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Short Review

Recent Progress in Electroless Ni Coatings for Magnesium Alloys

Xin SHU[1], Yuxin WANG[1], Jingguang PENG[2], Pengfei YAN[2], Biao YAN[2], Xumin FANG[3], Yewen XU[3]

[1] Department of Chemical & Materials Engineering, the University of Auckland, PB 92019, Auckland 1142, New Zealand
[2] School of Materials Science and Engineering, Tongji University, Shanghai 200092, China
[3] Laboratory of detection and sensing of near surface targets, Wuxi 214035, China
[*]E-mail: xshu441@aucklanduni.ac.nz

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Electroless Nickel (EN) plating is a widely used surface modification technology due to superior hardness and corrosion resistance of the deposit. Appling EN coating on magnesium alloy components can enhance the wear and corrosion performance of the components greatly. However, delicate pre-treat of the substrates and precise control of the plating parameters are essential to get good quality EN coating on Mg alloys. This work reviews the EN coatings on magnesium alloys with emphasis in pretreatment steps, showing the improvement achieved, the limitations exist still and shed light on the future trend of this technology on Mg alloys.

Keywords: electroless Ni plating, magnesium alloy, pre-treatment methods

1. INTRODUCTION

Brenner and Riddell [1] fabricated bright and dense Ni coatings via chemical reduction of Nickel by sodium hypophosphite on specific catalytic surfaces in 1946 and named this technology ‘electroless’ [2]. The technology gained a lot interest as surface modification method due to relative low cost of operation and unique properties of EN coatings. These promising properties include but not limit to: excellent corrosion and wear resistance, uniform thickness at sharp edge as well as blind holes, good soldering and diffusion barrier properties. Properties of EN coatings can be tailored by elaborate control of plating parameters and post heat-treatment strategy. Fundamentals of electroless plating technology can be found in books [3, 4] or review articles [5, 6].

Magnesium alloys, as the lightest structural metallic materials, have received increasing interest for applications in automotive, aircraft, aerospace and electronic device industries due to their unique properties such as low density, high specific strength, good thermal conductivity, high dimensional stability and good electromagnetic shielding property [7-10]. However, the industrial application of magnesium alloys is still hindered by their high chemical reactivity, which makes most magnesium alloys highly susceptible to corrosive environment [11]. Efforts have been made to protect Mg alloys [12-17] from corrosion and wear. Among these methodologies, EN coating is of interest due to decorative metal finish with good solderability and electrical conductivity, combined with outstanding wear and corrosion resistance of the coating itself. It has been pointed out and emphasized in many articles in regard to metal coatings for Mg alloys [18, 19] that "metal coating/Mg substrate" system is typical cathodic coating on an anodic substrate since most metals are nobler than Mg. Therefore, metal coatings on Mg alloy substrate are only physical barriers against the corrosion environment. The coating must be uniform, adherent, and pore-free. Penetrating defects in the coating will accelerate the corrosion speed of Mg substrate and results in peeling off of the coating. What make things complicated is that compared with other substrate, Mg alloy is hard to plate due to two main reasons. First, Mg alloy shows high reactivity with air to form passive oxide layer, which must be removed before plating. Second is the rapid dissolution of Mg in most plating solution. The development of non-traditional plating baths is essential and careful pretreatments are indispensable.

Current work specially reviews electroless coating technology on magnesium alloy substrate with emphases in pretreatment procedures, followed by the corrosion and mechanical properties of typical EN coatings on Mg alloy substrate. Composite and multi-layered coatings show great potential for protecting Mg substrate, which is also reviewed in this article.

2. PRETREATMENT OF Mg SUBSTRATE FOR EN PLATING

Mg alloys are hard to plate because they are electrochemically highly active. Composition of Mg alloys and surface roughness of the substrates all influence the deposited coating [20]. Careful designed pretreatment steps play a key role in obtaining good performance of final coatings on Mg substrate. The functions of pretreatment steps can be viewed as one protective film replaces the other [21]. Traditional pretreatment sequences for EN coating of Mg, known as Dow process, are illustrated as below:

Mechanical cleaning → alkaline cleaning → acid pickling → zinc immersion → cyanide Cu plating → electroless plating (same plating bath for Cu)

This pretreatment route has to use toxic cyanide after zinc immersion. The replaced zinc layer shows low adherent strength if the Al content of Mg alloy is high (such as AZ91). Direct EN pretreatment method for Mg is introduced with fluorination followed by plating in fluorine ion containing coating bath. Typical route is as below:

Mechanical cleaning → alkaline cleaning → acid pickling → HF activation → electroless plating (bath contain hydrofluoric acid or fluoride)

The use of fluoride containing solutions in the procedures not only emerges dangers to operators but also increases the cost for waste chemical management. What's more, MgF_2 film is very stable in subsequent plating procedures and will be sandwiched between subsequent coating and substrate [22, 23], resulting a loose adhesive layer.

Both the above mentioned pretreatment methods can be viewed as 'traditional' sequence for plating Mg alloy. For convenience, this paper use zincate EN pretreatment to represent pretreatment route using zinc immersion step, use direct EN pretreatment to represent pretreatment route using acid pickling and HF activation. In both aforementioned pretreatment routes, acid pickling has to use chromic acid and nitric acid, which has dramatic drawbacks both from health concern caused by hexavalent chromium and from severe intergranular corrosion of substrate caused by nitric acid. Fig. 1 shows the surface of AZ31 Mg alloy after pickling with 110mL/L HNO_3 and 125g/L CrO_3 at room temperature for different time. Severe intergranular corrosion happened with deep holes left in the grain boundary zone. These deep blind holes will easily accumulate residuary solution during following treatment steps. During EN plating, slurry may be encapsulated in these holes between EN coating and substrate, dramatically decreasing the quality of the final coating.

