S E S 2 0 1 5
Eleventh Scientific Conference with International Participation
SPACE, ECOLOGY, SAFETY
4 – 6 November 2015, Sofia, Bulgaria

ELECTROLESS DEPOSITION OF METALIC COATINGS ON MAGNESIUM ALLOYS

Zdravka Karaguiozova

Space Research and Technology Institute – Bulgarian Academy of Sciences
e-mail: karazuzi@yahoo.com, aleksander.ciski@imp.edu.pl

Keywords: *Electroless coatings, nickel coatings, zinn coatings, copper coatings, magnesium alloys*

Abstract: *Magnesium is the subject of interest from scientists due to his lightness combined with strength. Magnesium density is only two thirds of the aluminum's. This is a reason magnesium and its alloys to be widely applicable in areas of the industry as aircraft production, automotive and missile construction. This leads to fuel economy and reduced weight.*

A big problem for the magnesium and its alloys utilizing is its high chemical activity, which generates corrosion of the surfaces. To achieve optimum results in term of corrosion and wear protection of magnesium alloys a proper electroless and electrochemical coating deposition technique could be used.

The complicated behavior of the magnesium and its alloys during plating or chemical treatment processes requires the use of a specific pretreatment leading to equipotential material surface the technically and economically viable coating systems to be produced.

ОТЛАГАНЕ НА МЕТАЛНИ ПОКРИТИЯ ПО БЕЗТОКОВ МЕТОД ВЪРХУ МАГНЕЗИЕВИ СПЛАВИ

Здравка Карагьозова

Институт за космически изследвания и технологии – Българска академия на науките
e-mail: karazuzi@yahoo.com, aleksander.ciski@imp.edu.pl

Ключови думи: *Безтокови имерсионни покрития, калаено покритие, печатни платки, ецване, ъгъл на омокряне*

Резюме: *Магнезият представлява интерес за учените поради комбинацията на две негови основни свойства: той е лек и ковък елемент. Плътността на магнезия е две трети от тази на алуминия.Това обяснява широката употреба на магнезий и негови сплави в области на индустрията като самолетостроене, автомобило- и ракетостроенето,което води до икономия на гориво и редукция на теглото.*

Голям проблем при използване на магнезий и негови сплави е високата му химическа активност, причина за корозия на повърхността. За постигане на оптимални резултати по отношение на корозионо- и износоустойчивост на магнезиевите сплави се предлага приложение на подходящи методи за безтоково и електрохимично нанасяне на покрития.

Комплицираното поведение на магнезий и негови сплави по време на нанасяне на покрития и химическо третиране изисква специфични предварителни подготовки, водещи до еквипотенциална повърхност. По този начин се осигуряват технически и икономически изгодни условия за получаване на качествени покрития.

Introduction

This short review presents some methods for surface treatment of Magnesium and Magnesium alloys in order their high chemical activity to be reduced and their corrosion and wear resistance to be improved.

Since magnesium is less dense than aluminum, with a density of only two thirds of the aluminum, it has countless applications in cases where weight reducing is important, i.e. in aircraft and missile construction, space industry. Magnesium alloys are prized for its properties of lightness combined with strength [1].

As of 2013, magnesium alloy consumption was less than one million tons per year, compared with 50 million tons of aluminum alloys [2, 3]. Its use has been historically limited by its tendency to corrode, high-temperature deformation, and flammability [4].

For the chemical resistance improvement of Magnesium and its alloys research and development are carried out an expanding the application areas to be achieved. One preferred method for surface properties improvement is metal deposition by electroless or electrochemical methods.

According to the authors [5, 6] only complex and multilayer coatings are able to produce optimum results for surface protection of magnesium alloys, and a great deal of research has to be done furthermore to develop technically and economically viable coating systems.

The coating that acts as a barrier between the metal substrate and the environment has to be uniform, adherent, pore and crack free and self-healing in the applications where damage of the coating can occur [7].

Methods for magnesium surface pretreatment by plating deposition

The most widely used commercial magnesium 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.

