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Electroless and Electrochemical Deposition of Metallic Coatings on Magnesium Alloys

Critical Literature Review

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1. Introduction

A critical review pertaining to surface treatments on magnesium alloys was published in 2002 (Gray & Luan, 2002). Two years later, another review paper on the same subject was published (Natarajan et al., 2004). According to the authors of both reviews, only complex and multilayer coatings are able to produce optimum results in term of corrosion and wear protection of magnesium alloys, and a great deal of research has to be done furthermore to develop technically and economically viable coating systems.

One of the main challenges in the plating treatments of magnesium alloys is their susceptibility to corrosion. A way to prevent corrosion is by providing a barrier between the metal substrate and the environment. A coating has to be uniform, adherent, pore and crack free, and self-healing in the applications where damage of the coating can occur. The high reactivity of magnesium alloys causes the formation of a natural oxide when the metal is in contact with air and water. A treatment process for cleaning and removal of these oxides, that are unfavourable for coatings adhesion, is necessary before any electroplating and electroless plating treatment.

The electrochemical and electroless depositions of coatings on magnesium alloys demand significant technical requirements. In fact, magnesium is subjected to corrosion in acidic aqueous environments and is only partly protected by an hydroxide layer that forms at pH higher than 9-10. Moreover, the most widely used commercial alloys, i.e. AZ91D and AM60B, contain alloying elements which form intermetallic phases (Fig. 1a). From an electrochemical point of view those phases have different behavior when the alloy is immersed into a solution for plating or chemical treatment. This means that the surface must be made equipotential by modifying the metallurgical structure before the coating process or by a specific surface pretreatment. Lunder reported that the corrosion potential of β -Mg₁₇Al₁₂ phase in 5% NaCl saturated with Mg(OH)₂ is approximately -1.2 V vs. SCE, whereas the values for pure Mg and AZ91 are -1.66 V and -1.62 V vs SCE, respectively (Lunder et al., 1989). The heterogeneous structure of the alloys affects their corrosion resistance behavior and has a strong influence on the behavior of the alloy in the aqueous treatments processes, such as electroless and electrochemical depositions, and chemical conversions. A successful electroless or

electrochemical deposition process depends greatly on metallurgical process of fabrication. Casting defects, such as porosity, incomplete mold filling and flash, can make magnesium alloys difficult to plate (Bellemare, 2010).

2. Electroless plating

2.1 Introduction

Electroless plating consists in the deposition of a coating from a solution of metallic salts and reducing agents and, as consequence of the chemical and autocatalytic nature of the process, uniform layers are deposited onto the substrates irrespective of their shape. Most important electroless coatings are nickel based coatings (EN), which are used as protective layers against wear and corrosion of the substrate. Electroless Ni-P coatings on magnesium are usually preferred to the electrodeposited ones because of the corrosion resistance and the uniformity of the coatings on complex shapes. The corrosion potential E_{corr} of Ni-P alloys becomes more noble with increasing phosphorus content. Recently, the treatment has been performed successfully on wrought magnesium alloys such as AZ31B, AE42 and ZRE1 previously coated by a zinc layer. An improvement in corrosion resistance of the magnesium alloys is achieved especially after heat treatment, typically at 400°C for 1 hour.

Xiang published a paper on the state of the surface after the pretreatment stages (alkaline cleaning + chromate acid etch + fluoride activation) and a second paper on the initial mechanism of EN plating on AZ91D alloy from carbonate bath (Xiang et al., 2001 and 2001b). Electroless nickel deposition nucleates preferentially on β -phase and according to the authors the initial stage of deposition is due to a galvanic coupling between β -phase and eutectic structure and primary α -phase. The electrons produced by the anodic dissolution of magnesium from the α -phase are consumed by the cathodic deposition of nickel on β -phase. The absence of phosphorus in the region of nucleation supports the galvanic displacement mechanism, i.e. the initial deposition is not a process involving hypophosphite. They showed also that different F/O ratios due to different pretreatments followed by direct EN deposition result in different deposition rates, higher in the case of a lower F/O ratio. Similar results on initial mechanism of EN nucleation on AZ91D alloy were reported by Ambat using similar plating procedure (Fig. 1) (Ambat and Zhou, 2004).

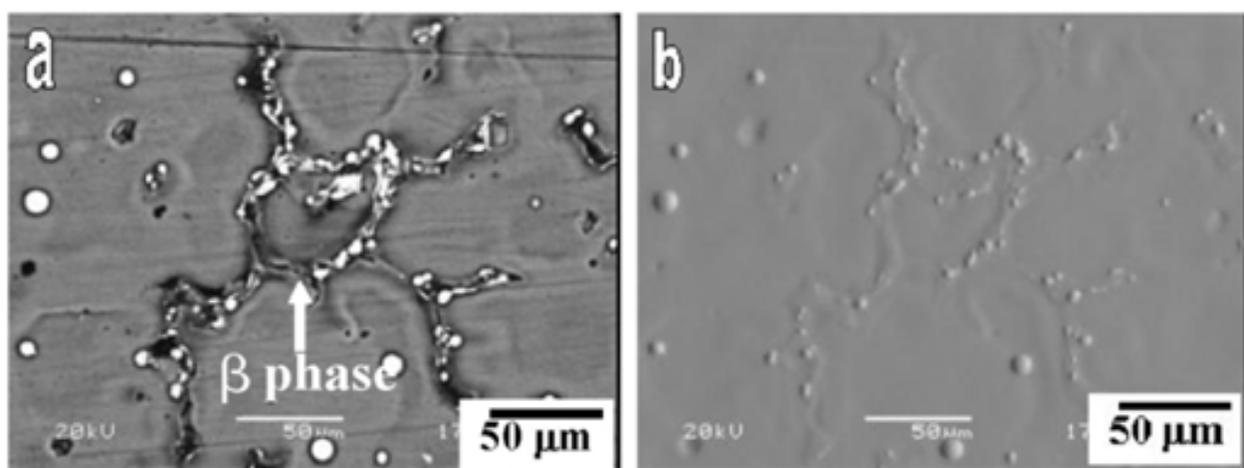


Fig. 1. Initial stages of nickel growth on AZ91 alloy (after 1 min): a) secondary and (b) topographic mode (Ambat & Zhou., 2004).

2.2 Surface preparation

After surface cleaning in alkaline solutions followed by surface etching in solutions of chromates and fluorides, or phosphates and fluorides, the magnesium alloys are generally plated with a zinc layer, referred also as zinc transition layer, obtained by immersion in alkaline zincate solutions. However, zinc transition layers obtained by immersion are too thin, therefore a double-zincate treatment is performed (Kushner, 2009) or a compact film can be produced by electroplating a second zinc layer on the single-zincate layer. With a double-zincate process zinc layer has a better coverage of the magnesium surface as the crystal grains are finer and adhesion is improved. Chen recently proposed a new galvanizing process that eliminates the need to deposit a layer of copper, and it is based on the deposition of a zinc film by immersion followed by the deposition of a layer of electroplated zinc (Chen et al., 2006). The addition of FeCl_3 salts to the zincate bath helped to change the zinc crystal structure and then the coverage and adhesion of the zinc layer (Fig. 2).

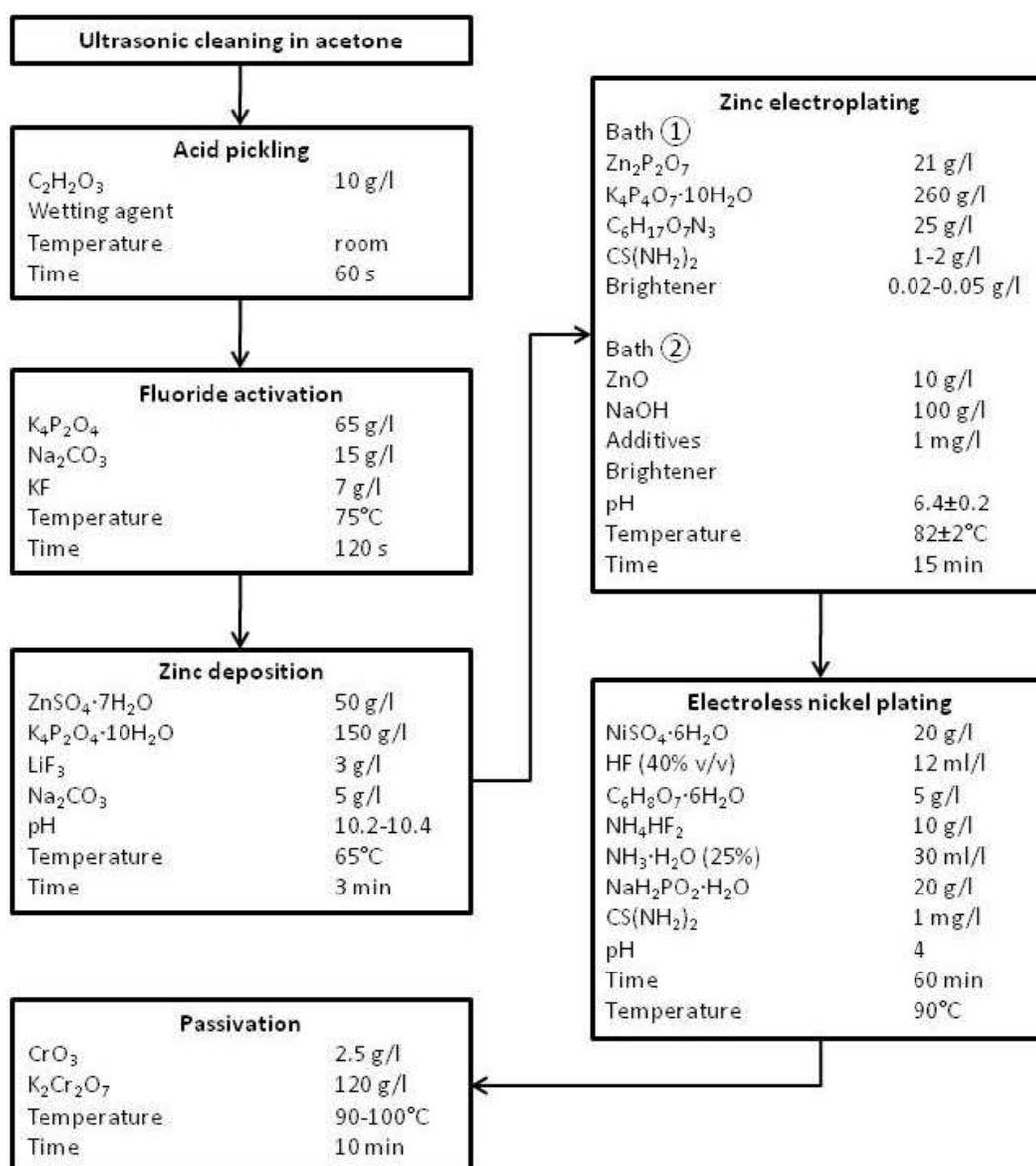


Fig. 2. Flowchart of the overall procedure for coating on the AZ91D magnesium alloy (Chen et al., 2006).

Before the electroless plating or the electrodeposition on magnesium alloys, a copper strike layer, usually cyanide bath, is electrodeposited on zinc layer in order to provide a uniform coverage. Yu studied the deposition (displacement + electrodeposition) of copper from a pyrophosphate solution over a zinc transition layer deposited from pyrophosphate solution (Yu et al., 2005).

In another study, a protective copper film on AZ31 magnesium alloy, without zinc pretreatment, was proposed. The aqueous solution containing 0.4M $\text{Na}_4\text{P}_2\text{O}_7$ + 0.08M $\text{Cu}_2\text{P}_2\text{O}_7$ + 0.24M CuSO_4 + 0.05M NaF was used. A galvanic displacement reaction occurs between copper and magnesium, then copper film is formed on magnesium substrate. After that, electroplating is carried out applying direct current and pulse current using the same copper solution.

Yang proposed a procedure in which a copper layer is deposited onto AZ91D, by immersion plating, before EN plating. The solution was optimized in term of temperature, pH and fluoride content by searching the maximum coverage (Yang et al., 2005, 2005b, and 2006). Ultrasonication was found effective in improving the copper immersion coating process, particularly during extended deposition times, beyond the initial stages (Yang et al., 2005c). Higher coverage of magnesium alloy surface (> 80%) by copper immersion coating were also achieved by using an alkaline bath. The procedure proposed by Yang is schematically represented in Fig. 3 (Yang et al., 2006).