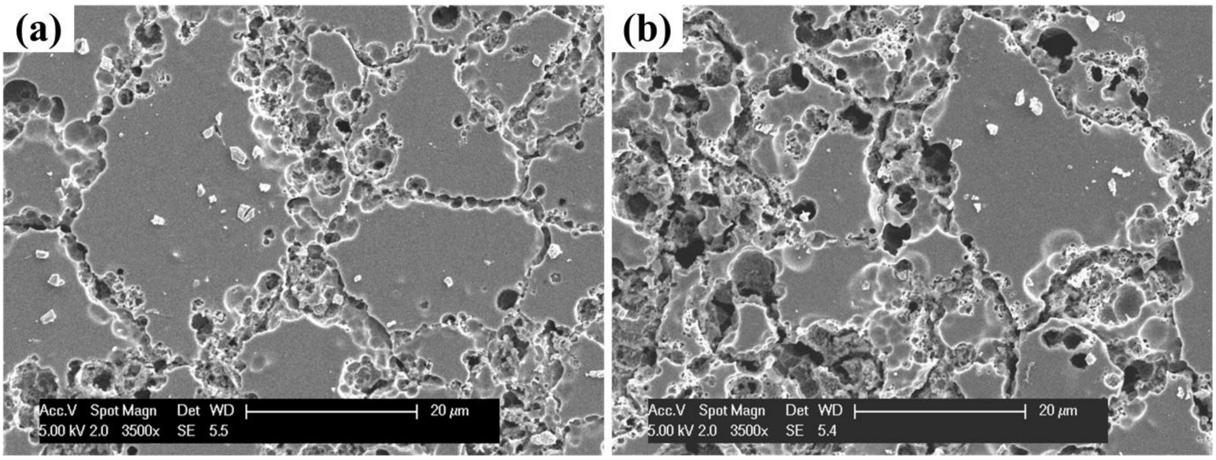

Figure 1. Surface morphology showing deep holes of Mg alloy AZ31 after acid pickling with 110mL/L HNO_3 and 125g/L CrO_3 for (a) 30s, (b) 60s

Researchers have done a lot of work to solve the aforementioned problems, mainly focus on following aspects: try to avoid using hazardous chemicals such as CrO_3 and HF in pretreatment steps by selecting alternative chemicals (section 2.1 in this article); try to pre-coat Mg alloy substrate with other form of coatings (section 2.2 in this article); try to simplify pretreatment steps by optimizing coating conditions (section 2.3 in this article).

2.1. Optimizing chemical selections

Efforts have been done mainly in two aspects for pretreatment of Mg alloys: to overcome the use of hazardous chemicals in traditional pretreatment routes; to enhance the adherence and uniformity of EN coating.

Direct EN pretreatment on magnesium alloys has gained more attention in recent years due to fewer pretreatment steps and ease to operate. The avoiding of CrO_3 and HF in pretreatment steps has been extensively studied. HNO_3 plus H_3PO_4 [24], H_3PO_4 plus Na_2MoO_4 [25], CH_3COOH [26] etc. have been investigated as environmentally friendly acid picking reagent. More complicated formula such as the mixture of H_3PO_4, $Mn(H_2PO_4)_2$, HNO_3 and CH_3COOH is also proposed [27]. NH_4HF_2 is mainly used to replace HF in activation step [24, 25] because the chemical NH_4HF_2 is in solid phase and safer to handle. A comparative study of interaction of AZ91D alloy with various pretreatment solutions [28] show that different acid reagent result in different corrosive rate and surface roughness. The following activation can remove the corrosive products and form a new activation film on the substrate surface. Authors confirmed that different plating methods needed corresponding pretreatment processes.

As for zincate EN pretreatment, much effort has been done to avoid the use of cyanide after the deposition of thin zinc layer. Copper plating with $Cu_2P_2O_7$ based bath [29], pulse nickel electroplating [30], zinc electroplating [31] etc. all have been tested as alternatives for copper cyanide. Modified zinc immersion solution containing Fe^{3+} [31], Sn^{2+} [32] showed very uniform distribution of zinc layer. Evenly-distributed zinc layer can also achieved by double zinc immersion treatment [30] or careful designed activation treatment with trace amount of Cu^{2+} before zincate treatment [24]. One advantage of zinc immersion pretreatment is that zinc layer can insulate magnesium substrate to obtain homogeneous surface conditions for further plating. Rare earth containing magnesium alloys have been successfully plated by novel zinc immersion treatment [33, 34]. A universal pretreatment sequence is also proposed for coating different magnesium alloys [35] by virtue of zincate pretreatment.

The main challenge in pretreat Mg alloy substrate for EN plating is to remove the oxide layer without severe grain erosion. The final surface should show similar potential for following treatment. More recently, the concept of ‘tailoring’ surface chemistry has been proposed [36]. Authors successfully remove second phase on magnesium alloy substrate by careful designed pretreatment sequence. Same authors further investigate the pretreatment method for Mg alloy and get very uniform zinc immersion layer [37]. The obtained zinc layer can be utilized to both electroplating and conversion coatings.

