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The synthesis of super-hydrophilic and hard MgB_2 coatings as an alternative to electroless nickel coatings

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Abstract

In this study, we report the electroless deposition using an alternative technique for the fabrication of hard and super-hydrophilic MgB_2 films. MgB_2 films on AZ91 magnesium alloys were prepared using an electroless bath containing magnesium diboride nanopowders, sodium hypophosphite, sodium succinate, sodium acetate, and dimethyl sulfoxide. The electroless deposition was carried out in a bath kept at a bath temperature of 95 °C for 60 min. After deposition, the coated samples were annealed at 300 °C for 60 min to investigate crystallization, morphology, and the changes in the hardness and wettability. The phase composition, morphology, the hardness, and the contact angle of produced coatings were studied by X-ray diffractometer, scanning electron microscopy, microhardness tester, and contact angle measurement system, respectively. The coatings exhibited a dense and nodular structure with strong grain connections. As-deposited and annealed MgB_2 films showed an orientation with the (101) reflection, and the highest hardness value (500 $HV_{0.01}$) was obtained from the annealed coating. Both synthesized coatings had a super-hydrophilic surface.

Key words: MgB_2, electroless, superhydrophilic, magnesium

1. Introduction

AZ91 magnesium alloys have achieved many superior properties such as high specific strength, high creep strength, good machinability, weldability, high impact resistance, high recyclability by aluminum and zinc addition although magnesium has several limitations such as low strength, toughness, and corrosion resistance, and is easily flammable with oxygen. Some techniques have been used to modify the surface properties of magnesium alloys. Some of these methods contain harmful inorganic or toxic organic electrolytes [1, 2]. Some require complex equipment and high costs [3]. In recent years there has been great attention in producing superconducting films of magnesium diboride (MgB_2) because of its superior properties [4, 5]. Many techniques have been developed for its synthesis [6–17]. However, they have high processing costs [18].

In recent years, electroless plating has attracted attention due to its unique advantages, such as excellent uniformity, ability to be soldered and brazed, being relatively well-understood and well-characterized process, widely accepted in industrial processing, and low labor costs [3]. Electroless deposition may be defined as "deposition of a metallic coating by controlled chemical reduction that is catalyzed by the metal or alloy being deposited" (ASTM 6-374) [19–21]. To date, the most of previous investigations on the electroless deposition of magnesium alloys have been on the deposition of Ni-P or Ni-B [20–38] coatings. So far too few studies [18, 39, 40] exist to explain electroless deposition of MgB_2 materials. Moreover, there are few studies on the electroless deposition of MgB_2 materials on magnesium alloys. This paper reports the experimental results obtained on electroless MgB_2 of AZ91 magnesium alloy, and an attempt has been made to evaluate the influence of the electroless magnesium diboride on the crystallographic texture, morphology, microhardness, and wettability of the magnesium alloy.

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Table 1. The chemical composition of bath solution and deposition conditions for electroless MgB_2

Quantity	Bath constituents
12 $g L^{-1}$	Magnesium diboride (MgB_2) nanoparticle
20.8 $g L^{-1}$	Sodium hypophosphite ($NaPO_2H_2$)
5 $g L^{-1}$	Sodium succinate ($C_4H_4Na_2O_4$)
24 $g L^{-1}$	Sodium acetate ($C_2H_2NaO_2$)
8 ml	Dimethyl sulfoxide $(CH_3)_2SO$
Conditions	
pH	6 ± 0.5
Temperature for as-deposited deposition	95 °C
Deposition and annealing duration	60 min
Annealing temperature	300 °C

2. Material and method

The die-cast flat cylindrical Mg alloy AZ91 (Al 9.09; Zn 0.88; Mn 0.45; Si 0.11; Fe 0.01; K 0.01; Mg 89.45 (in wt.%)) samples with 20 mm diameter and 3 mm height were used as substrate material. The top surface of all samples was mechanically hand ground to obtain a selected final roughness value (almost $Ra \approx 0.8$ μm) by 1200 grit SiC grinding paper. They were washed with distilled water, degreased with acetone and finally dried in air. Then the substrates were dipped for decontamination in the alkaline solution (a mixture of 50 $g L^{-1}$ NaOH and 10 $g L^{-1}$ Na_3PO_4) for 10 min to dissolve fats, grease, oils, and protein. Subsequently, they were etched with an acid mixture for 45 s to remove gross surface oxides and smear layers, thus to obtain a mechanical lock or suitable substrate for adhesion. The acid mixture consists of 125 $g L^{-1}$ CrO_3 and 110 $ml L^{-1}$ HNO_3. Surface activation and etching lead to numerous surface pits or holes which may act as initiation sites for mechanical interlocking to improve adhesion on the substrate [2]. Fluoride activation (385 $ml L^{-1}$ HF) was then applied for 10 min to remove residual oxides created in the above step and to replace it with a thin layer of MgF_2.