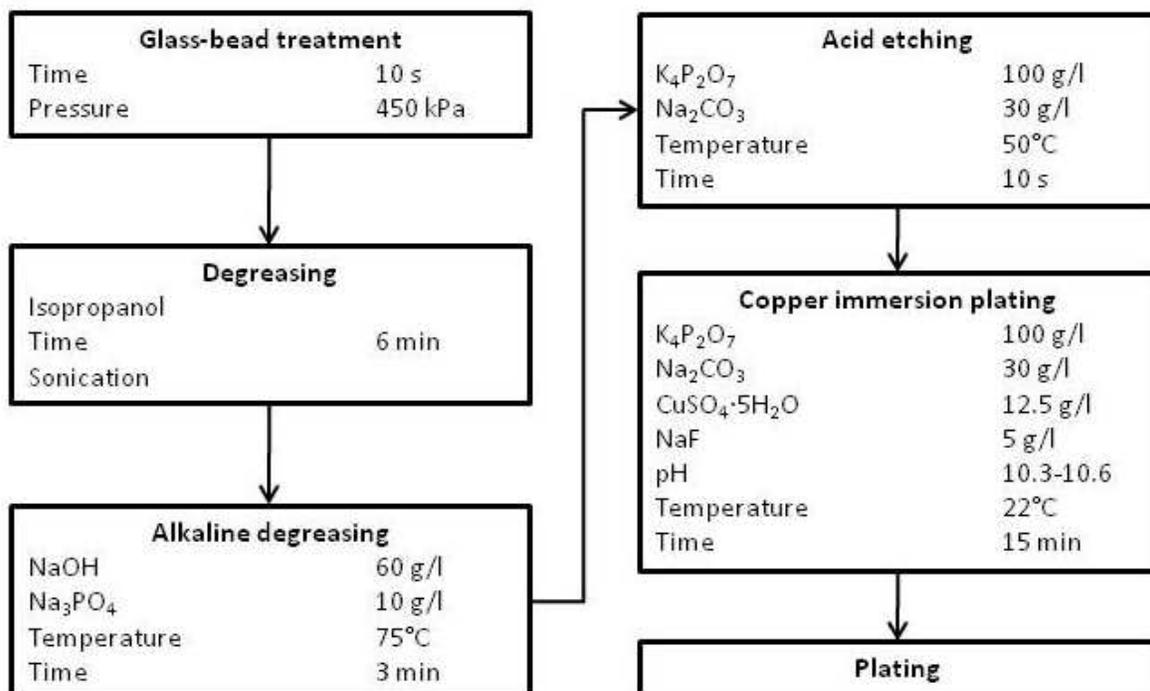


Fig. 3. Flowchart of the procedure for copper immersion coating on the AZ91D magnesium alloy (Yang et al., 2006).

2.2 Substrate morphology

The effect of the magnesium alloy AZ91 microstructure and roughness on the nucleation, deposition rate, coating microstructure, and mechanical properties of the EN coatings was recently investigated (Liu & Gao, 2006). Experimental results show that surface sandblasting pre-treatment ($R_a = 0.05 \mu\text{m}$) enhances the nucleation and coalescence of nickel crystallites.

Authors concluded that the sandblasting reduces the negative effect of microstructural heterogeneity of AZ91 alloy on EN plating, even though it increases the EN coating surface roughness. Moreover, while coating adhesion increases with roughness, wear tests show that the nickel coatings on roughened substrate have higher friction coefficients than those of polished surfaces ($R_a = 0.05 \mu\text{m}$).

2.3 Porosity

The nickel/magnesium system is a typical example of a “cathodic coating on an anodic substrate”. Therefore, the nickel layer provides only a physical barrier against the corrosion attack of magnesium substrate and, for this reason, it must be uniform, adherent and pore free. The assessment of the porosity in a coating deposited onto a magnesium alloy is a major issue in determining the quality of a protective layer. A study on the porosity in EN on AZ91D alloy was recently published (Li et al., 2006). The coated samples are dipped in corrodokote solution (5 ml HCl and 6 g NaCl in 100 ml H₂O) for 5 min, then they are immersed into an indicator solution for 3 min. The conclusion of the study is that eriochrome black T indicator offers more readable color point on filter paper than using magneson and sodium alizarin sulfonate indicators. The optimized solution composition for EN deposition, in relation to porosity assessment, contains sodium hypophosphite and nickel carbonate with a mass ratio equal to 1.75, 25 g/l of fluorides, 1.5 mg/l of thiourea, and 20 g/l of buffering chemicals (sodium acetate or sodium carbonate).

Zou described a way to seal the micropores of EN on magnesium by means of a post-treatment with fluoropolymers. The hardness of the coating reached 600 HV, the coefficient of friction of the coating was less than 0.15 suitable for to dry lubrication. The corrosion resistance was also excellent to endure 5% neutral salt spray test for 500 hours (Zou et al., 2005).

2.4 Alternatives to chromate and fluorides pre-treatment

The most difficult part of plating magnesium is the development of an appropriate pre-treatment. There are currently two alternatives to treat magnesium alloys before plating: zinc immersion and a treatment based on chromates etching and conversion with fluorides. Organic coatings are a popular, simple and cost effective mode for protection for metallic objects and structures. The use of an organo-silicon coating as primer has been studied by Zhao et al. as alternative to chromates and fluorides in the pre-treatment of the surface. They proposed a method for protecting AZ31 magnesium alloy using an organic layer as primer and an electroless silver layer (Zhao et al., 2007). In an another investigation an electroless copper film was deposited on AZ31 magnesium alloy using organic coatings as interlayer (Fig.5) (Zhao et al., 2008b). The surface of the organic interlayer must be sensitized and activated before electroless deposition. Fig.5 shows the surface and cross-section morphology of the coating. The organic interlayer is uniform and compact and with thickness of about 60 μm . The thickness of the metallic layer is about 7 μm and contains copper (99.5 wt%) and phosphorus (0.5 wt%). Electrochemical measurements in 3.5% NaCl showed that the corrosion potentials (E_{corr} vs SCE) of the AZ31 alloy and copper coated samples are -1569 mV and -1368 mV, respectively.

Electroless nickel-phosphorus layers were also deposited on AZ31 alloy coated with an organic interlayer of about 50 μm (Zhao et al., 2007b, 2008, and 2010). In a study the activation of the organic layer was carried out by means of palladium salts. The Ni-P coating (4 μm after 60 min of deposition) was found to contain 12.3% phosphorus.

Electrochemical measurements in 3.5% NaCl showed that the corrosion potentials (E_{corr} vs SCE) of the AZ31 alloy and copper coated samples are -1569 mV and -1316 mV, respectively (Zhao et al., 2007b).

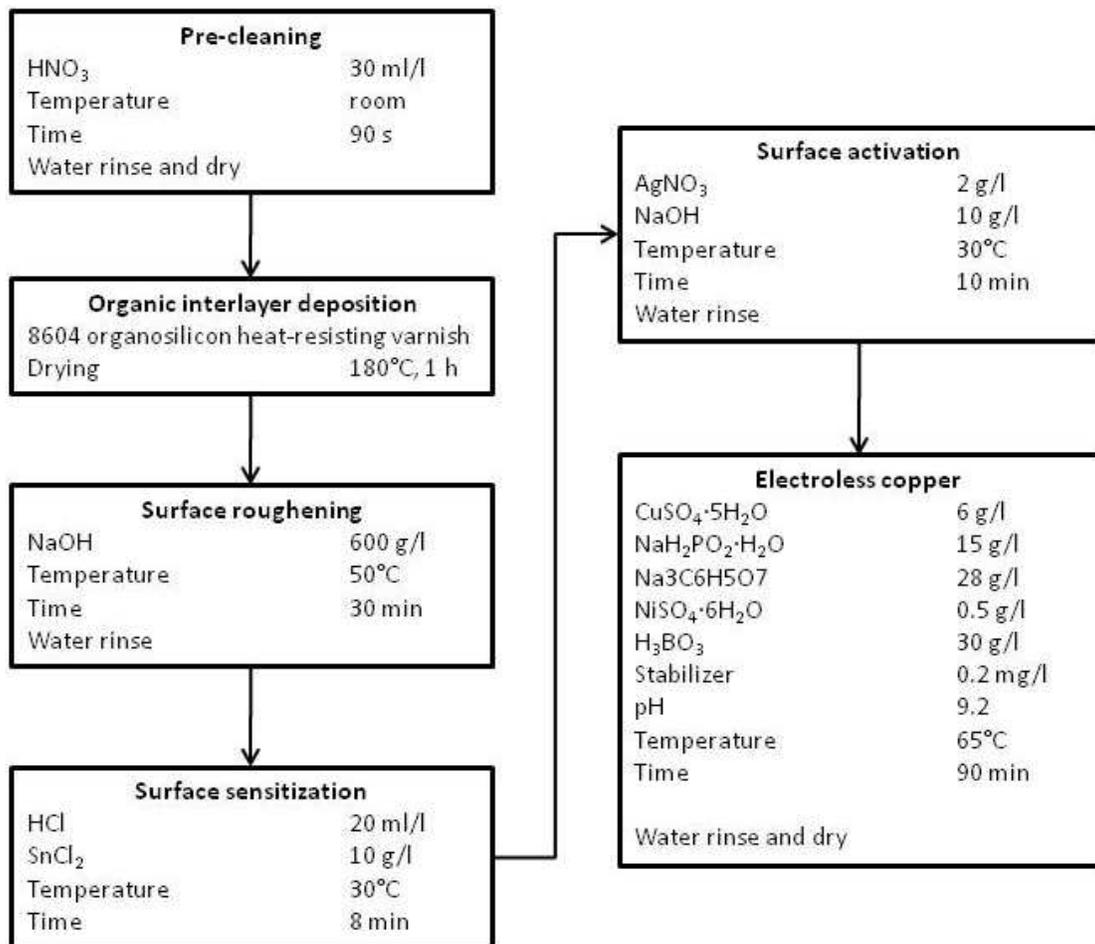


Fig. 4. Flowchart of the organic coating and electroless Cu deposition on the AZ31 magnesium alloy (Zhao et al., 2008). In Zhao et al., 2008b AgNO₃ was reported 12 g/l.

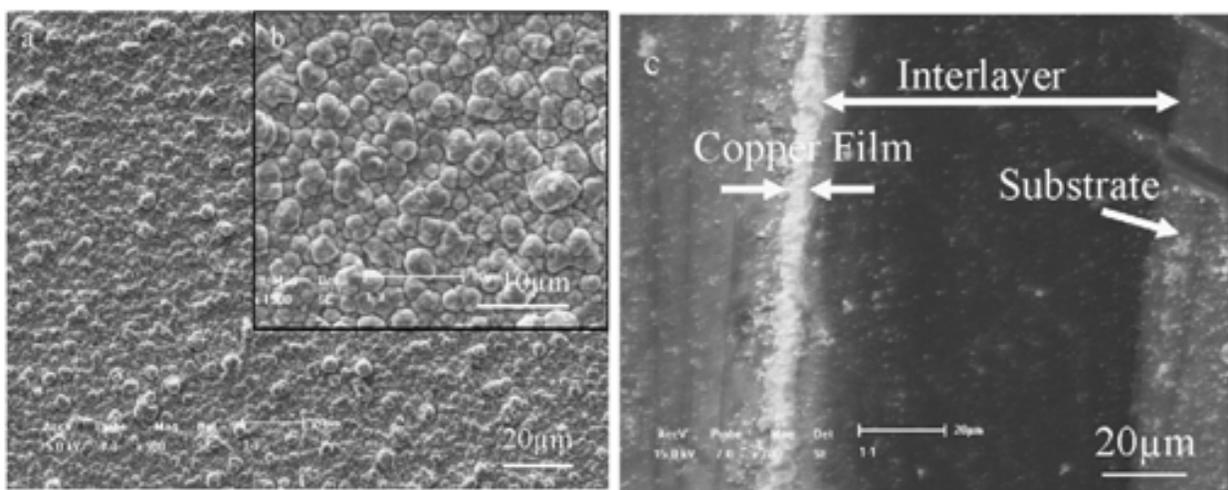


Fig. 5. Surface (a,b) and cross-section morphology (c) of electroless copper (90 min) deposited on AZ31D alloy with an organic interlayer (Zhao et al. 2008).

Electroless Ni-P plating	
NiSO ₄ ·6H ₂ O	16 g/l
Na ₂ H ₂ PO ₂ ·H ₂ O	16 g/l
Na ₄ P ₂ O ₇ ·10H ₂ O	60 g/l
NH ₃ ·H ₂ O (38%)	8 ml/l
Surfactant	20 mg/l
Stabilizer	1 mg/l
pH	9.5
Temperature	50°C

Fig. 6. Electroless Ni-P bath composition and operating conditions (Zhao et al., 2007).

Yang presented the results of a research on EN deposition (8 μm, 4.74% phosphorous) and molybdate conversion film pre-treatment on Mg-8Li alloy (Yang et al., 2009). (Fig.7)

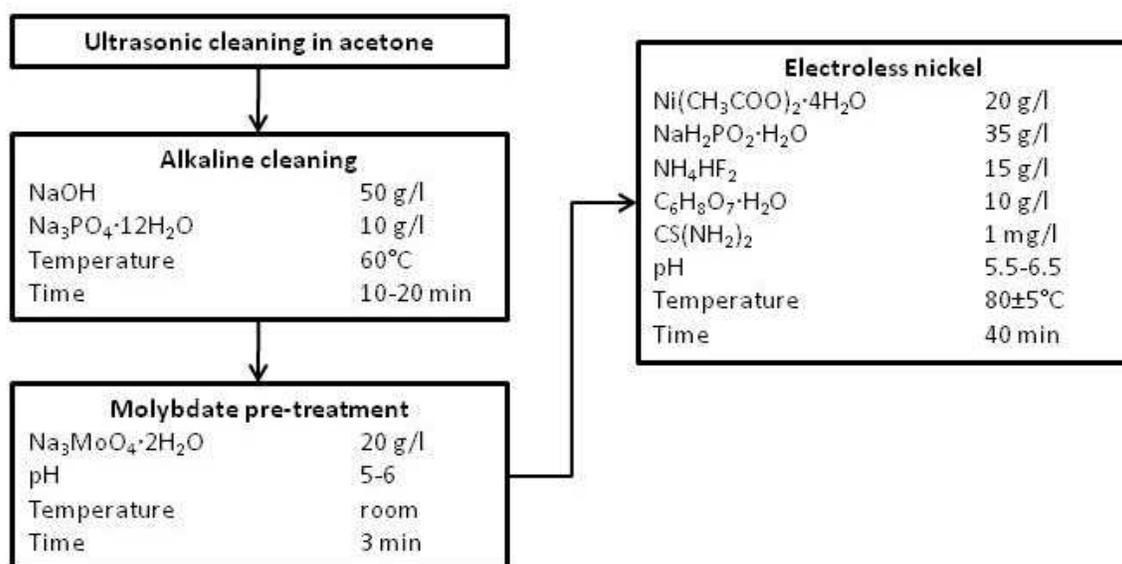


Fig. 7. Flowchart of the molybdate coating and electroless Ni deposition on the Mg-8Li magnesium alloy (Yang et al., 2009).

