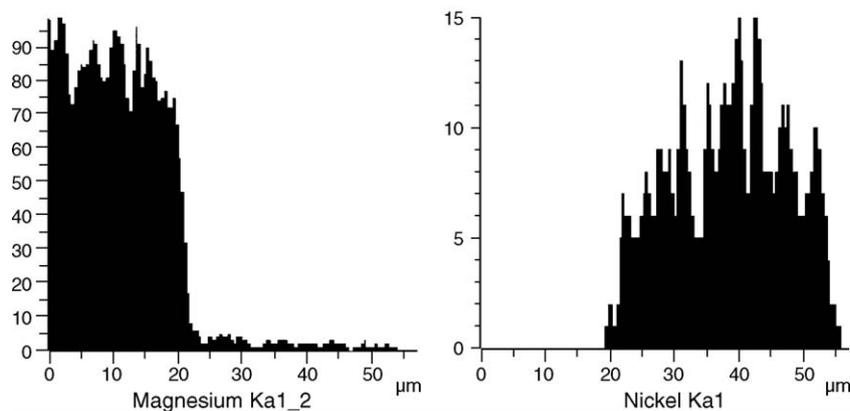


Fig. 5. (a) The cross-section morphology of the Ni coating on the AZ91D magnesium alloy, (b) the qualitative element analysis of coating on the AZ91D magnesium alloy by EDX analysis, scanning from the substrate to the coating surface along the line labeled in the figure.

Generally, nanocrystalline materials usually have improved hardness compared to the conventional polycrystalline materials [9,10]. In this study, the hardness of the nc Ni coating was about 580 VHN, which was far higher than that of the AZ91D magnesium alloy substrate (about 100 VHN). Therefore, the magnesium alloy coated by the nc Ni with high hardness would be expected to greatly improve its surface properties, for example the wear resistance.

### 3.2. Corrosion properties of the coatings

Fig. 6 gave the electrochemical polarization curves for the AZ91D magnesium alloy substrate and the various coatings on the magnesium alloy substrate in a 3 wt.% NaCl aqueous solution at room temperature. The cathodic reaction in the electrochemical polarization curves corresponded to the evolution of the hydrogen, and the anodic polarization curve was the most important features related to the corrosion resistance. For the magnesium alloy substrate and the substrate with 10  $\mu\text{m}$  electroless Ni alloy layer, when the applied potential increased into the anodic region, an activation-controlled anodic process was observed. The polarization current increased with increasing the applied anodic potential and no obvious passivation occurred. However, the corrosion potential  $E_{\text{corr}}$  of the substrate with 10  $\mu\text{m}$  electroless Ni layer was shifted positively about 80 mV compared with that of the substrate and the corrosion current density  $i_{\text{corr}}$  decreased from 1.546  $\text{mA}/\text{cm}^2$  of the substrate to 0.327  $\text{mA}/\text{cm}^2$  of the 10  $\mu\text{m}$  thickness electroless Ni layer. As for the electrochemical polarization curve of the substrate with 25  $\mu\text{m}$  thickness electroless Ni coating, the corrosion potential  $E_{\text{corr}}$  was shifted positively to  $-0.410$  V and the corrosion current density was only 9.8  $\mu\text{A}/\text{cm}^2$ . And when the applied potential increased to  $-0.287$  V, a thin passive film was formed on the surface of the coating with the corrosion current density of about 15.2  $\mu\text{A}/\text{cm}^2$ . However, at the potential of 0.085 V, nickel dissolution