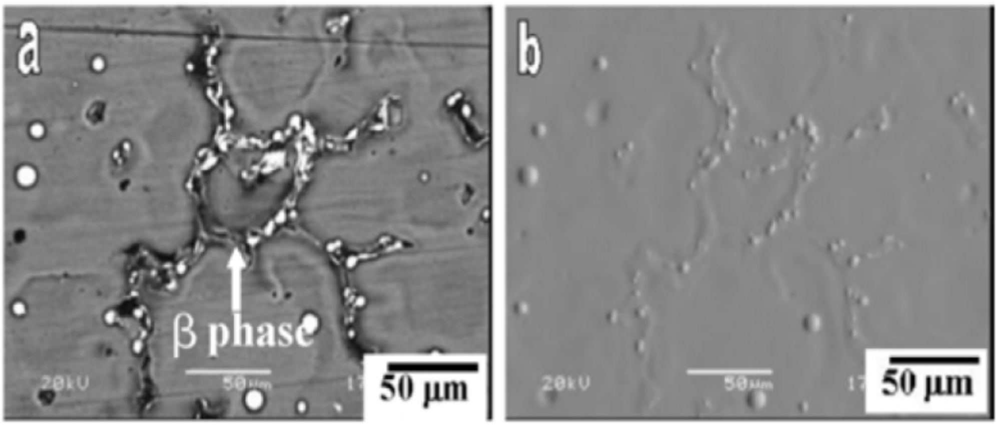


Fig. 1. Initial stages of nickel growth on AZ91 alloy (after 1 min): a) secondary and (b) topographic mode [8]

Chen [9] recently proposed a new galvanizing process based on the deposition of a zinc film by immersion followed by the deposition of a layer of electroplated zinc. 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). 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 + electrodepositon) of copper from a pyrophosphate solution over a zinc transition layer deposited from pyrophosphate solution [10].

In another study, a protective copper film on AZ31 magnesium alloy, without zinc pretreatment, was proposed. The aqueous solution containing 0.4M $Na_4P_2O_7$ + 0.08M $Cu_2P_2O_7$ + 0.24M $CuSO_4$ + 0.05M NaF was used. A galvanic displacement reaction occurrs 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 [11-13]. Ultrasonication was found effective in improving the copper immersion coating process, particularly during extended deposition times, beyond the initial stages [14]. Higher coverage of magnesium alloy surface (> 80%) by copper immersion coating was also achieved by using an alkaline bath. The procedure proposed by Yang is schematically represented in Fig. 3 [13].

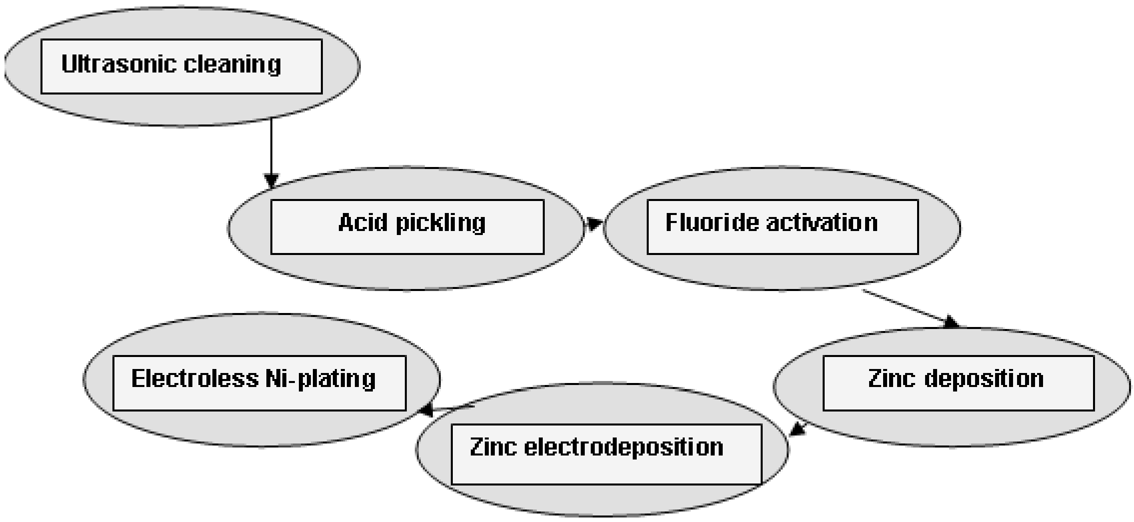


Fig. 2. Flowchart of the overall procedure for coating on the AZ91D magnesium alloy [9]