	E _{corr} (mV vs SCE)	i _{corr} (A cm ⁻²)
Mg-8Li substrate	-1594	1.046 ×10 ⁻³
Molybdate pre-treatment	-1466	1.213 ×10 ⁻⁴
Ni-P (8 μm)	-1083	2.247 ×10 ⁻⁵

Table 1. Electrochemical parameters of magnesium substrate, with molybdate pre-treatment and Ni-P coating (in 3.5% NaCl) (Yang et al., 2009).

A phosphate-manganese conversion film was proposed as pre-treatment layer on AZ91D magnesium alloy before EN plating from sulphate bath (Zhang et al., 2007)(Fig. 8). After the pre-treatment, α phase on the substrate was eroded and β phase (Mg₁₇Al₁₂) was exposed on the surface.

According to the authors, both the precipitation of phosphate and manganese and the increase of the volume fraction of β phase may improve the corrosion resistance of the substrate (Table 2).

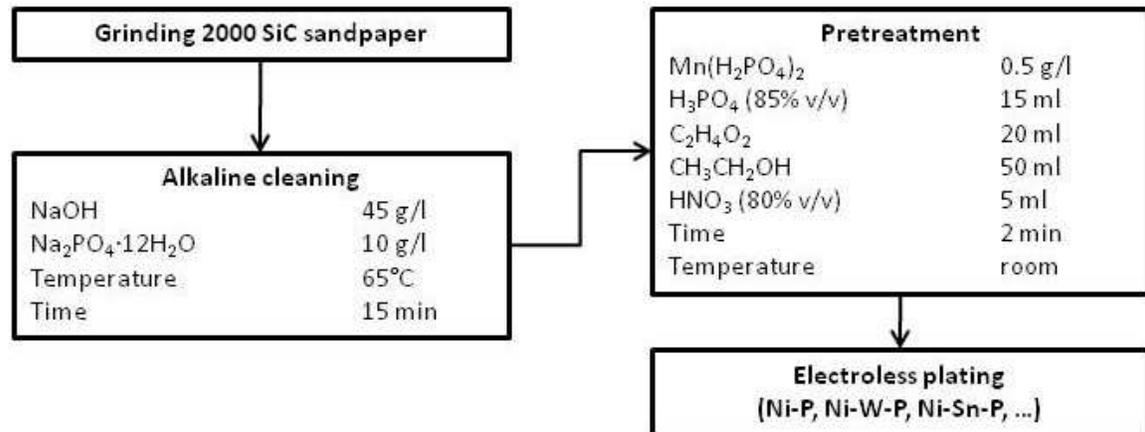


Fig. 8. Flowchart of the manganese-phosphate pretreatment and electroless plating on magnesium alloys (Zhang et al., 2007).

	E_{corr} (mV vs Ag/AgCl)	i_{corr} ($\mu\text{A cm}^{-2}$)
AZ91D	-1502	411.8
Phosphate - manganese pre-treatment	-1442	48.91
Ni-P (~20 μm , 5.6% P)	-599	15.98

Table 2. Electrochemical parameters of magnesium substrate, with phosphate-manganese pre-treatment and Ni-P coating (in 3% NaCl) (Zhang et al., 2007).

A zinc phosphating treatment before EN was proposed by some researchers (Lian et al., 2006). The composition of the phosphating solution is reported in Fig.9. The results show that metal zinc in the conversion coating acts as catalyst for nickel deposition. The addition of Na_2MoO_4 in the phosphating bath resulted in the increase of zinc content in the coating. Denser Ni-P coating were obtained on AZ91D alloy pretreated with a phosphating bath containing 2.0-2.5 g/l Na_2MoO_4 . Salt spray tests showed that the Ni-P coating can withstand for 150 h without corrosion (Lian et al., 2006).

Phosphating solution	
Phosphoric acid	17.5 g/l
Zinc oxide	3.2 g/l
Sodium fluoride	1.7 g/l
Nitroguanidine	0.2 g/l
Tartaric acid	2.2 g/l
Sodium nitrate	2.5 g/l
Sodium molybdate	0-2.5 g/l
pH	2.1-3.3
Temperature	45°C
Time	2-3 min

Fig. 9. Composition and operating conditions of the phosphate solution for AZ91D pretreatment before electroless Ni-P deposition (Lian et al., 2006).

Some authors proposed a double layer coating on magnesium alloys composed by a bottom layer obtained by anodic oxidation and an electroless metallic layer. Liu showed that the

presence of an anodic oxide on the AZ91 substrate provides high density of nucleation sites for nickel plating, resulting in the reduction of porosity of the metallic layer and providing better adhesion strength (Liu & Gao, 2006).

Zeng proposed the plasma electrolytic oxidation in silicate bath followed by electroless Ni-P deposition. The porous inner layer, mainly consisting of MgO and MgSiO₄, was activated in a solution of palladium salt. The electrochemical tests showed that the breakdown potential E_{bd} increased by 1.395 V, i.e. the pitting corrosion resistance was improved greatly in comparison with bare AZ91D alloy (Zeng et al., 2010)(Fig. 10).

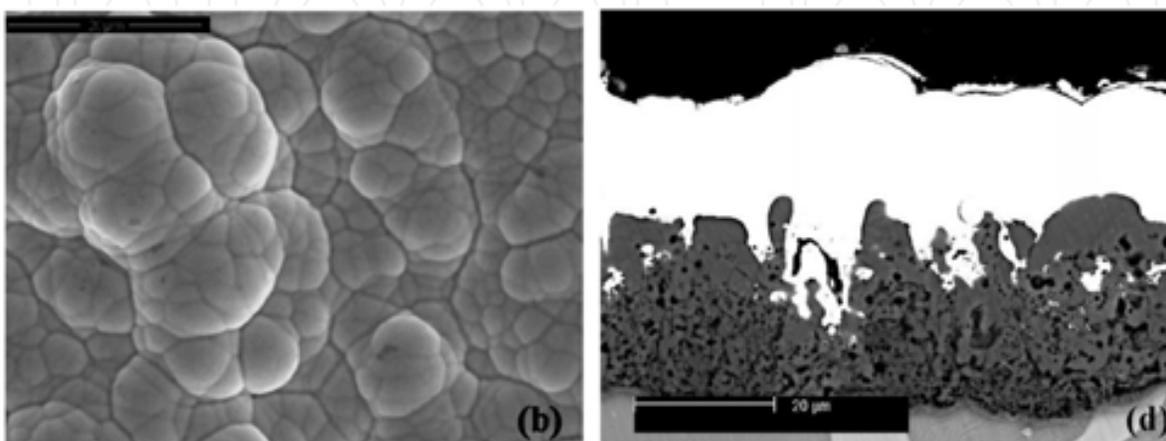


Fig. 10. Surface (left) and cross section (right) morphologies of a double layer coating PEO + EN (Zeng et al., 2008).

An EN plating process was established on the anodized (Dow process) AZ91D alloy that uses TiB₂ powders as catalyst instead of palladium (Sun et al., 2008). The catalytic powder of TiB₂ was mixed with the epoxy resin and curing agent to form a dilute solution with solvent addition. The weight ratio of TiB₂ with organic adhesive was 1.5:1. The anodized specimens were dipped in the solution for a certain time and then lift out to form a thin film on the surface. The specimens were finally cured at 70°C for 30 min. The thickness of catalytic layer film was about 10–15 μm. The deposition rate (10 μm/h) of the new process was close to that of the traditional process but somewhat lower than that of Pd-activation process on PEO film (Fig. 11).

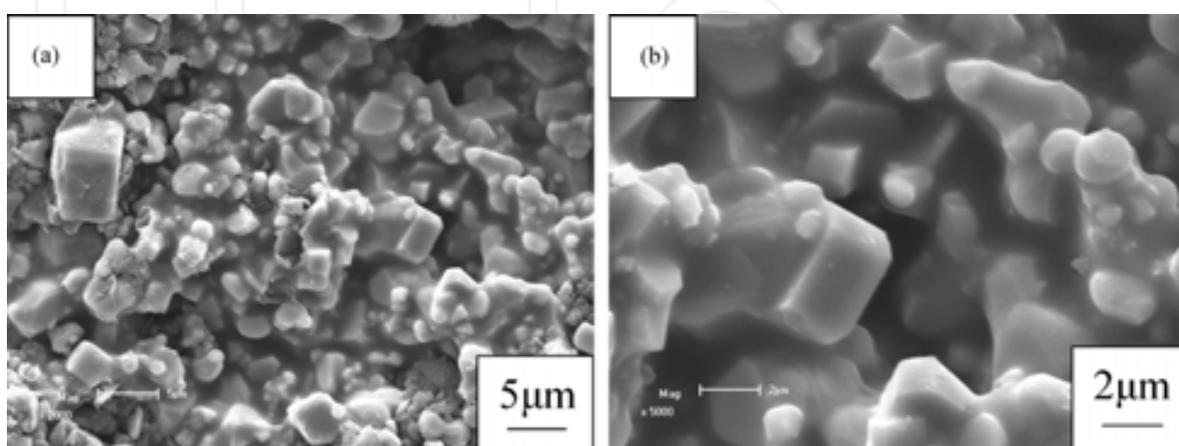


Fig. 11. Surface morphology of the catalytic TiB₂ layer before EN plating at two magnifications (Sun et al., 2008).

Jiang fabricated a composite coating on AZ91 by combining a PEO treatment and electroless copper plating passivated with benzotriazole (Jiang et al., 2010). In the paper the operating conditions are not specified, and it is shown that the composite coating has a positive corrosion potential shift in 5% NaCl solution of 300 mV, and no corrosion pits are visible after 168h of neutral salt spray test. The electroless copper layer adheres to the PEO oxide by mechanical interlocking of the metal in the oxide pores.

2.5 Ternary electroless coatings

The traditional nickel-plating baths are acidic with sulphate being the main salt. However, magnesium is readily corroded in acid solutions. For this reason Zhang investigated an alkaline bath for the deposition of Ni-W-P coatings. (Zhang et al., 2007b).

After grinding with 2000 SiC paper, the magnesium substrate was cleaned in 10% sodium hydroxide solution for 15 min to remove soils or greases on the surface and thoroughly rinsed with water to remove alkaline compounds. Then, the magnesium alloy sample was treated for 2 min in a bath where H_3PO_4 and $Mn(H_2PO_4)_2$ are the main ingredients to obtain a conversion film. The bath composition and operation parameters for the electroless Ni-W-P deposition are listed in Fig. 12.

Electroless Ni-W-P plating	
$NiSO_4 \cdot 6H_2O$	15 g/l
Na_4WO_4	10 g/l
$Na_2H_2PO_2 \cdot H_2O$	20 g/l
Na_4CO_3	20 g/l
$Na_3C_6H_5O_7 \cdot 2H_2O$	40 g/l
NH_4HF_2	8 g/l
$CS(NH_2)_2$	1 mg/l
pH	9
Temperature	$80 \pm 2^\circ C$

Fig. 12. Electroless Ni-W-P bath composition and operating conditions (Zhang et al., 2007b).

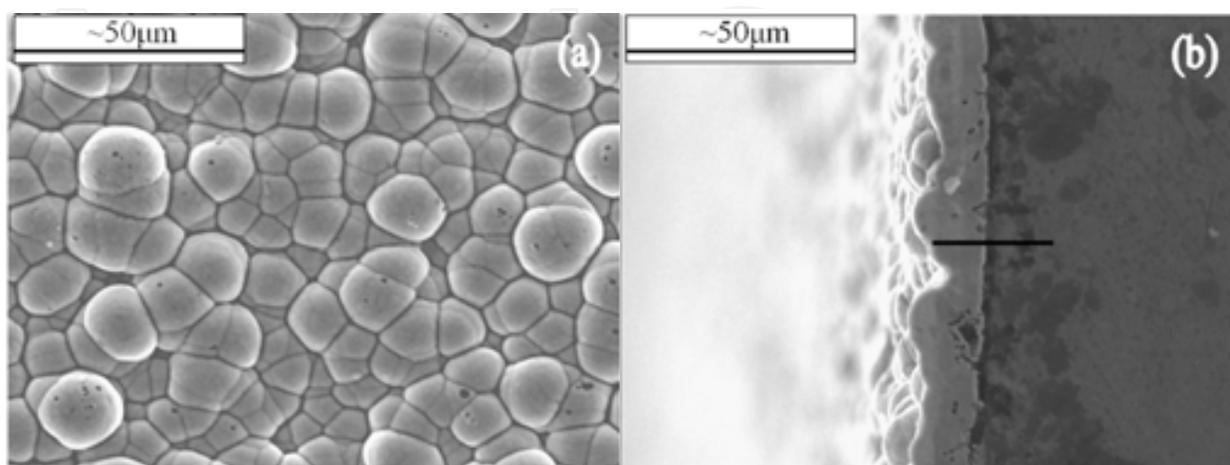


Fig. 13. Surface (a) and cross-section morphology (b) of the electroless Ni-W-P coating (Zhang et al., 2007).