The composition of bath solution and operation conditions used for electroless deposition are given in Table 1. Electrochemical nucleation of a metal on a foreign substrate takes place at the substrate/conducting electrolyte interface [41]. Overall, the initial nucleation and subsequent growth of the metal are strongly dependent on two factors, the binding energy of metal ad-atoms on foreign substrate S, ψ_{Me-S}, and the binding energy of metal ad-atoms on native substrates Me, ψ_{Me-Me} [41, 42]. The reactions occurring on the surface of magnesium-based substrate are as follows: Anodic: $Mg^{\circ} \rightarrow Mg^{2+} + 2e$, and Cathodic: $2B^{+} + 2e \rightarrow B^{\circ}$. The actual direction of the above reaction is dependent on the electrode potential, which can be calculated by Nernst equation [42]. Sodium hypophosphite (NaH_2PO_2) as reducing agent supplies electrons to reduce boron ion (Anodic: $NaH_2PO_{2(s)} + H_2O_{(l)} \rightarrow NaH_2PO_{3(aq)} + 2H^{+} + 2e$). Buffer of sodium acetate ($C_2H_3O_2Na$) sustains the pH for a long time ($C_2H_3O^{-}_{2(s)} + H_2O_{(l)} \rightarrow OH^{-}_{(aq)} + C_2H_3OH_{(aq)}$). Sodium succinate ($C_4H_4O_4Na_2$) as a complex agent controls the amount of free electrons for the reaction ($C_4H_4O_4Na_{2(s)} + H_2O_{(l)} \rightarrow OH^{-}_{(aq)} + C_4H_4O_4H_{2(aq)}$). Dimethyl sulfoxide $(CH_3)_2SO$ as a stabilizer, stabilizes the bath from decomposition by shielding catalytically active deposition which leads to the cathodic reaction (Cathodic: $[BDMSO]^{-} \rightarrow B^{+} + [DMSO]^{-} \rightarrow B^{\circ} + [DMSO]$).

The substrates were mounted in deposition bath, and the deposition was carried out at a bath temperature of 95 °C for 60 min. The plating bath was stirred by an adjustable speed motor equipped with a stirrer, and the stirring rate was set at 100 rpm. After deposition, the coated samples were thermally treated at 300 °C for 60 min to examine crystallization behavior and hardness change. The surface and cross-section morphologies of the treated coatings were characterized by scanning electron microscopy (ZEISS EVO40). TR-200 roughness tester was used to characterize the surface roughness. The XRD pattern of the coating was determined by XRD (Rigaku Advance Powder X-ray Diffractometer), and the coating was analyzed with CuKα ($\lambda = 0.154$ nm) radiation with 2θ between 10° and 100° (with a step size of 0.1°).

A microhardness tester ($HV_{0.01}$) was used to determine hardness. A static contact angle measurement (CAM-101 optical contact angle analyzer/KSV Instruments, Finland) was used to capture and analyze the contact angle before and after deposition. A distilled water droplet was suspended on the sample surfaces, and the contact angles were measured by using goniometer, which used a water drop of 6 μL and took Young-Laplace equation into account at the solid-liquid interface. The curvature of the interface and specific interfacial free energy of the interface are related to the pressure jump between the inside and

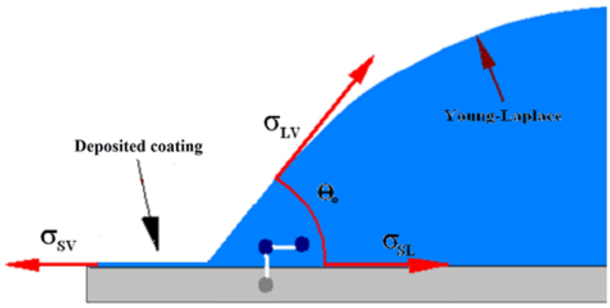

Fig.1. The contact angle of a liquid drop on an ideal solid surface under the action of three interfacial tensions.