occurred with increasing corrosion current density. For the electrochemical polarization curve of the substrate with the nc Ni coating, it should be noticed that the corrosion potential  $E_{\text{corr}}$  showed a significant shift to the positive direction compared with that of the substrate and the corrosion current density  $i_{\text{corr}}$  was largely decreased. Between the potential values of  $-0.174$  and  $0.162$  V, the formation of a thin passive film occurred resulting in a limited current at approximately 4.92  $\mu\text{A}/\text{cm}^2$ . This film, however, breaks down once the applied potential was beyond the value of  $0.162$  V. After the film has broken down, the nickel dissolution would have occurred through the pores of the nc Ni coating. So it can be seen that the corrosion potential  $E_{\text{corr}}$  of the electroless Ni coating on the AZ91D magnesium alloy increased greatly towards the positive direction when the coating thickness was increased. Therefore, the nc Ni coating possesses highest corrosion potential and lowest corrosion current density among all these studied coatings. In fact, the electrochemical techniques have been reported to study the relation between porosity and corrosion rate measurements for electroless nickel deposits on steel [19,20]. As the porosity of the electroless nickel coating is reduced, the value of corrosion potential  $E_{\text{corr}}$  would become more noble and the corrosion current becomes smaller. In a certain sense, the corrosion current density reflects the rate of corrosion of coatings. Therefore, it can be deduced from the above discussion that the nc Ni coating on the magnesium alloy has the lowest porosity among the studied coatings, which indicates the high corrosion resistance. Also, for the electroless Ni coating on the magnesium alloy, due to the decrease in porosity with increasing coating's thickness, the corrosion resistance appears to increase.

In the acid immersion tests, there were no hydrogen gas bubbles arising from the nc Ni coating on the AZ91D magnesium alloy after immersed in the 10% HCl solution for 2 h. However, the magnesium alloy with the electroless nickel coating with the same thickness of about 25  $\mu\text{m}$  could only endure about 8 min without corrosion of the magnesium substrate in the same corrosion solution. The great difference in corrosion resistance implied that the electroless Ni coating should exhibit some porosity and the nc Ni coating would be fully density. Moreover, according to [13], the high corrosion resistance of nc materials was attributed to the high degree of surface defects resulting from the high surface fractions of grain boundaries and triple junctions which provided an increased number of preferential attack sites and therefore dispersed the corrosion current density. So, the nc Ni coating on the magnesium alloy is an effective method to improve the corrosion resistance of the magnesium alloy dramatically.

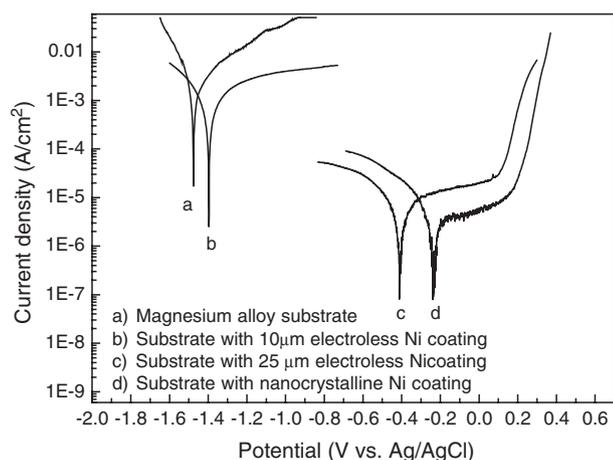


Fig. 6. The electrochemical polarization curves for the AZ91D magnesium alloy substrate and the various coatings on the magnesium alloy substrate in a 3 wt.% NaCl aqueous solution at room temperature.

## 4. Conclusions

In this study, a nanocrystalline Ni coating was applied to the AZ91D magnesium alloy substrate by a direct-current

electrodeposition using a direct electroless plating of nickel as the protective layer. The results could be summarized as follows:

1. The nc Ni coating had an average grain size of about 40 nm and an evident {200} preferred texture. And the as-deposited surface of the nc Ni coating showed more compact than that of the electroless Ni deposits.
2. In the acid immersion tests, the nc Ni coating exhibited very higher corrosion-resistance than the electroless Ni coating with the same thickness. The electrochemical measurements indicated that the nc Ni coating had the low porosity and a very low corrosion rate. The reasons for the high corrosion resistance of the nc Ni coating on the magnesium alloy should be attributable to its fine grain structure and the low porosity in the coating.
3. In addition, the hardness of the nc Ni coating was about 580 VHN, which was far higher than that of the AZ91D magnesium alloy substrate (about 100 VHN). Therefore, the nc Ni coating with a combination of high corrosion-resistance and high hardness would be expected to enlarge the applications of the magnesium alloy.

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