Codeposition of the tungsten resulted in ternary Ni-W-P coating with phosphorus content of 4.9 wt.% and tungsten content of 4.5 wt.%. The hardness of the as-deposited Ni-W-P coating is about 660 VHN, which is higher than that of the as-deposited Ni-P coating with similar phosphorus (5.6 wt.%) content on magnesium alloy (approximately 580 HV) and far higher than that of the AZ91D magnesium alloy substrate (about 100 HV).

The porosity test, acid immersion test and electrochemical measurements (Table 3) reveal that the presence of tungsten and the dense and pore-free microstructure make the coating suitable for corrosion resistance applications. The same researchers published a paper on electroless ternary Ni-Sn-P (Zhang et al., 2008).

Electroless Ni-Sn-P plating	
NiSO ₄ ·6H ₂ O	15 g/l
Na ₂ SnO ₃ ·3H ₂ O	4 g/l
Na ₂ H ₂ PO ₂ ·H ₂ O	20 g/l
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	80 g/l
NH ₄ HF ₂	15 g/l
CS(NH ₂) ₂	1 mg/l
pH	9±0.2
Temperature	90±2°C

Fig. 14. Electroless Ni-Sn-P bath composition and operating conditions (Zhang et al., 2008).

The ternary Ni-Sn-P coating grow at a rate of 6 μm/h, with phosphorus content of 8.51 wt.% and tin content of 2.48 wt.%. The hardness of the as-deposited Ni-Sn-P coating is about 670 HV. Due to the presence of tin in Ni-P, the porosity is low and the coating is compact.

	E _{corr} (mV vs Ag/AgCl)	i _{corr} (μA cm ⁻²)
AZ91D substrate	-1502	411.8
Ni-W-P (24 μm, 4.5% W, 4.9% P)	-701	7.809
Ni-Sn-P (25 μm, 2.48% Sn, 8.51% P)	-645	5.29
Ni-P (28 μm, 4.9% P)	-781	17.79

Table 3. Electrochemical parameters of magnesium substrate, with Ni-W-P, Ni-Sn-P and Ni-P coating (in 3% NaCl) (Zhang et al., 2007 and 2008).

2.6 Composites

Codeposition of ceramic, polymer, metal or other particles dispersed within a metal matrix can provide an increase of the properties such as wear and corrosion resistance, hardness, and self-lubricating behaviour.

Song investigated the corrosion properties of an electroless coating Ni-P-ZrO₂. The corrosion resistance of this coating has been demonstrated higher than that of Ni-P because of the effect of zirconia (diameter 20 nm). The greater corrosion resistance is due to a moderate anodic dissolution of Ni-P-ZrO₂ owing to the reduction of the active surface due to the presence of the inert ZrO₂ nanoparticles (Song et al., 2007). According to the authors Ni-P-ZrO₂ coatings are better in term of corrosion resistance in respect to Ni-P coatings, but in strong corrosive environment, the single Ni-P-ZrO₂ coatings cannot provide enough protection to the magnesium alloys substrate, therefore multilayer coatings have been proposed.

Electroless deposition of Ni-P-B₄C composite coating has been performed onto AZ91 alloy, and the micro hardness was higher than that of Ni-P of the same thickness (50 μm), but the presence of B₄C particles (diameter 1.5 μm) reduced the corrosion resistance. The cause is attributed to the presence of micro-cracks in the composite coatings. The pin-on-disc test showed that Ni-P-B₄C coating had better wear resistance than Ni-P coating (Araghi and Paydar, 2010)(Fig. 15).

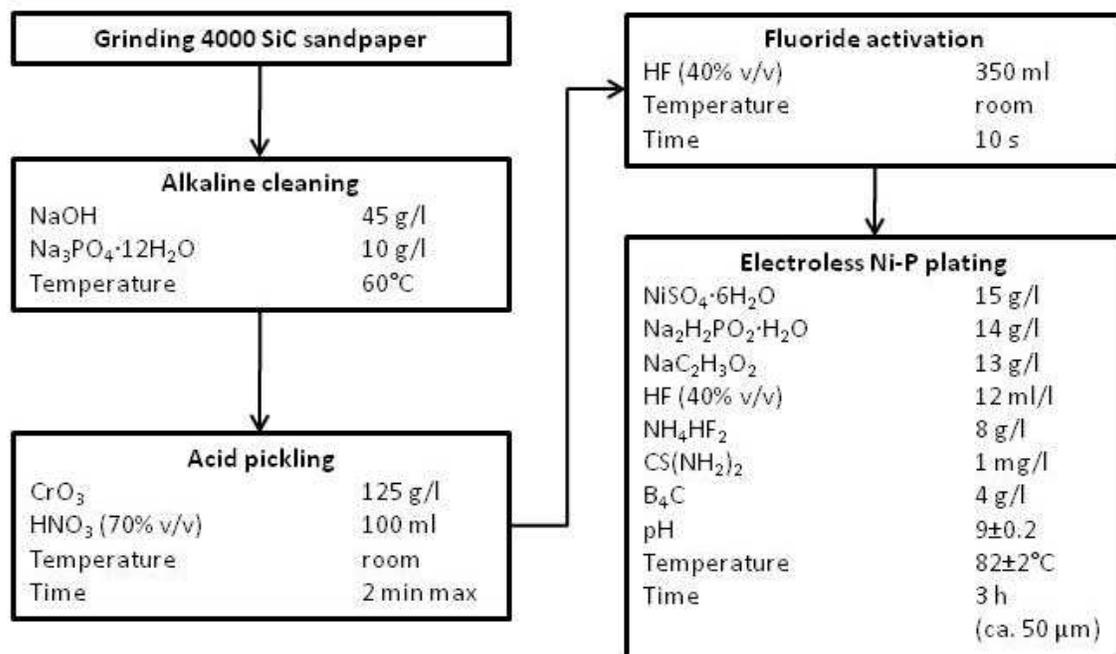


Fig. 15. Composition and operating conditions of the electroless Ni-P-B₄C composite coating on AZ91D magnesium alloy (Araghi and Paydar, 2010).

	E_{corr} (mV vs Ag/AgCl)	i_{corr} ($\mu\text{A cm}^{-2}$)	$HV_{50g,15s}$ (MPa)
AZ91D substrate	-1636	350	100
Ni-P (50 μm)	-808	7	700
Ni-P-B ₄ C (50 μm)	-1031	84	1200

Table 4. Electrochemical parameters of magnesium substrate, with Ni-P coating or Ni-P-B₄C coating (in 3% NaCl). Last column lists the microhardness values in MPa (Araghi and Paydar, 2010).

Fig. 16 shows the weight loss as a function of distance for both substrate alloy AZ91D and 50 μm-thickness Ni-P-B₄C composite coating obtained from a pin-on-disc test (load 10 N, disk rotation speed 0.06 m s⁻¹, distance 500 m).

A recent paper is about a composite coating on AZ91D alloy with electroless nickel coating as bottom layer and electrodeposited Ni-TiO₂ as top layer. The mean nominal diameter of TiO₂ particles was 10 nm and the TiO₂ content in the composite coatings amounted to 2.2±0.2 wt.% (Zhang et al., 2010)(Fig. 17).

The double layer structure improves corrosion resistance and mechanical protection of the AZ91D alloy compared with single electroless nickel coating (Table 5).

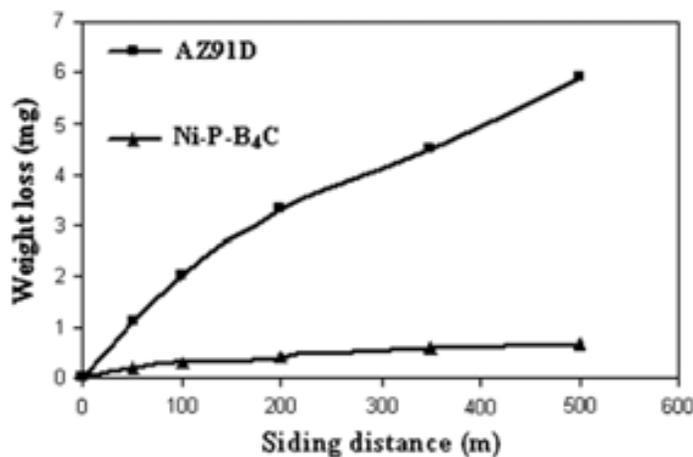


Fig. 16. Weight loss as a function of distance for both substrate and 50 μm thickness Ni-P-B₄C composite coating obtained from pin-on-disc test (Araghi and Paydar, 2010).

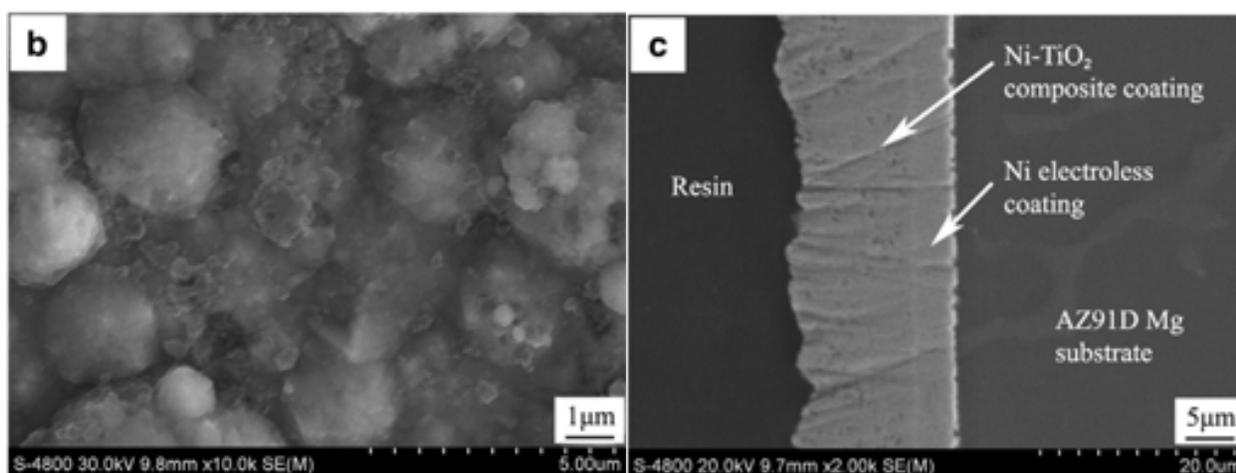


Fig. 17. Surface and cross section morphology of EN and electrodeposited Ni-TiO₂ coatings (Zhang et al., 2010).

	OCP (mV vs SCE)	E _{corr} (mV vs SCE)	i _{corr} (μA cm ⁻²)	Corrosion rate (mm y ⁻¹)	HV _{100g,15s}
AZ91D substrate	-1585	-1491	10.80	0.11	78
Electroless nickel coating	-514	-464	0.96	0.01	145
Ni-TiO ₂ composite coating	-251	-325	0.44	5.18e-3	445

Table 5. Electrochemical parameters of magnesium substrate, with EN coating and double layer EN + EDP Ni-TiO₂ coating (in 3.5% NaCl). Last column lists the microhardness values.

Electroless nickel deposited onto magnesium alloys increases the corrosion resistance and also the wear resistance. In addition, micro and nanoparticles can be codeposited into the electroless nickel matrix in order to improve hardness and friction coefficient. Table 6 shows the wear rate (Taber Wear Index, TWI) of some substrates and coatings.