2.2. Introducing interlayer coatings

Traditional methods of plating Mg alloys suffer from severe reaction of substrate with coating bath. Although pretreatment steps can provide temporary protective coating which can be removed in afterwards steps, concerns still exist for incomplete dissolve of such layers. What’s more, corrosion tendency increase if there is tiny holes in final coating. Introduce an interlayer coating can solve these problems by providing an insulated layer to corrosive environment. Currently, many kinds of interlayer have been utilized in pretreatment of electrochemical of Mg alloys such as organic coating [38], Plasma Electrolytic Oxidation (PEO) coating [39], anodizing coating [40] and chemical conversion coatings [41-48] etc. Recently, electroless Ni coating on laser surface treated (LST) AZ91 Mg alloy have been proposed [49], coatings with structure AZ91D/LST/EN show an increase in surface hardness and wear resistance and maintains a similar and high corrosion resistance. A simple replacement reaction pretreatment have been introduced [50] by using proper surfactant additives in replacement solution to form a Ni layer.

Both chemical conversion coating and PEO coating technology on Mg alloys have been widely studied [51, 52] as protective methods. The combination of these technologies with EN coating on Mg alloys is very promising to maximize the protection. The use of chemical conversion coating as interlayer gains much interest due to its simple solution composition and ease in operation. What is more, both chemical conversion and EN coating are insensitive to the substrate geometry. Chemical conversion coating can provide a good base for producing adherent top coatings. Research [53] indicated that different interlayer conversion coatings not only influence the morphology of top coating, but also changed the phosphors content of the electroless nickel deposits as well. It should point out that careful must be taken between each step to achieve enough adherent strength between each layer.

2.3. Directly plate on Mg alloys

It will be very attractive that Mg alloys substrates can be electrochemically coated with simple pretreatment like other metals such as steel. The idea of direct electro/electroless plating on Mg alloys has been long proposed. Some general principles are raised for directly plating onto Mg alloys in an electrolyte. First, the dissolution of the Mg alloy must not occur in the electrolyte. Moreover, the naturally formed hydroxide and oxide films must be removed in the electrolyte [54]. Petro and Schlesinger [55] established EN plating of copper from a highly alkaline deposition bath on AZ91D and AM50 magnesium alloys without chemical pretreatment. After this work they further proposed direct electroless procedures for low phosphorous Ni-P coating and ternary Ni-P-Zn coating on AZ91D magnesium alloy without any complex multi-stepped chemical pre-treatment [56, 57].

As a brief summary, pretreatment of Mg alloy for EN plating play a key role in obtaining good quality EN coating. General idea is to replace the oxide film on Mg alloy surface with an adherent interlayer with uniform potential over entire surface, controlling the redox reaction and preventing the dissolve of Mg in EN solution. Till now, the research status is still in a way that different researchers have their individual methods. There is no universal method dominate the research and industrial use. Another situation is that new Mg alloys are keep being investigated, such as Mg-Li as super light alloy, Mg-RE as super strong alloy. Particular coating strategies still need to be study for these particular alloys. The study of pretreatment of Mg alloy for EN coating (also for other coating types) must lead us to a universal method, with no use of toxic chemicals but get uniform and adherent protective final coating.

3. PROPERTIES OF EN COATINGS ON Mg ALLOYS

As a general rule, electroless Ni-P coatings show good hardness and outstanding corrosion resistance at deposited state. Heat treatment can further improve the hardness but sacrifice its corrosion performance [58]. Electroless Ni-B coatings have better hardness but less corrosion resistance than Ni-P. The main aim of deposit EN coating on Mg substrate is to improve surface hardness and corrosion resistance. Generally speaking, properties of EN coatings on Mg substrate should have no difference with coatings on other substrates. However, the following aspects must be bear in mind. The high reactivity of Mg alloy in coating solution results in replacement reaction at initial deposition stage. Thus the EN coating on Mg alloy substrates normally show high porosity and low adherent strength, both of which are pernicious of applying EN coating on Mg alloys. If the pretreatment method introduces another interlayer which totally seals Mg alloy, adherence strength of each layer has to be considered and tested.

3.1. Mechanical properties

Most commercial Mg alloys have low surface hardness [59, 60]. They would not be suitable to produce bearing surfaces without additional surface treatments [61]. EN coatings can greatly improve the surface hardness and anti-wear performance of Mg substrate. Figure 2 gives some hardness result of Mg alloy and EN coatings. Hardness of EN coatings on Mg alloys substrate depend on plating parameters such as bath PH [62, 63], bath composition [64-66], and coating temperature [67]. Generally the hardness of as plated coating lies in the range of 450~550HV. Heat treatment will increase in hardness of the coating due to precipitation of hard second phases [68].

The anti-wear properties of EN coatings benefit from there high hardness and surface morphology. EN coatings are nodular or cauliflower like, which allow the retention of lubricating fluids and reduce the contact surface. The wear rates of Mg and AZ91D magnesium alloy decreased by two orders of magnitude with electroless Ni-B coating [69]. Wear study of electroless Ni-P coating on AZ91 magnesium alloy shows that heat treatment has no significant influence on wear resistance [70]. Friction coefficient of electroless Ni-P coatings changes with roughness of substrate [71]. Wear loss of the coating decrease with increase coating hardness, which can be achieved by incorporating hard particles [72] or heat treatment [73].

It is emphasized here that heat treatment strategy of EN coating on Mg alloys must be careful designed because heat treatment of EN coating (normally between 200 to 600 degrees C) will incur microstructure transformation of most Mg alloys (Solid-solution heat treatment of Mg alloys generally lies in 375 to 520 degrees C, annealing of Mg alloys may occur above 120 degrees C). The designers must be aware of this during materials selection. Heat treatment of EN coating and Mg substrate can be done at the same time with elaborate design.