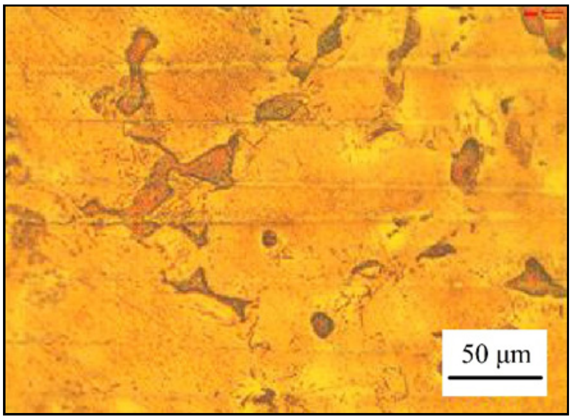

Fig. 2. The 500×-optical microscopy image of the etched AZ91 magnesium alloy.

outside of a liquid drop:

$$p_{\text{in}} - p_{\text{out}} - 2H\sigma_{\text{LV}} = 0. \quad (1)$$

As first described by Thomas Young [43] in 1805, the contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions (Fig. 1):

$$\sigma_{\text{SV}} - \sigma_{\text{SL}} = \sigma_{\text{LV}} \cos\theta, \quad (2)$$

where σ_{SV}, σ_{SL}, and σ_{LV} represent the solid-vapor, solid-liquid, and liquid-vapor interfacial tensions, respectively, and θ is the contact angle. The contact angle for a three-phase region is the main variable in Young's equation. Equation (2) is usually referred to as Young's equation, and θ is Young's contact angle.

3. Results and discussion

An image of the pre-electrochemical etched AZ91 magnesium alloy substrate taken at 500× magnification using optical microscopy is given in Fig. 2 before electroless deposition. As seen in Fig. 2, the used etchant darkens the massive $Mg_{17}Al_{12}$ phase and reveals primary α grains surrounded by a non-equilibrium eutectic mixture of α and β (the intermetallic $Mg_{17}Al_{12}$) as dark and light areas. Figure 3 shows SEM micrographs (magnified 500× and 2000×) of polished AZ91 magnesium alloy substrate, as-deposited and annealed MgB_2 coatings, respectively. The scratches are seen on substrate sample after the mechanical polishing carried out by emery paper in Fig. 3a. The morphology of the coating in as-deposited state exhibits a nodular structure and non-uniform agglomerations of some nodules (Fig. 3b). It is observed that the grain size increased and the surface morphology of the coating changed from a nodular structure to a granular structure including individual and clustered ball-like particles, and even the detached grains coalesced as a result of annealing (Fig. 3c).

The use of the electroless process for the deposition of ceramic materials enables the deposition of uniform coatings on substrates of complex shapes. It is seen from Fig. 4 the thickness gained-deposition time relation that deposits weight increases with deposition time.

The XRD diffractograms obtained for the substrate, as-deposited, and annealed samples are shown in Fig. 5. The XRD pattern in Fig. 5a shows the two-phase crystalline structure, typically consisting of α-Mg and β($Mg_{17}Al_{12}$) phase belonging to AZ91 magnesium alloy substrate. As shown from the XRD spectrum in Fig. 5b, the diffracted intensity of the substrate is reduced by deposition and develops the MgB_2 coating with weak intensities of the (101) plane at approximately 42° diffraction angle. Figure 5b also reveals that there is (321) peak that correlates to the orthorhombic phase of MgB_4 at approximately 61° diffraction angle. After annealing process, it is observed that three minor peaks [(001), (002), and (112)] at approximately 28°, 52°, and 81° diffraction angles, assigned to the hexagonal phase of MgB_2, form, and MgB_4 (321) phase is more pronounced, as well as these orientations (Fig. 5c). However, the pattern in Fig. 6c indicates that partial oxidation occurs on the coated sample surfaces after post-deposition annealing although the annealing process is performed under an argon atmosphere and oxidation product is MgB_2O_5 at approximately 18° diffraction angle. The oxidation of a coated film after annealing treatment may be harmful to the properties of the film. Actually, as for the oxidization of MgB_2, a lot of previous studies have been carried out [44–52]. Our work shows that the low-temperature annealing applied to electroless MgB_2 coatings can decrease the oxidation of MgB_2 film.

Comparison of hardness values of the substrate, the MgB_2-coated samples before and after annealing is shown in Fig. 6. The surface hardness of magnesium alloy substrate having a hardness value of about 140 $HV_{0.01}$ increased to 200 $HV_{0.01}$ after deposition