Ishihara evaluated the corrosion fatigue resistance of AZ31 alloy plated with EN (24 μm, 8% P), polished and glass bead-blasted (Ishihara et al., 2008). In laboratory air, the effect of surface treatments on the fatigue lives of specimens was found to be minimal. However, in 3% NaCl solution, the EN-plated specimens were found to have shorter fatigue lives than

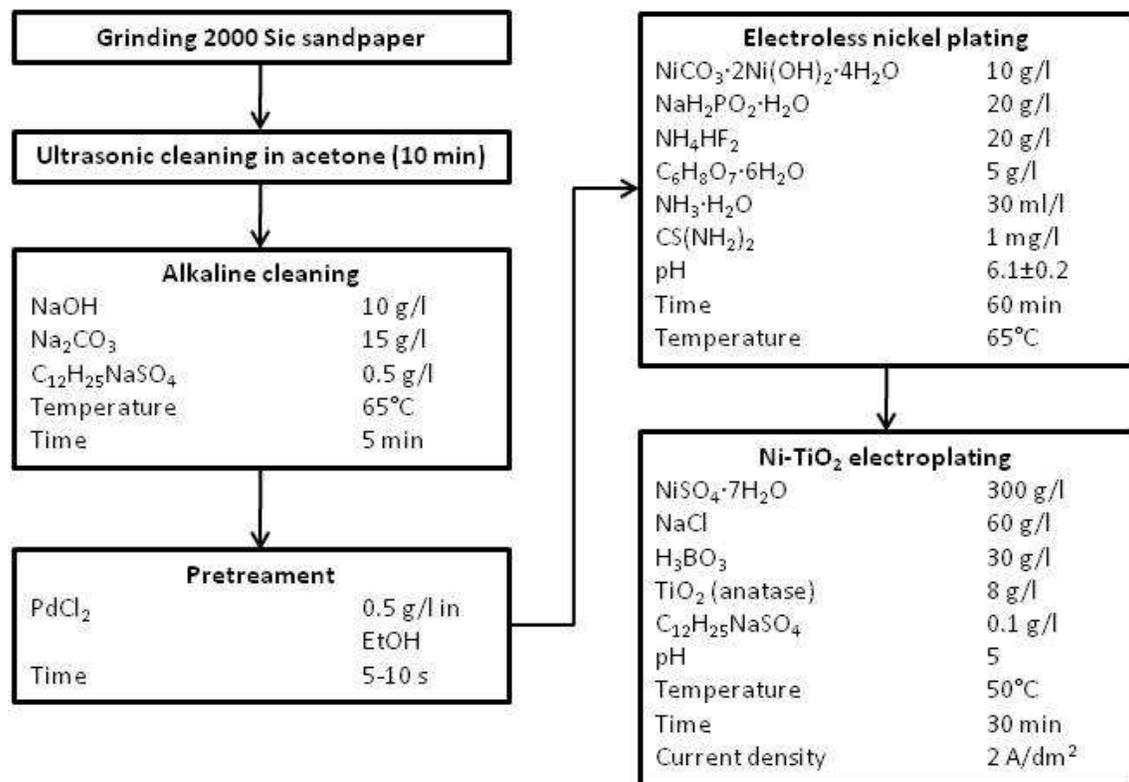


Fig. 18. Composition and operating conditions of the electroless Ni coating and Ni-TiO₂ composite coating on AZ91D magnesium alloy (Zhang et al., 2010).

	TWI (mg/1000 cycles)
AZ91D	49.98
Al 356	13.77
Electroless nickel	13.95
Hard chrome	0.9

Table 6. Wear data of some substrates and coatings (Shahin, 2001).

those of the polished and blasted specimens. Their electroless Ni-P coatings were characterized by compressive stresses, but the experimental data indicate that those are not sufficient to increase the fatigue life of EN. According to the authors, aggressive components infiltrate from the deposition solution through the pores of the Ni-P coating arriving to the interface between substrate and coating, and leading to pits formation. A crack initiates at the bottom of the pit and leads to the failure of the sample (Fig. 19).

A similar study was recently carried out by Ishihara on corrosion fatigue resistance of AZ31 alloy electroplated with a 20 µm thick multilayer coating of copper, semi gloss nickel, gloss nickel and chromium top layer. The crack initiation and the propagation behavior of both coated and uncoated specimens were also investigated to estimate the effect of the multilayer coating.

Experimental observations lead to conclude that two kinds of crack initiation mechanism occur. The cracks initiated from depressions on the surface or from depressions at the interface between the substrate and copper layer. The authors conclude that the fatigue life

of Ni plated specimens could be improved by eliminating surface and interface depressions produced during the electrodeposition, which are sites of stresses concentration and therefore responsible for cracks formation (Fig. 20).

EP Ni-P coatings are hardened by thermal treatment at high temperature to transform the crystal structure from amorphous to crystalline. As a consequence of the treatment, cracks form in the coating thus exposing the magnesium alloy substrate to corrosion.

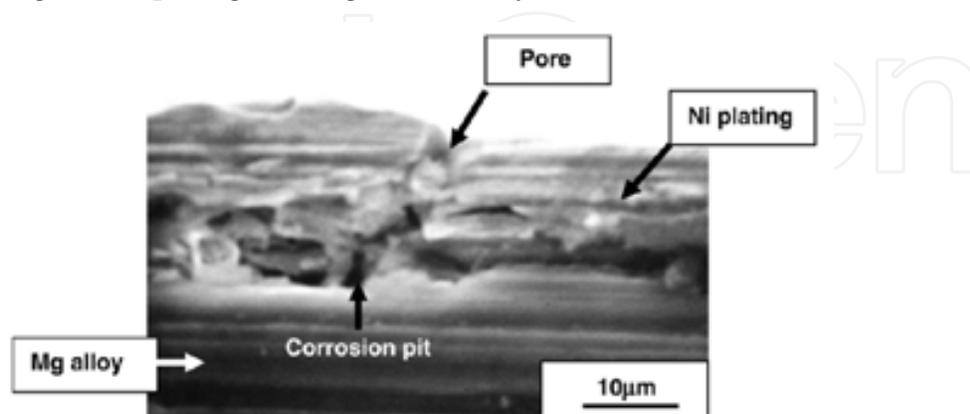


Fig. 19. Cross section of the electroless Ni plated specimen, tested and interrupted during fatigue in sodium chloride solution (Ishihara et al., 2008).

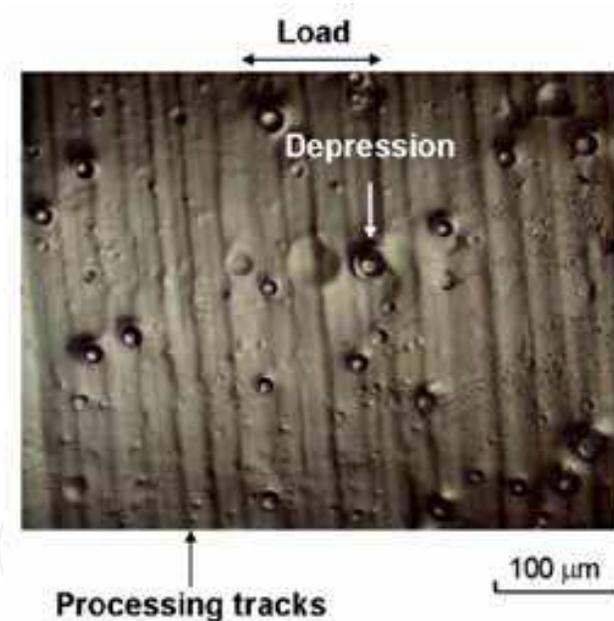


Fig. 20. Optical micrograph of the plated surface (Cu, Ni semi-gloss, Ni gloss, Cr; 20 μm). (Ishihara et al., 2010).

3. Electroplating

3.1 Introduction

Among surface treatments of magnesium, metal electrodeposition is considered as one of the most effective ways to produce corrosion and wear resistant coatings. Magnesium is a very reactive metal and electroplated metal coatings, such as copper, nickel, zinc and chromium act as physical barrier to prevent corrosion attack of the substrate. Magnesium is

classified as a difficult to plate metal due to the extreme corrosion attack on magnesium substrates by aqueous electrolyte, high reactivity that quickly forms poor immersion layers on the surface by galvanic displacement. Because of these layers, the subsequent electrochemical deposition is inhibited and it's equally hindered by the rapid formation of magnesium oxide/hydroxide films.

Process	Solution compositions	Operating conditions
(1) Alkaline cleaning		
NaOH	50 g/l	60±5°C
Na ₃ PO ₄ ·12H ₂ O	10 g/l	10-15 min
OP emulgator	3 ml/l	
(2) Acid pickling A		
CrO ₃	125 g/l	T room
HNO ₃ (68%)	110 ml/l	30 s - 1 min
(2) Acid pickling B		
H ₃ PO ₄ (85%)	605 ml/l	T room
HNO ₃ (68%)	30 ml/l	40 s
(2) Pickling activation C		
Na ₃ PO ₄ ·12H ₂ O	100 g/l	T room
H ₃ PO ₄	30 g/l	1-9 min
KMnO ₄	20 g/l	pH 4-5
Additives		
(3) Activation A		
HF (40% v/v)	385 ml/l	20°C
		10 min
(3) Activation B		
K ₄ P ₄ O ₇ ·3H ₂ O	76 g/l	75°C
Na ₂ CO ₃	15 g/l	2 min
KF·2H ₂ O	7 g/l	
(4) Zinc immersion		
ZnSO ₄ ·7H ₂ O	50 g/l	65°C
K ₄ P ₄ O ₇ ·3H ₂ O	175 g/l	70 s for AZ91D
Na ₂ CO ₃	5 g/l	150 s for AM60B
KF·2H ₂ O	10 g/l	

Fig. 21. Pretreatment solutions and operating conditions (Lei et al., 2010).

Electroplated coatings are generally comprised of a sequence of layers. There is no a single galvanic layer that protects the magnesium alloy but a sequence of layers. Cibis (Cibis et al., 2010) observed in pilot plant tests that corrosion resistance in the salt spray chamber of AZ91D and AM Lite alloys improves significantly by making a vibro finish pre-treatment before the deposition of a nickel layer from sulphamate bath in place of the deposition of copper (cyanide and then acid). This is important if pores and cracks are present in the magnesium alloys and become exposed or enhanced as a consequence of the chemical surface preparation. The operation of vibratory finishing allows to "close" the cracks and defects, thereby facilitating the adhesion of galvanic coatings.

The authors of a recent paper consider electrodeposition on magnesium alloys more advantageous compared with electroless nickel plating, in term of lower production cost, higher coatings thickness, lower porosity, better corrosion resistance and higher production efficiency (Lei et al., 2010). Pretreatment and pre-plating stages are critical for a protective coating system and in their paper they describe three pre-plating processes, i.e. Ni-P alloy, Ni and Cu as interlayers on industrial components (AZ91D engine shell and AM60B wheel hub) of magnesium alloys using different pretreatments before electrodeposition of Cu/Ni/Cr coatings from cyanide free solutions.

Before any pre-plating stage, the following process sequence was used: alkaline cleaning, pickling, activation and zinc immersion. Fig. 21 shows the solutions composition and the operating conditions for the above mentioned pretreatment processes.

Process	Solution compositions	Operating conditions
(1) Electroless nickel-phosphorus		
NiSO ₄ ·6H ₂ O	20 g/l	70°C
HF (40%)	12 ml/l	pH 5.5. – 7.0
NH ₄ HF ₂	10 g/l	
Na ₂ H ₂ PO ₂ ·H ₂ O	20 g/l	
NH ₃ ·H ₂ O (25%)	30 ml/l	
CS(NH ₂) ₂	1 mg/l	
Ligands (3)		
(2) Nickel plating		
NiSO ₄ ·6H ₂ O	110-130 g/l	45-55°C,
F ⁻	1.0-1.5 mol/l	2.0-3.5 A/dm ² (pref. 3.0)
Buffer agent		Time 15-20 min (pref. 20)
		pH 4.8-5.4
(3) Copper plating		
Cu ₂ P ₂ O ₇	60 g/l	45°C
K ₄ P ₄ O ₇ ·3H ₂ O	300 g/l	0.8-2 A/dm ² (pref. 1.5)
(NH ₄) ₃ C ₆ H ₅ O ₇	25 g/l	Time 20 min

Fig. 22. Compositions and operating conditions of electroless nickel-phosphorus, nickel electroplating and copper electroplating solutions (Lei et al., 2010).

Among the different possibilities to pretreat the magnesium alloys before electroless Ni-P deposition, the authors suggest the following sequence: alkaline cleaning, acid pickling A, activation A, electroless nickel plating (Fig. 22). Electrodeposited nickel can be used as intermediate layer instead of EN. The pretreatment before Ni electrodeposition consists of: alkaline cleaning, acid pickling B, activation B, zinc immersion, Ni electrodeposition (Fig. 22). A third preplating procedure was proposed by the authors: alkaline cleaning, acid pickling activation C, zinc immersion, Cu electrodeposition from pyrophosphate solution (Fig. 22).

Because of the good adhesion and enhanced corrosion resistance, these coatings play a role of improved protection for these substrates.

Electroless Ni-P for both even and complex shapes, electrodeposited nickel and electrodeposited copper are suitable interlayers between the magnesium substrate and Cu/Ni/Cr composite multilayers, as they provide good adhesion and corrosion resistance (see Table 7 for corrosion potentials in 3.5% NaCl solution).

	E_{corr} (mV vs SCE)
AZ91D	-1510
AM60B	-1530
Electroless Ni-P	-682
Electroplated Ni	-832
Electroplated Cu	+63.2

Table 7. Electrochemical parameters of magnesium substrates, with different pre-plating layers in 3.5% NaCl (Lei et al., 2010).

3.2 Dual coatings

Gu (Gu et al., 2005 and 2006) proposed a combination of a nickel electroless intermediate layer plus an electrodeposited layer of nanocrystalline nickel to obtain high corrosion resistance with good wear resistance on magnesium AZ91D (Fig.23).

To date only zinc and nickel have been directly plated onto magnesium and have been used as intermediate layer before the subsequent metal deposition. Cu-Ni-Cr plating is useful for many applications in indoor and in mild outdoor. The pretreatments currently used for magnesium alloys are zinc immersion and electroless nickel plating from a fluoride containing bath. A zinc layer by galvanic displacement is usually deposited onto magnesium alloys before a strike of copper from cyanide bath and multilayer electrodeposited coatings, typically Cu-Ni-Cr. In the papers and patents about this process, it is stressed that magnesium alloys with an aluminium content greater than 6-7% are difficult to treat and the deposit is not satisfactory. Nickel electroless plating has been proposed instead of zinc immersion treatment for AZ91 alloy. It was found that electroless nickel coating shows a good adherence on AZ91D magnesium alloy after pre-treatment and excellent properties including corrosion resistance and conductivity, therefore it's an excellent interlayer for electrodeposition (Jia et al., 2007).