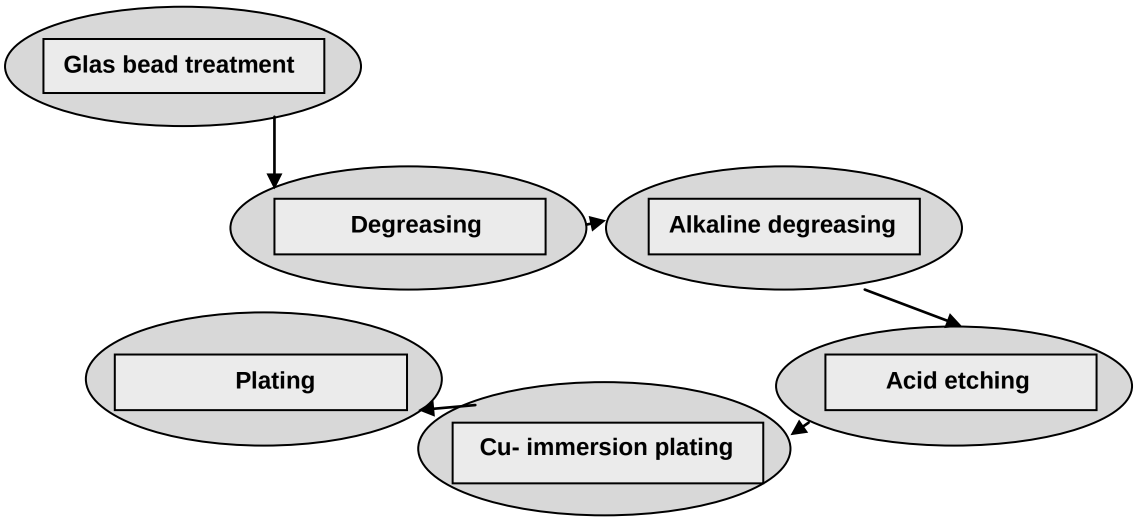


Fig. 3. Flowchart of the procedure for copper immersion coating on the AZ91D magnesium alloy [13]

Methods for surface activation for direct electroless nickel plating on magnesium alloy

Yang presented the results of a research on EN deposition (8 μm, 4.74% phosphorous) and molybdate conversion film pretreatment on Mg-8Li alloy [15] (Fig.4).

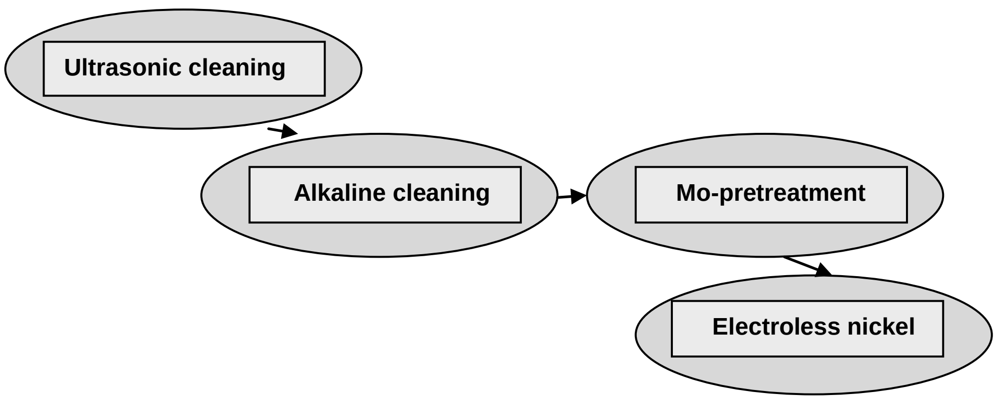


Fig. 4. Flowchart of the molybdate coating and electroless Ni deposition on the Mg-8Li magnesium alloy [15]

Magnesium alloy is disposed by three kinds of acid pickling formula and activation formula and the effect of the three kinds of acid activation formula on magnesium alloy is studied by contrast experiment. The experimental results indicated that after disposed by acid pickling formula of HNO_3 25 ml/L, H_3PO_4 25 ml/L, room temperature and activation formula of $NH_4H_2PO_4$ 80–100 g/L, NH_4F 30–50 g/L, room temperature, magnesium alloy could realize electroless nickel plating directly. The results showe that the structure of Ni–P coating is amorphous, the Ni–P coating is very meticulous and uniform, the activation coating is mainly MgF_2 and $Mg_2P_2O_7$, and comparing with magnesium substrate, the corrosion potential of magnesium alloys increases by about 1.1 V and the corrosion current density declines obviously. Tested by thermal shock test and file test, the adhesion of magnesium alloy and Ni–P coating is good. Fig. 5 shows the section figure of magnesium alloy electroless nickel plating, it is seen from the figure that nickel plating is well combined with the substrate.