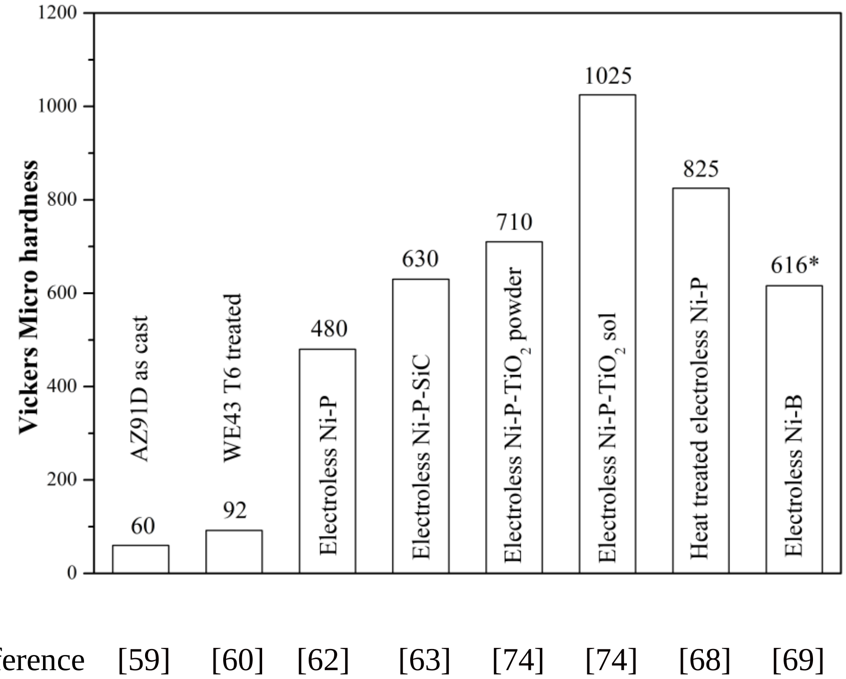

Figure 2. Typical microhardness of some commercial Mg alloys and electroless Ni coatings *: Result is in knoop microhardness scale

3.2. Corrosion resistance

The general accepted conclusions of anti-corrosion properties of EN coatings are also suitable for Mg alloy substrate. Electroless Ni-P coatings with high P content show better corrosion resistance than low P coatings [75]. Introducing ternary alloy element such as W [48, 76, 77] or Sn [47] in EN coating can further enhance the corrosion resistance. On the other hand, heat treatment decreases the corrosion resistance, mainly due to micro-crack formation [78].

Electrochemical testing methods such as potentiodynamic polarization and electrochemical impedance spectroscopy are normally used for corrosion resistance evaluation [79]. Compared with bare magnesium alloys, the corrosion resistance of EN coatings significantly improved in different testing solutions such as 3.5 wt%, 5 wt % NaCl solution [42, 80] as well as artificial sweat solution [81].

However, evaluation the corrosion performance of EN coatings on Mg alloy substrate by virtue of electrochemical methods have question mark for reliability and reproducibility. The corrosion resistance of EN coating on Mg alloy is essentially the penetrating defects density of the coating [82]. A decrease in the corrosion fatigue behavior of electroless Ni deposited Mg alloy under sodium chloride environment was reported due to the acceleration of the crack initiation process in the electroless Ni plated specimens [83]. Mechanical attribution-enhanced electroless Ni-P plating shows improved corrosion resistance due to much compact and fine-grained coating, free of pores and cracks [84].

EN coatings on magnesium and its alloys must be pore and defects free, totally insulating Mg substrate from corrosive environment. Any penetrating defects will dramatically increase the corrosion speed of Mg alloy substrate. In literatures, different methods to evaluate the porosity of EN coatings have been proposed. Corrosion resistance assessments based on these methods are more suitable for coatings on Mg alloy substrates.

One method is to immerse the coated sample in 3.5 wt.% NaCl for 2h, porosity can be checked by the corrosion spots be observed [24, 25]. Another method is to utilize NaCl solution which contains phenolphthalein as indicator. The porosity was evaluated by check red area after certain times of wetting [85].

Table 1 shows the corrosion resistance of electroless coatings on Mg alloys substrates by immersion test and salt spray test. It can be seen that the barrier properties of Ni-P can be improved by thicker coating or multi-layer coatings. For long term service of EN coated Mg alloy components. Multi-layered EN coatings or combinations of EN coating with other coatings are practical methods. The demands for further increasing hardness and wear resistance can be achieved by EN composite coatings. These are reviewed as follow.

Table 1. List of corrosion evaluation of EN coatings on Mg alloys substrates

Substrate	Coating	Testing method	Results	Ref.
AZ91D	~25μm Ni-P	10%HCl immersion	67 min	[44]
AZ31	Ni-P/ Organic interlayer	10%HCl immersion	More than 5 h	[38]
AZ91D	Ni-P/ stannate conversion layer	3.5% NaCl immersion	More than 100h	[86]
AZ91D	~15μm Ni-P	Salt spray test	102h	[87]
Mg-RE	~52μm Ni-P	Salt spray test	210h	[34]
AZ91	Ni-P/ PEO interlayer	Salt spray test	168h	[39]
AZ91D	~40μm Ni–P–ZrO_2/Ni/Ni-P	Salt spray test	1000h	[88]

4. MULTI-LAYERED AND COMPOSITE COATINGS

The critical review by Gray and Luan [89] pointed out that only complex and multilayer coatings are able to produce optimum results for corrosion protection of magnesium alloys. Two or more layered structure is superior to one layered one because the development of defects in the coatings will be disrupted at the interface of coatings. The importance of getting defects free EN coatings for Mg alloys is greater than for other substrates because Ni coating on Mg is typical cathodic coatings on anodic substrate. The corrosion performance of the coatings on Mg is essentially the porosity of the coating.