Recently, a galvanostatic etching followed by copper electrodeposition from the same alkaline bath has been proposed as a pretreatment of AZ31 alloy surface (Huang et al., 2008). After a mechanical grinding of the surface, the alloy is anodically etched at 25 mA cm⁻² for 500 s in the bath used for copper electrodeposition, i.e. an alkaline solution of copper sulfate. The layer of copper was deposited at constant plating charge of 24 C cm⁻². As shown in Fig. 24 the copper layer is quite uniform and the coverage of the alloy is complete. The interface between the copper layer and the magnesium alloy is dense and pore-free, and free of any oxide or hydroxide-rich interlayer.

Such pre-treatment was used as basis for depositing multilayer coatings on magnesium alloys such as those shown in Fig. 25 (Huang et al., 2008, 2008b and 2010).

Zhu proposed a protective multilayer coating process on AZ91D alloy schematized in the flowsheet in Fig. 26 (Zhu et al., 2006). In this process a final thermal treatment in air is performed in order to improve the adhesion of the coating to the substrate. After thermal treatment, tin diffused through the zinc layer and reached the magnesium alloy, where it formed the compound Mg₂Sn.

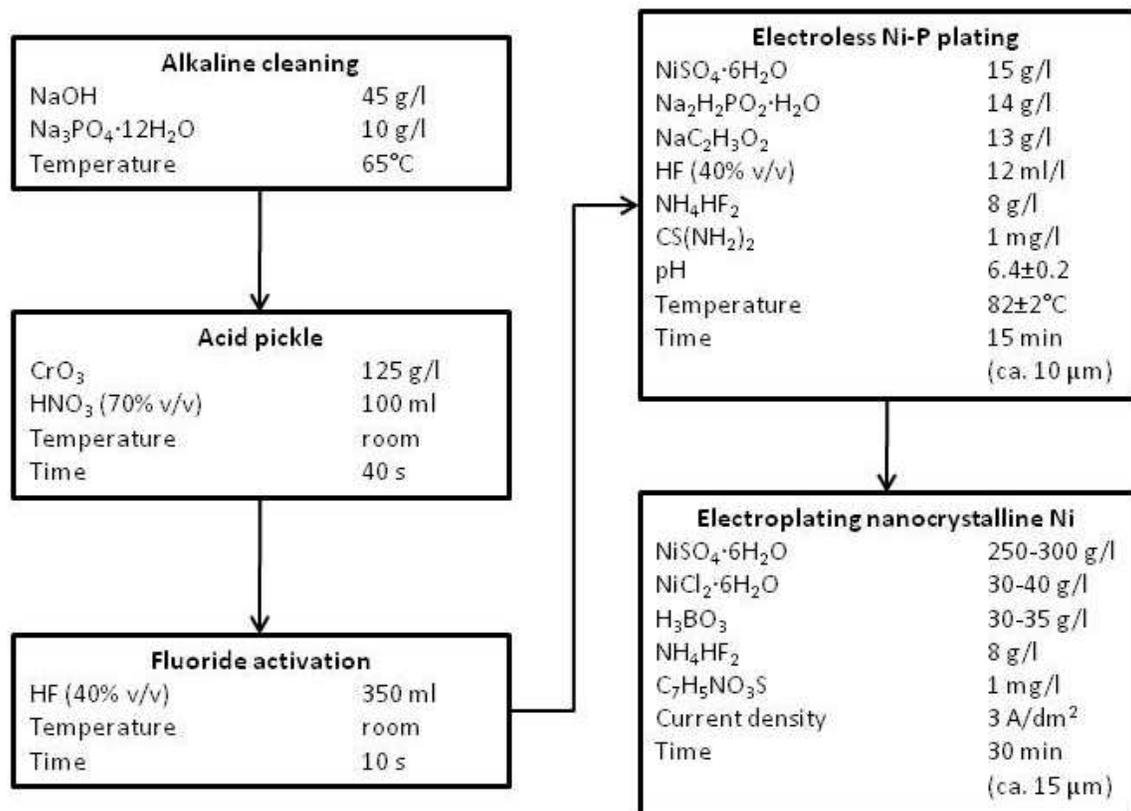


Fig. 23. Flowchart of the electroless Ni and electroplated nanocrystalline Ni on the AZ91D magnesium alloy (Gu et al., 2005 and 2006).

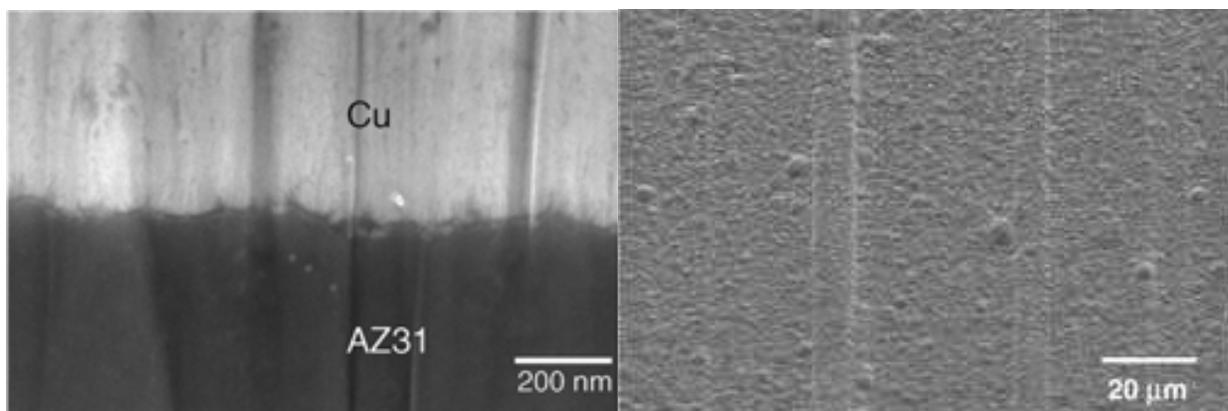


Fig. 24. SEM surface morphology of copper plated AZ31 alloy (left). Interface between the AZ31 alloy and electrodeposited copper layer (right). (Huang et al., 2008).

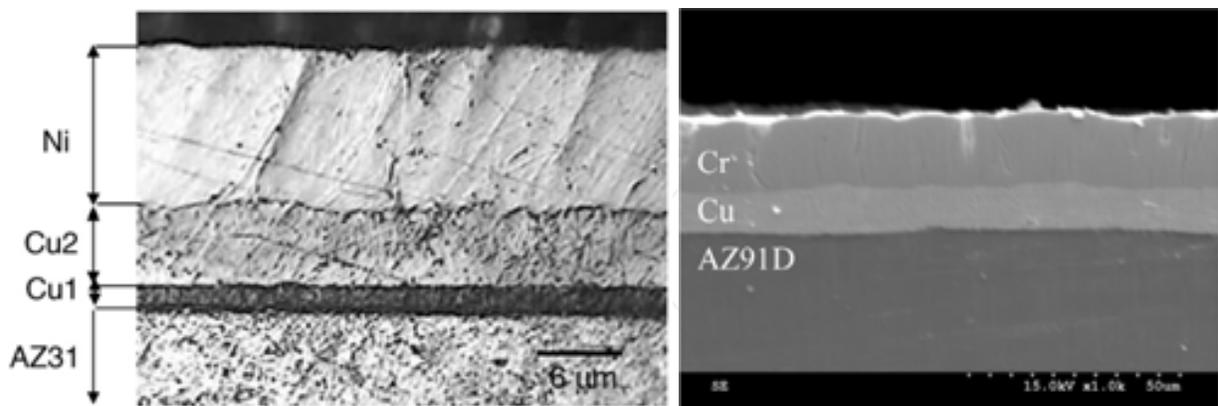


Fig. 25. Cross section morphologies of multilayer coatings on magnesium alloys. Left: Cu1 / Cu2 / Ni on AZ31 (Huang et al., 2008). Right: Cu / Cr in AZ91D (Huang et al., 2010).

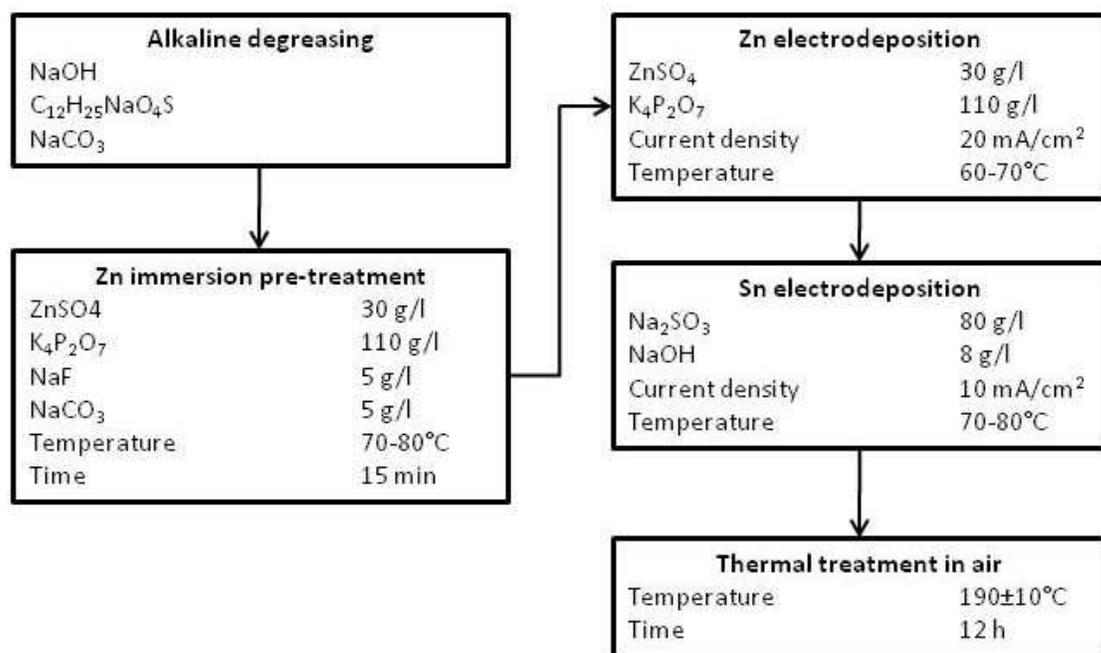


Fig. 26. Flowchart of the zinc and tin electroplating process on the AZ91D magnesium alloy (Zhu et al., 2006).

The coating has a three layers structure, shown in Fig. 27. A bottom layer, compact and pore free Sn and Mg₂Sn layer, formed by reaction of Mg and Sn; a middle layer, Zn and ZnO, formed by electroplating; an upper, loose and porous Sn layer formed by electroplating. The authors demonstrated that such three-layer structure provides better corrosion protection for the AZ91D alloy in comparison to the as plated Zn-Sn alloy without thermal treatment.

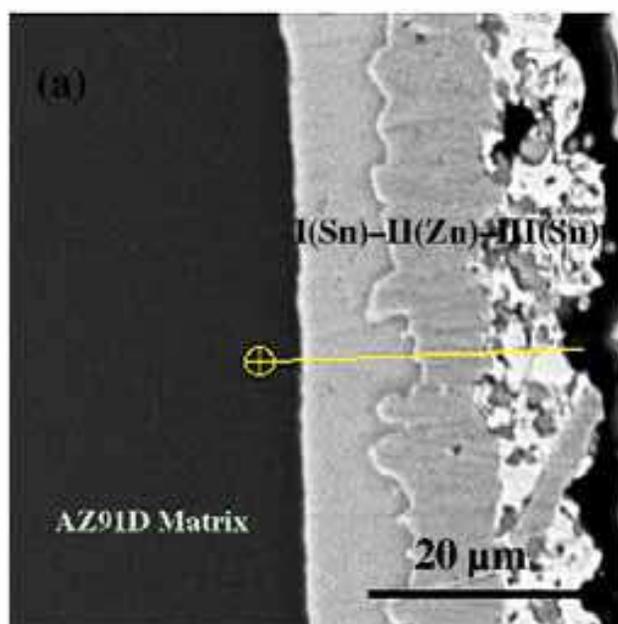


Fig. 27. Cross-section image of the Zn-Sn plated coating on AZ91D alloy after thermal treatment at 190°C for 12 h (Zhu et al., 2006).

3.3 Alloys electrodeposition from aqueous solutions

The pulse plating of Zn-Ni coatings on AZ91 alloy was investigated by Jiang (Jiang et al., 2003, 2005 and 2005b) for protecting the alloy from corrosion. The process is schematized in Fig. 28. Zinc-nickel coatings have anticorrosion properties when the content of Ni is 12-14% due to the presence of the intermetallic phase $Zn_{12}Ni_5$. The pulse electrodeposition induces a high rate of nucleation and the coating structure has a grain refined structure. The thickness of Zn-Ni layers increases almost linearly along with the increase of both deposition time and electric current density while there is no obvious relationship between the thickness of Zn-Ni layers and the value of t_{on} / t_{off} . The Ni content in Zn-Ni coating generally increases with both electric frequency and electric current density and increases with t_{on} / t_{off} firstly and then decreases. The maximum value of Ni content is about 18% when t_{on} / t_{off} is about 30%. The microhardness of Zn-Ni coatings also increases with the increase of processing time, electric current density, electric frequency and mostly with the increase of t_{on} / t_{off} (140 - 240 HV).