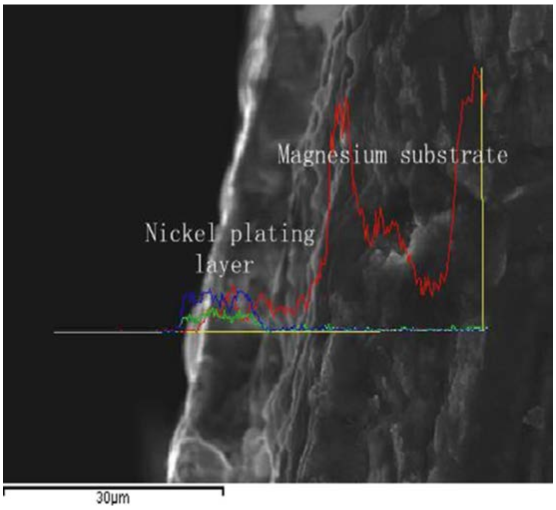


Fig. 5. Cross section morphology of Ni–P coating on magnesium alloy.[16]

The surface morphology of nickel plating layer is observed to find out the early growth rule of nickel layer. Fig. 6 shows the surface morphology and energy spectrum analysis of the electroless nickel plating for magnesium alloys in the early growth process. Fig. 6(a)–(e) respectively shows the surface morphology and element distribution map during the plating time of 10 s, 30 s, 60 s, 120 s and 240 s.

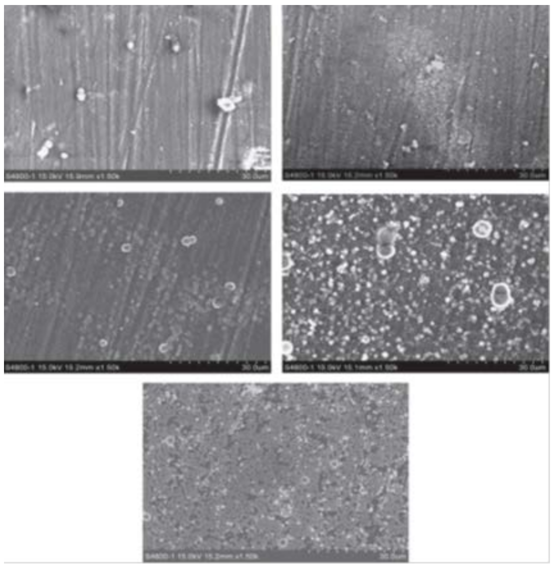


Fig. 6. Beginning growth process of electroless nickel plating on magnesium alloy.
(a: 10s, b: 30s, c: 60s, d: 120 s, e: 240 s)

After continuous plating for 30 min, the surface of plating is completely covered with nickel–phosphorus alloy layer and its structure is shown in Fig. 7: belonging to the sub- crystalline structure of coating.