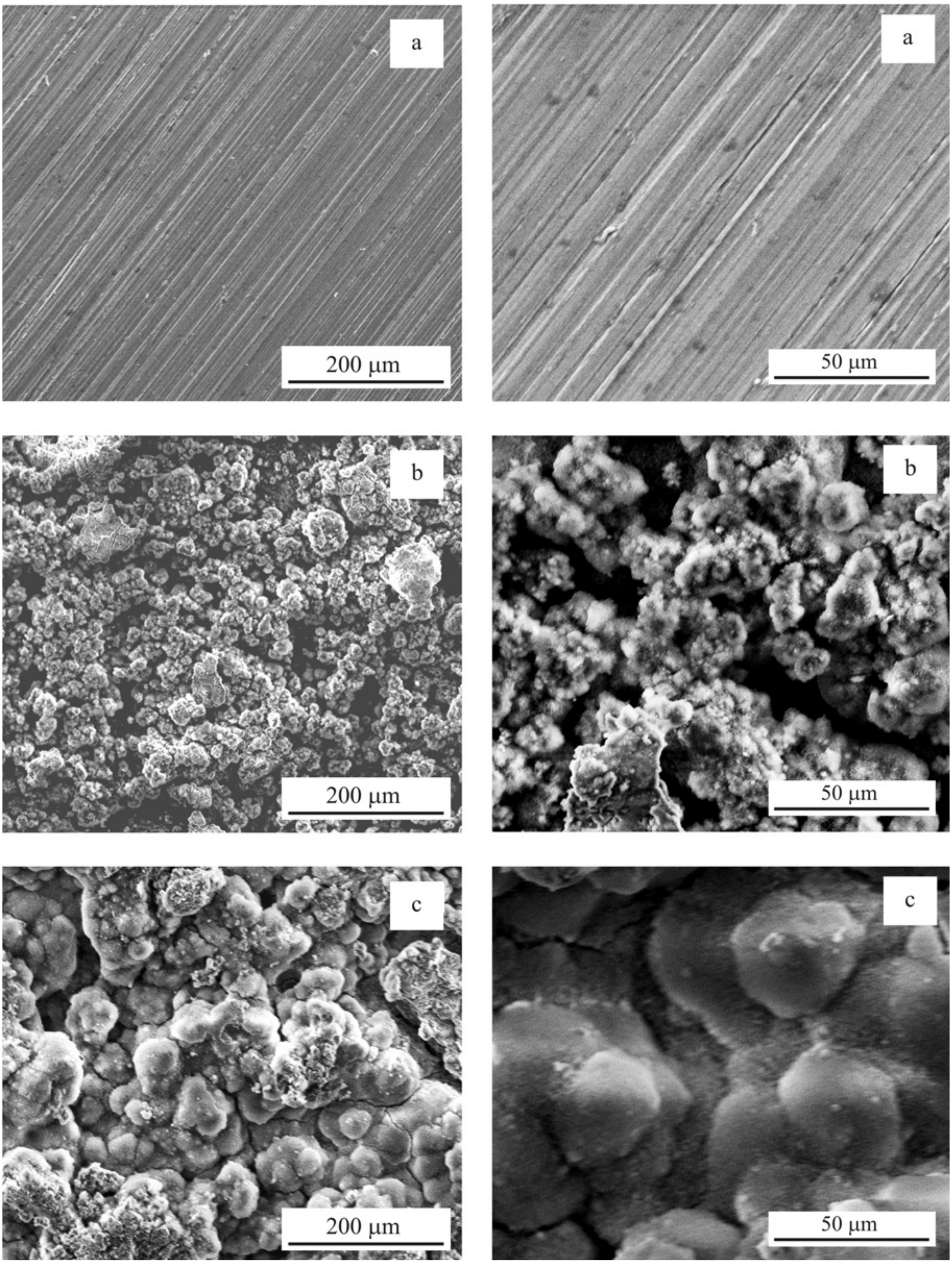

Fig. 3. The 500×- and 2000×-SEM images of (a) the substrate, (b) as-deposited, and (c) annealed MgB_2 coatings.

and further increased to 500 $HV_{0.01}$ by annealing. The partial increase in hardness is attributed to the development of MgB_2 (101), (002), and MgB_4 (321) crystalline phases and formation of the oxidants from partial oxidation when annealing. It is seen the electro-

less MgB_2 coating exhibits hardness values very close partial increase in hardness is attributed to the development of MgB_2 (101), (002), and MgB_4 (321) crystalline phases and formation of the oxidants from partial oxidation when annealing. It is seen the electro-

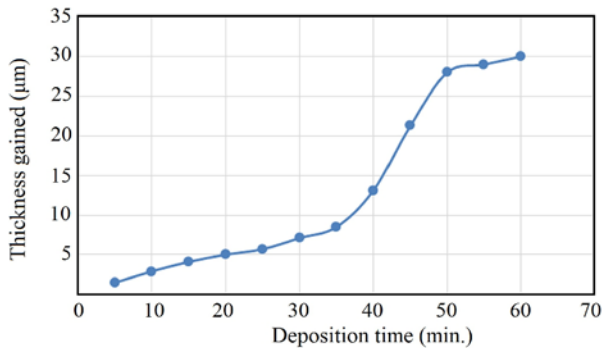

Fig. 4. The curve of thickness gained of the deposit on substrate against deposition time.