Many multi-layered coating combinations such as graded Ni-P [90, 91], Ni-P/Ni-B [92], Ni-P/Ni-W-P [93], Ni-P/ Ni [94-96] have been introduced to protect Mg substrate from corrosion and wear. All of them get better anti-corrosion performance. However, differences exist in approaches. Some believe the outer layer should have better corrosion performance but others disagree. Schematic coating structures are shown in figure 3. It is true that high corrosion resistance top coating (Fig. 3 (a)) such as high P electroless Ni coating [97] will show higher corrosion potential and greater corrosion resistance in electrochemical experiment. However, based on our knowledge, coating structure as Fig. 3 (b) will be preferred in long term service because in certain cases, if the top coating failed by external force, high corrosion bottom layer still can provide sufficient protection of Mg substrate. What's more, if the corrosion potential difference of coatings is great enough, high corrosion bottom layer will make top coating sacrificial [94]. Another privilege of this structure is that if a high corrosion resistance bottom coating is existing on Mg substrate, the top coating can be enhanced via deposit a composite coatings or undergo surface heat treatment [98]. Our recent study of sol enhanced EN coating on AZ31 magnesium alloy shows very good performance of both surface hardness and corrosion resistance by introducing high P EN bottom layer and sol enhanced low P composite layer [99]. The schematic diagram of coatings is shown in figure 4.

Multi-layered coatings with different coating technology can improve the protection of Mg substrate due to distinct function of each coating layer. Electroless Ni coating on anodized Mg substrate show good corrosion resistance and surface hardness [100-102]. Micro-arc oxide (MAO) or plasma electrolytic oxidation (PEO) coating technology show great potential as sub-coating on Mg surface because MAO/PEO technology is less sensitive to base alloy. After the oxide layer formed on Mg alloy surface, electroless coating can be carried out with better adhesive strength [102-104]. The corrosion performance also improved due to oxide layer [105]. Triple layer coating with MAO/polymer/ electroless Ni-P have been fabricated on AZ31 Mg alloy with better long term corrosion resistance and metallic surface [106]. Chemical conversion coatings are treated as pretreatment coating in this review, so they will not discussed here.

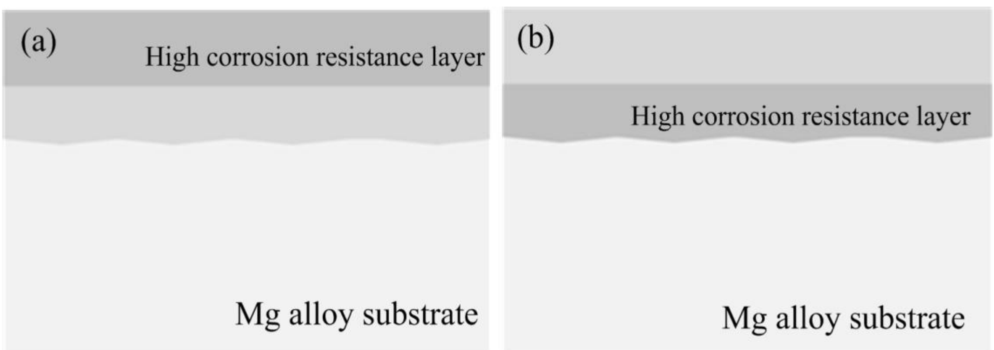

Figure 3. Schematic diagram of two types of multi-layer coatings on Mg substrate (a) High corrosion resistance layer as top layer (b) High corrosion resistance layer as bottom layer

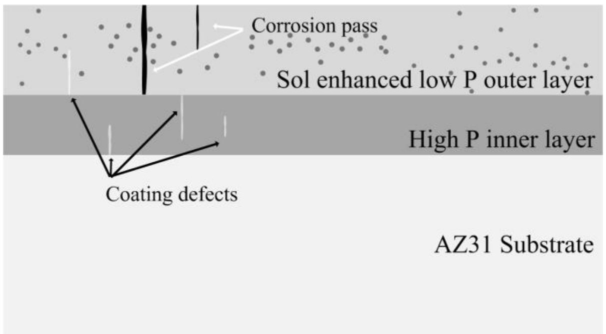

Figure 4. Schematic diagram of two layer electroless Ni-P coatings with high corrosion resistance bottom layer and high hardness top composite layer

Composite EN coatings on Mg alloys substrates with different micro or nano sized particles are studied to further increase mechanical properties [107, 108]. Although some works found improved corrosion resistance of composite coatings than bare EN coating on AZ91D Mg alloy [87]. It should be bear in mind that the introduction of embedded particles to EN coating may increase the risk of forming coating defects. Strengthen particles are only physically occluded in EN coating [109]. Embedded particle might break the integrity of EN coatings and increase corrosion path density. It has been reported that strengthen particles has a decreasing effect on corrosion resistance of EN coating due to the creating micro cracks in the coated microstructure [110]. Thus, multi-layered composite coatings with high corrosion resistance bottom layer are preferred for Mg alloys [88, 111].

5. CONCLUSION REMARK:

Magnesium and Mg alloys have found more and more applications as structure materials due to its high strength to weight ratio. EN coatings can provide hard surface finish and good anti-corrosion performance, at the same time maintaining metallic properties and good solderability. The research interest of EN coating on Mg alloys help promoting the application of Mg alloys in industry. Due to the distinct behavior of Mg in coating solution, careful pretreatment methods are needed to get good quality coating. More than half of research topics in this field focus on pretreatment methods. However, till now, most of them show disadvantages such as toxic chemical or complicated procedures. None of them gained general acceptance.