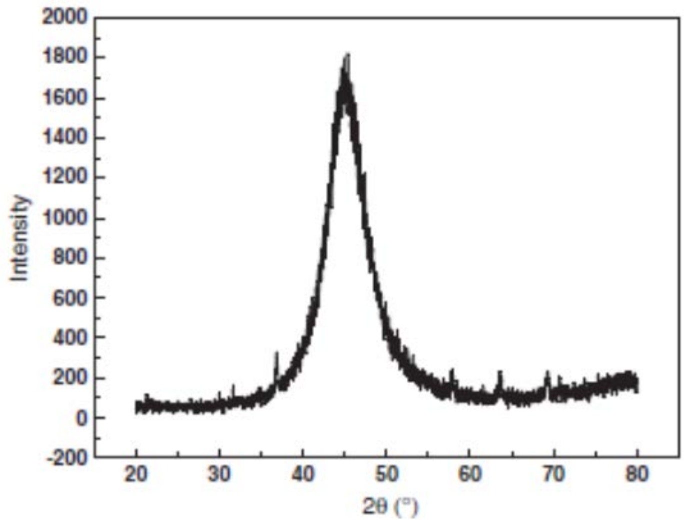
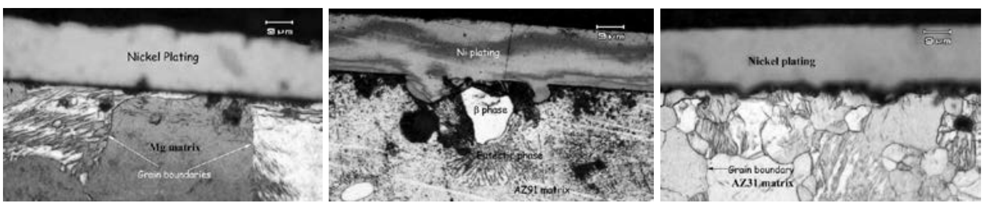


Fig. 7. X-Ray patterns of Ni_P coating on Magnesium alloy

Authors [17] investigate the influence of the chemical pretreatment before direct electroless nickel plating on the surface roughness (Fig. 8). It is found the substrate surface roughness increases significantly after pretreatment process, although to different degrees for different alloy substrates. The coating surface roughness on the pure Mg substrate increases compared to the chemical pretreated surface. On the contrary, the coating roughness on AZ31 and AZ91 alloys decreases after plating (Table 1). Figs.9-11 show that the interface between the coating and AZ31 substrate has a rather high roughness and a more uniform distribution than other interfacial systems, consistent to the highest Lc value of 13N. In contrast with the smallest Lc (8.7N) and rather smooth interface between pure Mg substrate and plating, it is believed that the interfacial mechanical interlocking effect plays a more important role in improving adhesion strength than the substrate hardness in this coating system. Nevertheless, various substrate composition and microstructure leads to different surface roughness after etching, influencing the coating performance.

Table 1. Surface roughness velue Ra (μm) and mechanical performance

Sample	Before etching	Before platin	After plating (110min)	Substrate hardness (HV50g)	Coating hardness (HV50g)	Adhesion strength Lc (N)
Mg	0.05±0.01	0.15±0.03	0,36±0,06	55±10	580-610	8,7
AZ31	0.05±0.01	0.37±0.06	0,22±0,04	75±10	580-610	13,1
AZ91	0.05±0.01	1.2±0.2	0,32±0,05	95±10	580-610	10,1



9 10 11

Fig. 9-11 Cross section optical micrograph of electroless Ni plating on 9- pure Magnesium, 10- AZ31, 11-AZ91 subtrates

Stage no.	Constituent or condition		Value or range
1	Ultrasonic degreasing	Ethanol	5–10 min
2	Alkaline cleaning	NaOH	50 g/L
		Na_3PO_4	10 g/L
		Temperature	333±5 K
		Agitation	Mild, magnetic
		Time	8–10 min
3	Acid etching (pickling)	CrO_3	125 g/L
		HNO_3 (70% V/V)	110 ml/L
		Temperature	Ambient (293K)
		Agitation	Vigorous, magnetic
		Time	30–60 s
4	Fluoride activation	HF (40%V/V)	385 ml/L
		Temperature	Ambient (293K)
		Agitation	Mild, magnetic
		Time	10 min
5	Electroless nickel plating and operating conditions	Basic nickel carbonate	10 g/L
		HF (40% V/V)	12 ml/L
		Citric acid	5 g/L
		Ammonium bifluoride	10 g/L
		Sodium hypophosphite	20 g/L
		Ammonium hydroxide 25%	30 ml/L
		pH (colorimetric)	4.5–6.8
		Temperature	349–353 K
		Agitation required	Mild mechanical

[1] Water rinse about 1–2 min is omitted after each step in this table.

Fig. 8 Sequences of operations

Conclusions and outlook

The study presents a short overview for some surface treatment of Magnesium and Magnesium Alloys the better corrosion and wear resistance of the surface to be achieved. Many Authors focus their attention on the electroless and electrochemical plating methods for production of high quality coatings to expand the application areas of these materials.