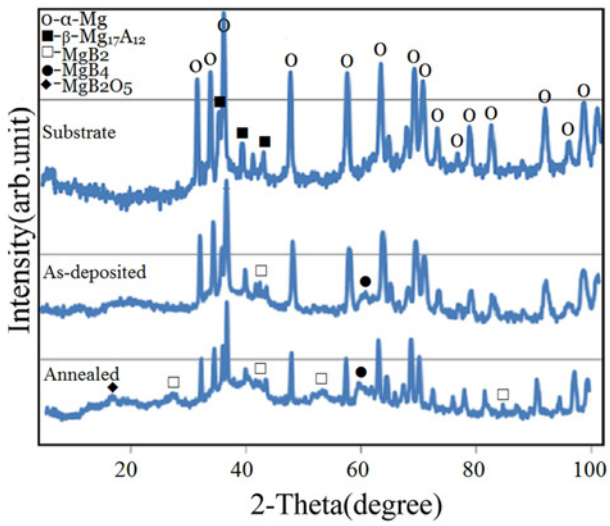

Fig. 5. X-ray diffraction spectra of the uncoated AZ91 magnesium alloy substrate, the as-deposited sample, and the annealed coating sample.

less MgB_2 coating exhibits hardness values very close to those of un-annealed Ni-B coating produced by the same deposition technique although their chemical compositions, morphologies, and crystallographic structures are different [38].

Figures 7a,b show the images of water droplets on the uncoated and the MgB_2 coated samples, respectively. Accordingly, while a hydrophilic ($56.32° < 90°$) surface was obtained from the uncoated magnesium alloy substrate, a superhydrophilic or water spreading (< 5) surface was achieved from both as-deposited and annealed MgB_2 coating samples.

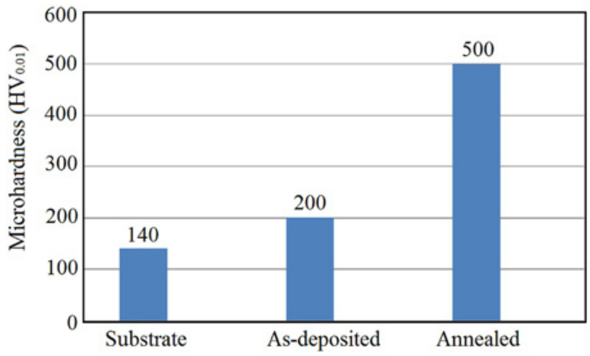

Fig. 6. Variation in microhardness after the electroless MgB_2 deposition on the AZ91 magnesium alloy substrate.

4. Conclusions

In present study, the electroless deposition process on AZ91 magnesium alloy substrate produced a uniform MgB_2 coating. MgB_2 coatings were thermally annealed at 300 °C for 60 min. The XRD diffractograms revealed that the thermally annealed film possessed an amorphous MgB_2 structure, with a preferred plane orientation along (101). SEM analysis showed a nearly similar surface morphology behavior for all the MgB_2 films. The coatings were dense and uniform. The most pronounced MgB_2 (101) was obtained from the as-deposited sample. With annealing, the intensity of MgB_2 (101) peak decreased, and partial oxidation was found to suffer the coating because only a very small amount of crystalline MgB_2O_5 was obtained, but coating hardness increased. The surfaces of the MgB_2 coatings produced were super-hydrophilic.

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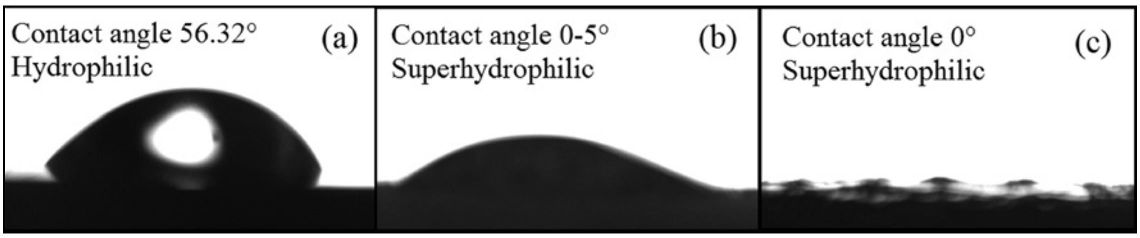

Fig. 7. Images of droplets on (a) uncoated, (b) as-deposited, and (c) annealed coating samples.

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