Properties of EN coatings on Mg alloy substrates show same trend with on other substrates. Hardness of the coating can be tailored by control of coating parameters and co-deposition of hard particles. However, it must be very careful to heat treat the coating because it will cause shrinkage of the coating. The main concern of corrosion of EN coated Mg alloy is the coating porosity. As general rule, corrosion protection EN coatings on Mg substrate must be thick enough to prevent any penetrating defects. Due to this certain concern, multi-layered coatings are researched a lot as protection coating on Mg alloys.

Successfully applying EN coatings on Mg alloys need better pretreatment strategy which is eco-friendly to carry out and cheap to run. Multi-layered coating system is a suitable solution to get sufficient long term protection. Much effort is needed to further research optimal coating combination. Processing technics especially heat treatment of EN coating on Mg alloys need further research in detail.

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References

1. A. Brenner and G. E. Riddell, *J. Frankl. Inst.*, 242 (1946) 64.
2. A. Brenner and G. Riddell, *J. Res. Nat. Bur. Stand.*, 39 (1947) 385.
3. W. Riedel, *Electroless nickel plating*, ASM International, Stevenage (1991).
4. G. O. Mallory and J. B. Hajdu, *Electroless plating fundamentals and applications*, William Andrew Publishing, New York (1990).
5. J. Sudagar, J. Lian and W. Sha, *J. Alloy. Compd*, 571 (2013) 183.
6. K. H. Krishnan, S. John and K. N. Srinivasan, *Metall. Mater. Trans. A*, 37A (2006) 1917.
7. W. A. Monteiro, *New Features on Magnesium Alloys*, Intech Publishing (2012).
8. S. R. Agnew and J. F. Nie, *Scripta Mater.*, 63 (2010) 671.
9. A. A. Luo, *Int. Mater. Rev.*, 49 (2004) 13.
10. M. O. Pekguleryuz and A. A. Kaya, *Adv. Eng. Mater.*, 5 (2003) 866.
11. G. Song and A. Atrens, *Adv. Eng. Mater.*, 9 (2007) 177.
12. C. Blawert, W. Dietzel, E. Ghali and G. L. Song, *Adv. Eng. Mater.*, 8 (2006) 511.
13. X. B. Chen, N. Birbilis and T. B. Abbott, *Corrosion*, 67 (2011).
14. H. Hornberger, S. Virtanen and A. R. Boccaccini, *Acta Biomater.*, 8 (2012) 2442.
15. R. G. Hu, S. Zhang, J. F. Bu, C. J. Lin and G. L. Song, *Prog. Org. Coat.*, 73 (2011) 129.
16. A. Singh and S. P. Harimkar, *JOM*, 64 (2012) 716.
17. N. Nassif and I. Ghayad, *Adv. Mat. Sci.Eng.*, 2013 (2013) 1.
18. J. E. Gray and B. Luan, *J. Alloy. Compd*, 336 (2002) 88.
19. X. B. Chen, H. Y. Yang, T. B. Abbott, M. A. Easton and N. Birbilis, *Corrosion*, 68 (2012) 518.
20. Z. Liu and W. Gao, *Surf. Coat. Technol.*, 200 (2006) 3553.
21. Y. Xiang, W. Hu, X. Liu, C. Zhao and W. Ding, *T. I. Met. Finish.*, 79 (2001) 30.
22. D. Guo, Z. G. Fan, Z. D. Yang, L. Zhao and P. Gao, *The Chinese Journal of Nonferrous Metals*, 17 (2007) 789.
23. Y. H. Xiang, W. B. Hu, B. Shen, C. Z. Zhao and W. J. Ding, *J. Shanghai Jiaotong University*, 34 (2000) 1638.
24. T. N. Tran, G. Yu, B. N. Hu, Z. H. Xie, R. Tang and X. Y. Zhang, *T. I. Met. Finish.*, 90 (2012) 209.
25. X. Lei, G. Yu, X. Gao, L. Ye, J. Zhang and B. Hu, *Surf. Coat. Technol.*, 205 (2011) 4058.
26. Z. C. Wang, F. Jia, L. Yu, Z. B. Qi, Y. Tang and G. L. Song, *Surf. Coat. Technol.*, 206 (2012) 3676.
27. H. Liu, S. Bi, L. Cao, Q. Bai, X. Teng and Y. Yu, *Int. J. Electrochem. Sci.*, 7 (2012) 8337.
28. Y. Zhu, G. Yu, B. Hu, X. Lei, H. Yi and J. Zhang, *Appl. Surf. Sci.*, 256 (2010) 2988.
29. S. Zhang, F. Cao, L. Chang, J. Zheng, Z. Zhang, J. Zhang and C. Cao, *Appl. Surf. Sci.*, 257 (2011) 9213.
30. M. J. Zhao, C. Cai, L. Wang, Z. Zhang and J. Q. Zhang, *Surf. Coat. Technol.*, 205 (2010) 2160.