Fig. 29 shows a typical cross section and surface morphology of a coating composed by a zinc layer of about 4 μm, a Zn-Cu layer of about 8 μm and a Zn-Ni layer of about 20 μm. Some microvoids can be observed at the interface between Zn-Cu and Zn-Ni layers.

More recently, a paper on Zn-Ni electroplating on AZ91D was published (Abdel Aal, 2008). Prior the deposition of the Zn-Ni coating, AZ91D substrate was treated in Zn(II) containing solution and then in a phosphate-permanganate solution to facilitate the adhesion of the Zn-Ni external layer (Fig. 30).

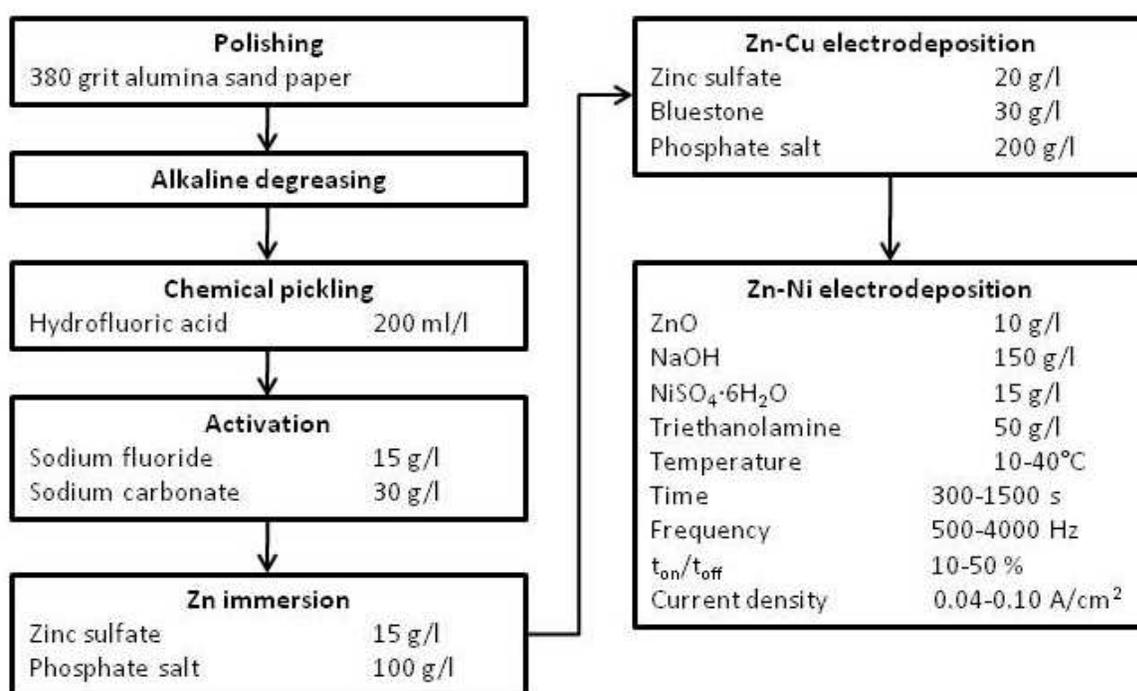


Fig. 28. Flowchart of the Zn-Ni electroplating process on the AZ91D magnesium alloy (Jiang et al., 2005b).

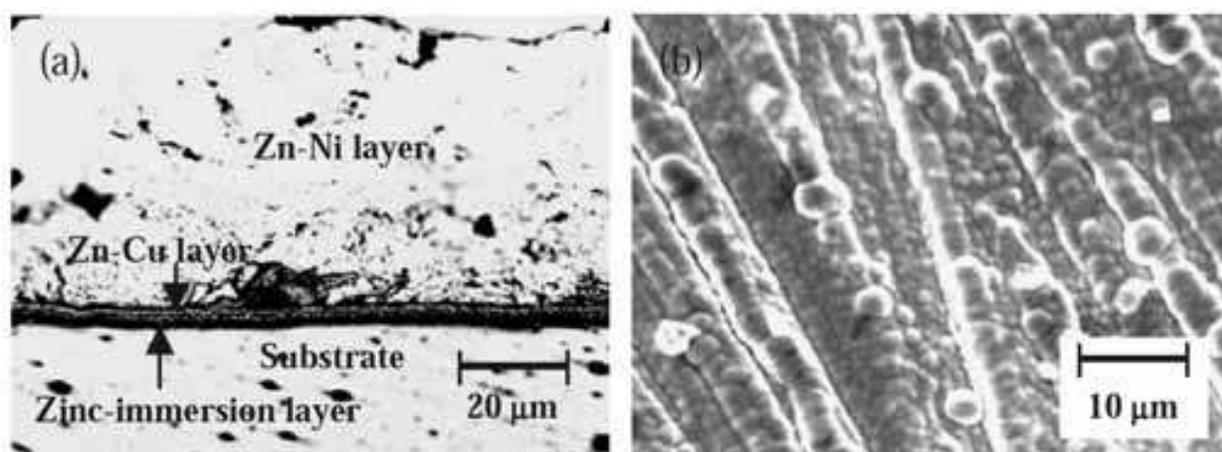


Fig. 29. Optical cross section (left) and SEM surface morphology (right) of a Zn / Zn-Cu / Zn-Ni coating (Zn-Ni: 600 s, 1 kHz, t_{on}/t_{off} 10%, 0.04 A/cm²). (Jiang et al., 2005b).

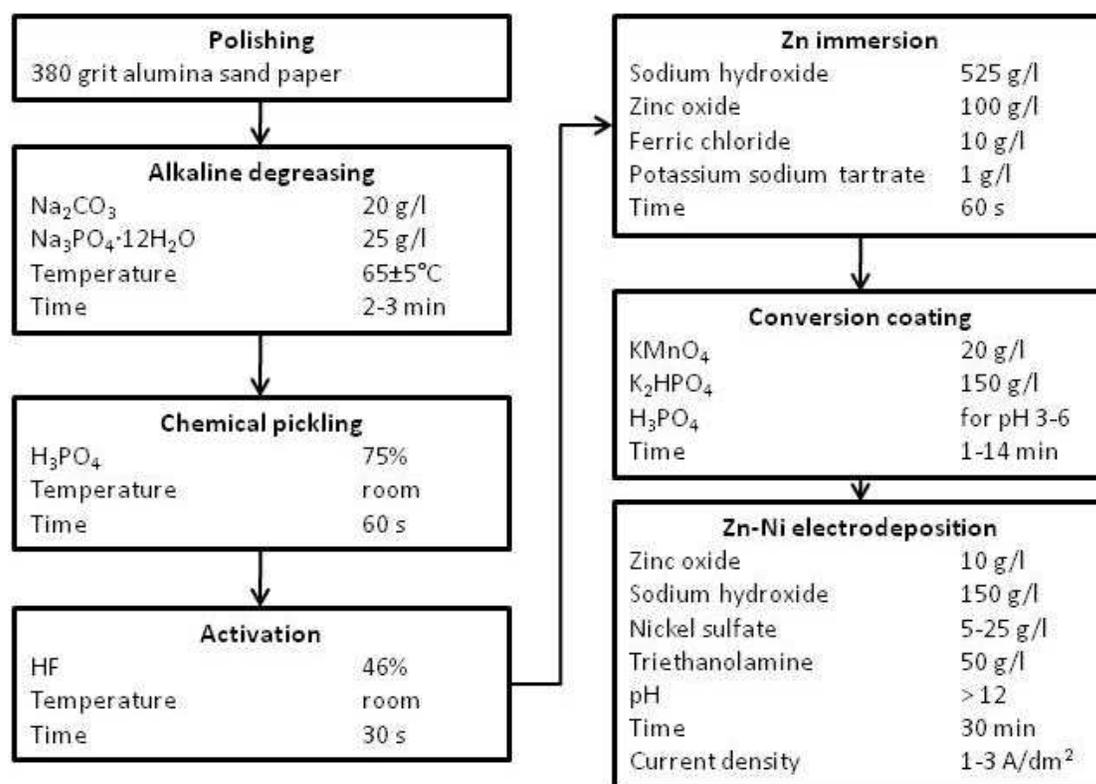


Fig. 30. Flowchart of the Zn-Ni electroplating process on the AZ91D magnesium alloy (Abdel Aal, 2008).

Fig. 31 displays the surface morphology of the coating obtained at a current density of 3 A/dm². When the Zn-Ni coating is exposed to corrosive environments, zinc dissolves preferentially leaving an external layer enriched with nickel, that acts as a barrier to further attack. The higher corrosion resistance is obtained for the alloy containing 13 wt.% Ni, and this could be explained by the lower porosity of the coating and its single γ -phase structure and hence the absence of local microgalvanic cells between different phases.

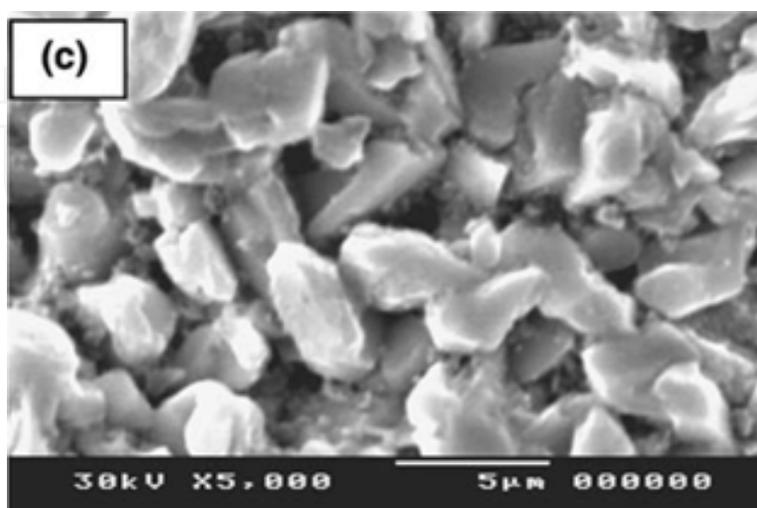


Fig. 31. SEM images of AZ91D Mg alloy coated with Zn-Ni at current density 3 A/dm². (Abdel Aal, 2008).

	E_{corr} (mV vs Ag/AgCl)	i_{corr} (A cm ⁻²)
Substrate AZ91D	-1685	5.6×10^{-4}
Phosphate - permanganate	-1635	5.1×10^{-5}
Zn - 13% Ni	-1515	5.8×10^{-5}

Table 8. Electrochemical parameters of magnesium substrate, with phosphate-permanganate and Zn-Ni coating (in 3.5% NaCl) (Abdel Aal, 2008).

3.4 Non-aqueous electroplating

Magnesium alloys are sensitive to aqueous environment and thus non-aqueous processes have been proposed for metal plating on magnesium alloys. The electrodeposition of zinc onto magnesium alloys from two types of ionic liquid, stable in air and in the presence of water, was recently proposed (Bakkar and Neubert, 2007). One type of ionic liquid is obtained by mixing (ratio 1:2) choline chloride (ChCl), as amine salt ($\text{HOC}_2\text{H}_4\text{N}(\text{CH}_3)_3^+\text{Cl}^-$), with a hydrogen bond donor such as urea (NH_2CONH_2), ethylene glycol ($\text{HOCH}_2\text{CH}_2\text{OH}$), malonic acid ($\text{HOOCCH}_2\text{COOH}$), or glycerol ($\text{HOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$). The other type is formed by mixing ChCl with a metal halide. The water content in the ionic liquid was in the range 3.5-7.2%. The electrodeposition solutions were prepared by dissolving 0.5 M of ZnCl_2 in the ionic liquid at 90°C. The magnesium substrates used for electrodeposition were: cp Mg, AZ31, AZ61, AZ91, AS41, AE42, WE43-T6, QE22, MgGd5Sc1 and MgY4Sc1.

The electrochemical tests showed that magnesium has the best corrosion resistance behavior in ChCl/urea 1:2 and therefore ionic liquids were suggested to test the possibility of electroplating magnesium alloys. Successful electrodeposition of metallic zinc layers onto Mg-RE alloys free of Al was obtained while the other ionic liquids produced either powdery deposits or corrosion of the substrate. Pulsed current produced uniform, shiny and dense deposits free of defects (Fig. 32). Potentiodynamic polarisation tests in 0.1M NaCl showed that the zinc deposited by pulsed current densities exhibits a corrosion behaviour similar to that of pure zinc (Table 9).