Considering Magnesium lightness combined with strength it is too promising to investigate novel coatings with improved properties for application in areas of the industry as aircraft production, automotive and missile construction, also space technology.

Our achievements in recent Years about improved properties of electroless nickel and composite nickel coatings give us a reason to be optimistic about possibilities for using these coatings to ensure a bright future of Magnesium and its alloys.

References:

1. Aghionm, E., Bronfin B. "Mg Alloys Development towards the 21 –st Century". Materials Science Forum, 350-351, 2000, pp.19-30.
2. Miteva, A. "Possibilities for aluminum and aluminum alloys strengthening on the base of the structure analysis". Proceedings of the Annual Academic Scientific Conference with International participation, 8, Veliko Tarnovo, 2011, pp. 126-129.
3. Miteva, A., "On the microstructure and strengthening of aluminum and aluminum alloys". Tribological Journal BULTRIB, III, 2013, pp. 367-370.
4. Ddodson, B. "Stainless magnesium breakthrough bodes well for manufacturing industries". Gizmag.com, Retrieved 29 08.2013.
5. Gray, J. E., B. Luan B. "Protective coatings on magnesium and its alloys — a critical review". Journal of Alloys and Compounds, 336, 1-2, 2002, pp.88-113.
6. Natarajan, S., V. Sivan, P.G. Tennyson, V.R. Kiran. "Protective coatings on magnesium and its alloys - a critical review". Journal of Corrosion prevention & Control, 51, 4, 2004, pp. 142-163.
7. Massimiliano, B., A. Da Forno. "Electroless and Electrochemical Deposition of Metallic Coatings on Magnesium Alloys Critical Literature Review". Magnesium Alloys - Corrosion and Surface Treatments, Frank Czerwinski (Ed.), InTech, http://www.intechopen.com/books/magnesium-alloys-corrosion-and-

surface-treatments/electroless-andelectrochemical-deposition-of-metallic-coatings-on-magnesium-alloys-critical-literat].

8. Ambat, R., W. Zhou. " Electroless nickel-plating on AZ91D magnesium alloy: Effect of substrate microstructure and plating parameters". Surface and Coatings Technology, 179, 2-3, 2004, pp. 124-134.
9. Chen, J., G. Yu, B. Hu, Z. Liu, L. Ye, Z. Wang. "A zinc transition layer in electroless nickel plating". Surface and Coatings Technology, 201, 3-4, 2006, pp. 686-690.
10. Yu, G., Y. E. Liu, B.N. Hu, Z. Liu, L.Y. Ye. "Investigation of electroplating copper in pyrophosphate on magnesium alloy". Journal of Hunan University Natural Sciences, 32, 4, 2005, pp.77-81.
11. Yang, L., B. Luan. "Copper immersion deposition on magnesium alloy: The effect of fluoride and temperature". Journal of the Electrochemical Society, 152, 7, 2005, pp. C474-C481.
12. Yang, L., B. Luan, W.J. Cheong, J. Jiang. "Optimization and performance analysis of copper immersion coating on AZ91 magnesium alloy". Journal of Coatings Technology Research, 2, 2005b, pp. 493-498.
13. Yang, L., B. Luan, J. Nagata. "Novel copper immersion coating on magnesium alloy AZ91D in an alkaline bath". Journal of Coatings Technology Research, 3, 3, 2006, pp. 241-246.
14. Yang, L., B. Luan, W.J. Cheong, J. Jiang. "Sono-immersion deposition on magnesium alloy". Journal of the Electrochemical Society, 152, 3, 2005c, pp. C131-C136.
15. Yang, L., J. Li, Y. Zheng, W. Jiang, M. Zhang. "Electroless Ni-P plating with molybdate pretreatment on Mg-8Li alloy". Journal of Alloys and Compounds, 467, 1-2, 2009, pp. 562-566.
16. Shao, Z., Cai Z., Hu R., Wei S. "The study of electroless nickel plating directly on magnesium alloy". Surface & Coatings Technology , 249, 2014, pp. 42–47.
17. Liu, Z., Gao W. "The effect of substrate on the electroless nickel plating of Mg and Mgalloys". Surface&Coatings Technology, 200 , 2006, pp. 3553–3560.