31. J. Chen, G. Yu, B. Hu, Z. Liu, L. Ye and Z. Wang, *Surf. Coat. Technol.*, 201 (2006) 686.
32. Y. R. Gao, C. M. Liu, S. L. Fu, H. Z. Li, X. Shu and Y. H. Gao, *Journal of Central South University*, 42 (2011) 1248.
33. Y. Gao, C. Liu, S. Fu, J. Jin, X. Shu and Y. Gao, *Surf. Coat. Technol.*, 204 (2010) 3629.
34. J. Jin, C. Liu, S. Fu, Y. Gao and X. Shu, *Surf. Coat. Technol.*, 206 (2011) 348.
35. N. El Mahallawy, A. Bakkar, M. Shoeib, H. Palkowski and V. Neubert, *Surf. Coat. Technol.*, 202 (2008) 5151.
36. H. Y. Yang, X. B. Chen, X. W. Guo, G. H. Wu, W. J. Ding and N. Birbilis, *Appl. Surf. Sci.*, 258 (2012) 5472.
37. H. Yang, X. Guo, X. Chen and N. Birbilis, *Corros. Sci.*, 79 (2014) 41.
38. H. Zhao, Z. Huang and J. Cui, *Surf. Coat. Technol.*, 202 (2007) 133.
39. Z. Liu and W. Gao, *Appl. Surf. Sci.*, 253 (2006) 2988.
40. S. Sun, J. Liu, C. Yan and F. Wang, *Appl. Surf. Sci.*, 254 (2008) 5016.
41. L. P. Wu, Z. D. Yang, J. J. Zhao and Y. P. Xie, *Adv. Mat. Res.*, 154-155 (2010) 1330.
42. H. H. Elsentriecy and K. Azumi, *J. Electrochem. Soc.*, 156 (2009) D70.
43. J. Sudagar, J. S. Lian, Y. Q. Liang and J. A. Liu, *T. I. Met. Finish.*, 90 (2012) 129.
44. W. X. Zhang, J. G. He, Z. H. Jiang, Q. Jiang and J. S. Lian, *Surf. Coat. Technol.*, 201 (2007) 4594.
45. L. Yang, J. Li, Y. Zheng, W. Jiang and M. Zhang, *J. Alloy. Compd*, 467 (2009) 562.
46. D. Seifzadeh and Z. Rajabalizadeh, *Surf. Coat. Technol.*, 218 (2013) 119.
47. W. X. Zhang, Z. H. Jiang, G. Y. Li, Q. Jiang and J. S. Lian, *Surf. Coat. Technol.*, 202 (2008) 2570.
48. W. X. Zhang, N. Huang, J. G. He, Z. H. Jiang, Q. Jiang and J. S. Lian, *Appl. Surf. Sci.*, 253 (2007) 5116.
49. J. Sudagar, R. Dewen, J. S. Lian, B. J. Zheng and K. Venkateswarlu, *Laser. Eng.*, 26 (2013) 321.
50. D. Guo, B. Wang, L. Mao and Z. G. Fan, *T. I. Met. Finish.*, 89 (2011) 109.
51. X. B. Chen, N. Birbilis and T. B. Abbott, *Corrosion*, 67 (2011).
52. C. Blawert, W. Dietzel, E. Ghali and G. Song, *Adv. Eng. Mater.*, 8 (2006) 511.
53. J. Sudagar, G. Bi, Z. Jiang, G. Li, Q. Jiang and J. Lian, *Int. J. Electrochem. Sci.*, 6 (2011) 2767.
54. J. Lee, W. Chung, U. Jung and Y. Kim, *Surf. Coat. Technol.*, 205 (2011) 4018.
55. R. Petro and M. Schlesinger, *Electrochem. Solid. St.*, 14 (2011) D37.
56. R. Petro and M. Schlesinger, *J. Electrochem. Soc.*, 159 (2012) D455.
57. R. Petro and M. Schlesinger, *J. Electrochem. Soc.*, 160 (2013) D349.
58. C. M. Wang, J. Q. Wang, B. Zhang, R. B. Niu, J. K. Yu and Q. Jing, *Rare Metals*, 32 (2013) 465.
59. Y. Lü, Q. Wang, X. Zeng, W. Ding, C. Zhai and Y. Zhu, *Mat. Sci. Eng. A-Struct.*, 278 (2000) 66.
60. G. Riontino, M. Massazza, D. Lussana, P. Mengucci, G. Barucca and R. Ferragut, *Mat. Sci. Eng. A-Struct.*, 494 (2008) 445.
61. P. J. Blau and M. Walukas, *Tribol. Int.*, 33 (2000) 573.
62. G. Mao, Y. Sun, G. Zhang and Q. Liu, *Rare Metal Materials and Engineering*, 39 (2010) 2039.
63. Y. GOU, W. HUANG, R. ZENG and Y. ZHU, *T. Nonferr. Metal. Soc.*, 20 (2010) s674.
64. J. Sudagar, J. S. Lian, Q. Jiang, Z. H. Jiang, G. Y. Li and R. Elansezhian, *Prog. Org. Coat.*, 74 (2012) 788.
65. W. J. Huang and Y. Xue, *Journal of Materials Engineering*, (2010) 23.
66. H. H. Shao, G. W. Liu and C. X. Zhang, *Corrosion Science and Protection Technology*, 22 (2010) 139.
67. S. Z. Shang, G. M. Lu, Z. X. Zhao and Y. J. Wan, *Corrosion and Protection*, 31 (2010) 125.
68. J. W. Zhang, L. F. Hou and B. S. Xu, *Transactions of Materials and Heat Treatment*, 31 (2010) 137.
69. E. Correa, A. A. Zuleta, L. Guerra, M. A. Gómez, J. G. Castaño, F. Echeverría, H. Liu, P. Skeldon and G. E. Thompson, *Wear*, 305 (2013) 115.
70. M. Novák, D. Vojtech, P. Novák and T. Vítu, *Appl. Surf. Sci.*, 257 (2011) 9982.
71. Z. Liu and W. Gao, *Surf. Coat. Technol.*, 200 (2006) 5087.