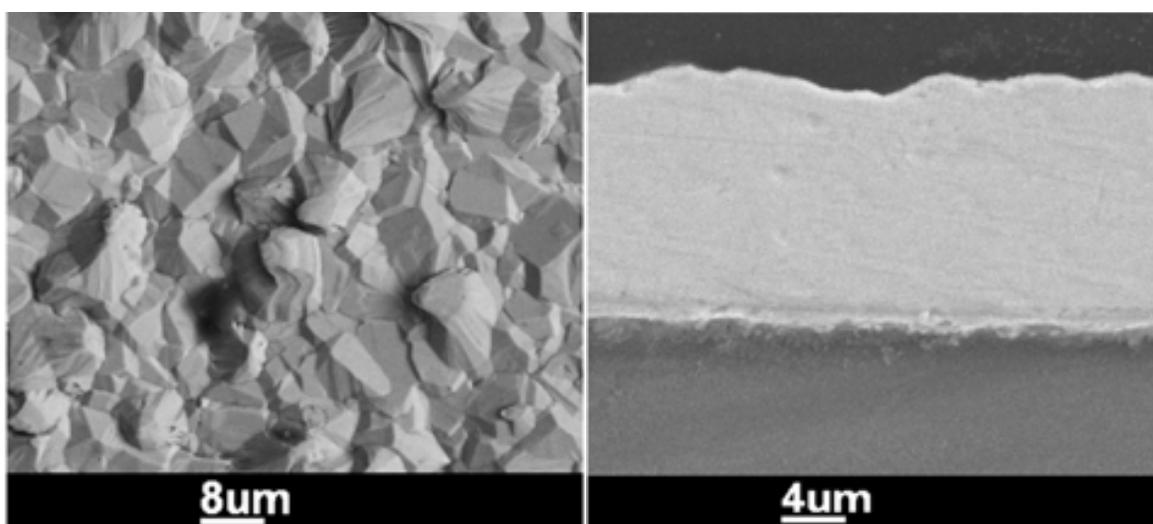


Fig. 32. SEM surface (left) and cross section (right) micrographs of electrodeposited Zn onto WE43 Mg alloy from ChCl/urea + 0.5M ZnCl_2 at $\text{CD} = 5 \text{ mA/cm}^2$, $T = 60^\circ\text{C}$. Pulsed current (2 s on-time, 1 s off-time).

	E_{corr} (mV vs SCE)	i_{corr} ($\mu\text{A cm}^{-2}$)
WE43 substrate	-1705	14.67
Zinc coating on WE43 (pulsed)	-1129	1.38
Zinc sheet	-1006	1.89

Table 9. Electrochemical parameters of zinc sheet, WE43 alloy and Zn coating on the magnesium alloy (0.1 M NaCl) (Bakkar and Neubert, 2007).

Several papers on Al (Chang et al., 2007, 2008 and 2008b) and Al-Zn (Pan et al., 2010) electrodeposition from EMIC (1-ethyl-methylimidazolium chloride) has been recently published. In the electrodeposition of aluminium on AZ91D, a solution of AlCl_3 -EMIC (1.5:1) was prepared and handled in a glove box under nitrogen atmosphere, in which the moisture and oxygen content were maintained below 1 ppm. Before electrodeposition, each sample was ground with SiC paper to 1000 grit. Electrodeposition tests were carried out both at constant potential (-0.2 V and -0.4 V vs Al wire) (Chang et al., 2007) and at constant current density (Chang et al., 2008). The surface and cross-section morphologies of the sample produced at -0.2 V are shown in Fig. 33. On the contrary, samples deposited at -0.4 V were less compact, with nodular microstructure and cracks.

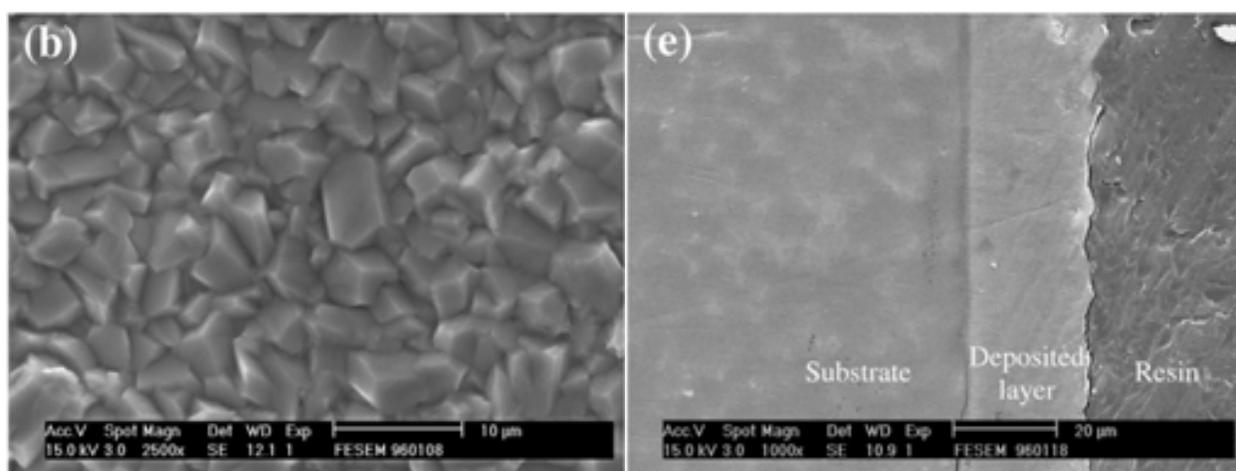


Fig. 33. SEM surface (left) and cross section (right) micrographs of electrodeposited Al onto AZ91D alloy from AlCl_3 -EMIC at -0.2 V vs Al wire for 2550 s (5 C) at 25°C (Chang et al., 2007).

Experimental results show that aluminium coatings give satisfactory protection for the AZ91D alloy against corrosion (Fig. 34). The deposition current density is the factor that controls the coating properties and the corrosion resistance of the Al layer deposited. In fact, a lower deposition rate results in a more uniform and compact coating layer and also thicker and, consequently, give rise to a better performance for corrosion protection.

Pan demonstrated the possibility of plating thick coatings of Al-Zn alloys on AZ91D substrate from AlCl_3 -EMIC (60:40 molar ratio) ionic liquid containing 1wt.% ZnCl_2 (Pan et al., 2010). The zinc content in the coating can be controlled in the range 20-100% by varying the potential of deposition. Uniformity in the coating composition was obtained when the deposition was performed at -0.2 V vs Al.

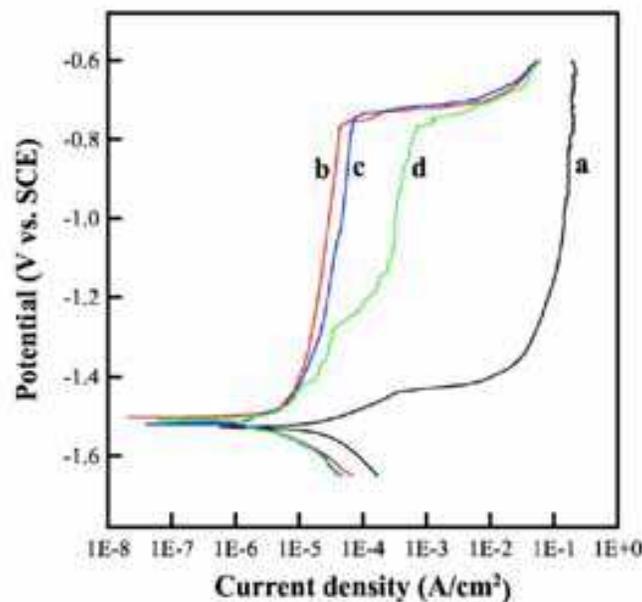


Fig. 34. Polarization curves of AZ91D alloy (a) and Al-deposited Mg electrodes (b -15, c -20, and d -40 mA/cm²) in 3.5% NaCl at 25°C (Chang et al., 2008).

The effects of different acid pickling processes on the adhesion between the AZ91D magnesium alloy substrate and aluminum coatings electrodeposited from the acid AlCl₃-EMIC room temperature molten salts were studied by Qian (Qian et al., 2009). The results show that the aluminum coating is not dense and the adhesion between the coatings and substrate is not good after mechanical pretreatment on AZ91D substrate. Dense and uniform coatings can be electrodeposited on the AZ91D substrate after hydrofluoric acid pickling. The density of coatings and the adhesion can be improved simultaneously by using diluted phosphoric acid as pickling solution, and thus, the coating provides good protection to the substrate.

The electrodeposition of Al-Mn coatings on AZ31B magnesium alloy was investigated by Zhang (Zhang et al., 2009). Experiments were carried out by using molten AlCl₃-NaCl-KCl-MnCl₂ at 170°C. The substrate was pre-plated with a zinc layer (5 μm) as interlayer to prevent corrosion during Al-Mn deposition in molten salts. The addition of MnCl₂ to the molten bath results in compact coatings. The coating of Fig. 35 (right) has a content of Mn of about 22.5 %. By increasing the Mn content in the coating, the structure change from partly crystalline (Fig. 35 left) to amorphous (Fig. 35 right). Table 10 lists the electrochemical parameter obtained from corrosion tests (Al-Mn coating thickness of about 16 μm).

Corrosion resistance of magnesium alloys can be improved by addition of rare earth elements. Recently the electrodeposition of Mg-Yb alloy film on magnesium from molten LiCl-KCl-YbCl₃ (2wt.%) at 500°C under argon atmosphere was investigated by Chen (Chen et al., 2010). A thin film of about 200 nm of Mg₂Yb was formed at -1.85 V (vs Ag/AgCl) for 12 h, and a film of about 450 nm was obtained at -2.5 V for 2.5 h.

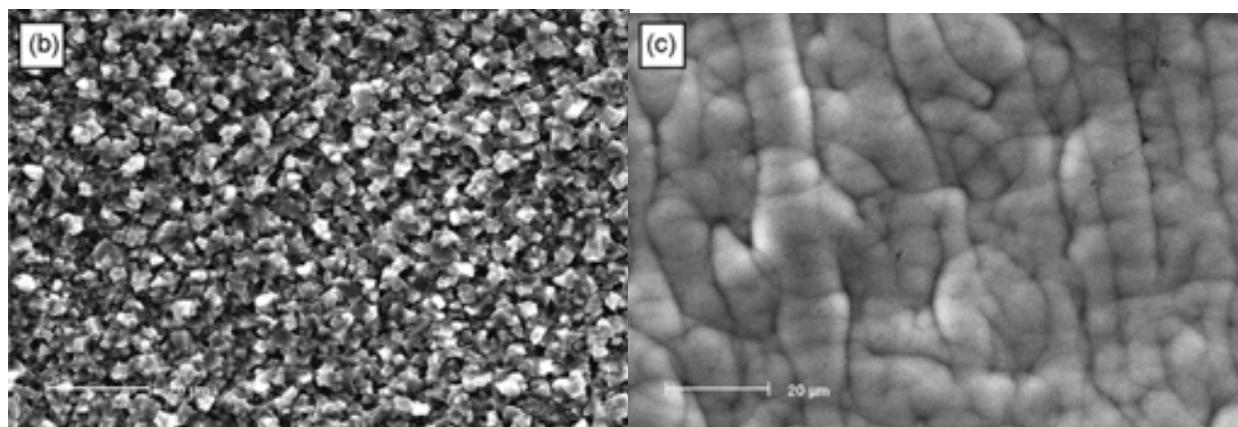


Fig. 35. SEM surface morphologies of Al-Mn coatings from molten salts with various MnCl₂ content (left 0.5%, right 1%) (Zhang et al., 2009).

	E_{corr} (mV vs SCE)	i_{corr} (A cm ⁻²)
AZ31B	-1523	1.60×10^{-5}
Zn layer	-1463	2.02×10^{-4}
9.2 Mn	-1276	5.15×10^{-5}
22.7 Mn	-1271	2.89×10^{-7}
25.4 Mn	-1162	2.59×10^{-8}
29.3 Mn	-713	3.71×10^{-9}

Table 10. Electrochemical parameters of different specimens in 3.5% NaCl) (Zhang et al., 2009).

4. Conclusions

The review on the scientific literature on coatings deposited by electroless and electroplating processes shows that magnesium alloys are difficult to plate substrates. However, processes based on metal deposition by electroless and electrodeposition are used and a great deal of research is done in order to develop environmentally friendly processes. The problem of electroless and electroplating magnesium alloys can be solved by using complex schemes, that combine surface preparation procedures with multilayer coating systems.

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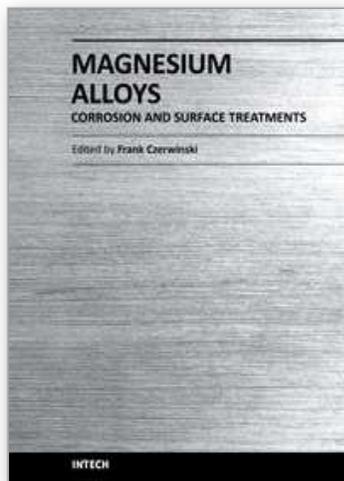
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A resistance of magnesium alloys to surface degradation is paramount for their applications in automotive, aerospace, consumer electronics and general-purpose markets. An emphasis of this book is on oxidation, corrosion and surface modifications, designed to enhance the alloy surface stability. It covers a nature of oxides grown at elevated temperatures and oxidation characteristics of selected alloys along with elements of general and electrochemical corrosion. Medical applications are considered that explore bio-compatibility of magnesium alloys. Also techniques of surface modifications, designed to improve not only corrosion resistance but also corrosion fatigue, wear and other behaviors, are described. The book represents a valuable resource for scientists and engineers from academia and industry.

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