72. X. L. Ge, D. Wei, C. J. Wang, Z. Bing and Z. C. Chen, *Appl. Mech. Mater.*, 66-68 (2011) 1078.
73. X. Ge, Z. Bing, Z. Chen, D. Wei and C. Wang, *Appl. Mech. Mater.*, 43 (2011) 510.
74. W. Chen, W. Gao and Y. He, *Surf. Coat. Technol.*, 204 (2010) 2493.
75. L. Yuan, L. Q. Ma, T. N. Qin and Y. Ding, *Corrosion and Protection*, 31 (2010) 696.
76. Q. Zhou, W. C. Sun, M. Zhu and M. F. Tan, *Adv. Mat. Res.*, 79-82 (2009) 997.
77. Y. Liao, S. T. Zhang and R. Dryfe, *Materialwiss. Werkst.*, 42 (2011) 833.
78. N. Iranipour, R. Azari Khosroshahi and N. Parvini Ahmadi, *Surf. Coat. Technol.*, 205 (2010) 2281.
79. H. Zhang, S. Wang, G. Yao and Z. Hua, *J. Alloy. Compd*, 474 (2009) 306.
80. J. Chen, G. Yu, B. Hu, Z. Liu, L. Ye and Z. Wang, *Surf. Coat. Technol.*, 201 (2006) 686.
81. Y. W. Song, D. Y. Shan and E. H. Han, *Electrochim. Acta*, 53 (2007) 2009.
82. C. Gu, J. Lian, J. He, Z. Jiang and Q. Jiang, *Surf. Coat. Technol.*, 200 (2006) 5413.
83. S. Ishihara, H. Notoya, A. Okada, Z. Y. Nan and T. Goshima, *Surf. Coat. Technol.*, 202 (2008) 2085.
84. Y. D. He, H. F. Fu, X. G. Li and W. Gao, *Scripta Mater.*, 58 (2008) 504.
85. J. S. Lian, G. Y. Li, L. Y. Niu, C. D. Gu, Z. H. Jiang and Q. Jiang, *Surf. Coat. Technol.*, 200 (2006) 5956.
86. H. Huo, Y. Li and F. Wang, *Corros. Sci.*, 46 (2004) 1467.
87. Y. W. Song, D. Y. Shan and E. H. Han, *Materials and Corrosion*, 58 (2007) 506.
88. Y. W. Song, D. Y. Shan and E. H. Han, *Electrochim. Acta*, 53 (2008) 2135.
89. J. E. Gray and B. Luan, *J. Alloy. Compd*, 336 (2002) 88.
90. E. Georgiza, J. Novakovic and P. Vassiliou, *Surf. Coat. Technol.*, 232 (2013) 432.
91. C. Gu, J. Lian and Z. Jiang, *Adv. Eng. Mater.*, 7 (2005) 1032.
92. W. X. Zhang, Z. H. Jiang, G. Y. Li, Q. Jiang and J. S. Lian, *Appl. Surf. Sci.*, 254 (2008) 4949.
93. X. CHEN, G. LI and J. LIAN, *T. Nonferr. Metal. Soc.*, Supplement 1 (2008) s323.
94. Y. W. Song, D. Y. Shan, R. S. Chen and E. H. Han, *T. Nonferr. Metal. Soc.*, 18 (2008) s339.
95. C. Gu, J. Lian, J. He, Z. Jiang and Q. Jiang, *Surf. Coat. Technol.*, 200 (2006) 5413.
96. S. Y. Zhang, Q. Li, X. K. Yang, X. K. Zhong, Y. Dai and F. Luo, *Mater. Charact.*, 61 (2010) 269.
97. T. S. N. Sankara Narayanan, I. Baskaran, K. Krishnaveni and S. Parthiban, *Surf. Coat. Technol.*, 200 (2006) 3438.
98. H. Liu, R. X. Guo, J. S. Bian and Z. Liu, *Cryst. Res. Technol.*, 48 (2013) 100.
99. X. SHU, Y. WANG, C. LIU, A. Aljaafari and W. GAO, *In Practice*.
100. Z. M. Liu and W. Gao, *Appl. Surf. Sci.*, 253 (2006) 2988.
101. P. Shi and X. D. Han, *Adv. Mat. Res.*, 299-300 (2011) 663.
102. X. Z. Fan, Y. Wang, B. L. Zou, L. J. Gu, W. Z. Huang and X. Q. Cao, *Appl. Surf. Sci.*, 277 (2013) 272.
103. H. T. Hsu and T. J. Yang, *Adv. Mat. Res.*, 509 (2012) 90.
104. L. Zeng, S. Yang, W. Zhang, Y. Guo and C. Yan, *Electrochim. Acta*, 55 (2010) 3376.
105. M. A. Chen, N. Cheng, J. M. Li and S. Y. Liu, *Surf. Eng.*, 28 (2012) 491.
106. M. A. Chen, N. Cheng, Y. C. Ou and J. M. Li, *Surf. Coat. Technol.*, 232 (2013) 726.
107. Y. W. Song, D. Y. Shan, R. S. Chen and E. H. Han, *Surf. Eng.*, 23 (2007) 334.
108. L. Yu, W. Huang and X. Zhao, *J. Alloy. Compd*, 509 (2011) 4154.
109. F. N. Hubbell, *T. I. Met. Finish.*, 56 (1978) 65.
110. A. Araghi and M. H. Paydar, *Mater. Design*, 31 (2010) 3095.
111. E. Georgiza, J. Novakovic and P. Vassiliou, *Surf. Coat. Technol.*, 232 (2013) 432.