Modern Chemistry & Applications

Review Article Open Access

Development of Anti-Corrosion Processing on Magnesium Alloys

Sun Rujian, Guan Yingchun* and Zhu Ying

Beihang University, 37 Xueyuan Road, Beijing 100191, P.R. China

Abstract

Magnesium alloys have been increasingly used in the industries and biomaterial fields due to their low density, high specific strength and biodegradability. However, poor surface-related properties are major factors that limit their practical applications. This paper will begin with a brief review of conventional methods for anti-corrosion of Mg alloys, and demonstrate the feasibility of laser shock processing in achieving the enhanced corrosion resistance, especially for stress corrosion cracking.

Keywords: Stress corrosion; Metal corrosion; Aerospace; Organic coating

Introduction

Metal corrosion has been considered as common phenomenon, ranging from daily life to wide industrial applications including metallurgy, chemical industry, energy industry, transportation, aeronautics, agriculture, marine engineering. For instance, annual economic loss due to corrosion accounts for 2 to 4 percent of the gross domestic product in China. The economic losses caused by corrosion reached to 500 billion Yuan in 1999, while the economic losses jumped to 819 billion Yuan in 2004, which stands for an increase of 64 percent only within five years [1]. Therefore, the impact of corrosion damage to the national economy is critical, thus is no doubt a serious problem in urgent need of being resolved.

Magnesium is one of the lightest metallic element, and magnesium alloys have unique properties including high strength to weight ratio, low density, effective damping qualities, good absorbing electromagnetic radiation performance, as well as more than 80% recyclable rate. This makes it consistent with the concept of "21st Century Green Engineering Material" [2]. The need for lightweight structural as well as functional parts, particularly in the aerospace, automotive and electronic industries, has stimulated engineers to be more adventurous in their choice of materials. Mg and its alloys, with one quarter of the density of steel and only two thirds that of aluminum, and a strength to weight ratio that far exceeds either, fulfills the role admirably as an "ultra-light" alloy [3]. Moreover, Mg-based metal implants have attracted much attention in the fields of bio-medicals nowadays due to their biodegradability [4]. Witte claimed that this groundbreaking approach to temporary metallic implants was one of the latest developments in bio-materials science that was being rediscovered [5] (Figure 1).

However, Mg is a highly active element, which is susceptible to becoming corroded within its working condition, especially when Mg alloy serving as structural materials are immersed in corrosive media and combined with stress [5-7]. This limits the wide use of Mg alloys; therefore magnesium alloy anti-corrosion becomes an important issue. This review starts with looking back to conventional surface treatment methods for improving corrosion resistance of Mg alloy, subsequently, provides a new approach using laser shock processing technique for stress corrosion cracks.

Brief Review of Conventional Anti-Corrosion Technologies

According to previous study, conventional surface treatment technologies for anti-corrosion of Mg alloys mainly include chemical conversion, anodic oxidation, micro-arc oxidation, organic coating, thermal spraying, physical vapor deposition (PVD), etc. [8]. The advantages and disadvantages of these methods can be mainly summarized in Table 1.

Laser Shock Processing for Mg Alloy

Laser surface processing has been considered as an advanced alternative over conventional counterparts to improve the surface properties of materials [7,9]. It has been recognized that laser surface engineering can produce surface layers with a fine microstructure that reduce the size of galvanic couples and expand the solid solution range of alloying elements [6,9]. Such factors can potentially improve surface performance of laser-treated metallic alloys. Moreover, short

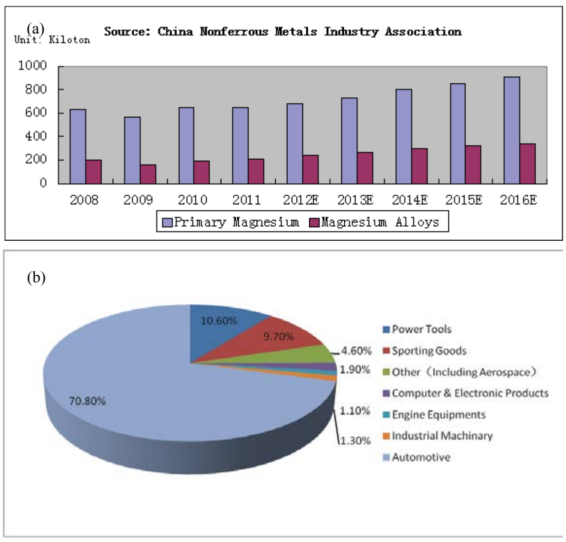

Figure 1: (a) Output of primary magnesium and magnesium alloy in China, 2008-2016 (Unit: kiloton); (b) Classification of Mg casting shipments in United States based on different applications in the year 2008 [6].

***Corresponding author:** Guan Yingchun, Beihang University, 37 Xueyuan Road, Beijing 100191, P.R. China, Tel: 86-082-339-961; Fax: 86-823-399-61; E-mail: guanyingchun@buaa.edu.cn

Received April 30, 2015; **Accepted** May 25, 2015; **Published** May 29, 2015

Citation: Rujian S, Yingchun G, Ying Z (2015) Development of Anti-Corrosion Processing on Magnesium Alloys. Mod Chem appl 3: 153. doi:10.4172/2329-6798.1000153

Surface treatment technique	Advantages	Disadvantages
Chemical conversion	Easy process; Low cost; No electricity.	Harmful Cr^{+6}; Waste products difficult to deal with; Environmental pollution.
Anodic oxidation	Widely used; Coating properties better than Chemical Conversion.	Large coating pores; Uneven distribution.
Micro-arc oxidation	Easy and quick process; Cheap equipment; Alkaline solution, environmentally friendly.	Small crack on the surface; Complex improving process; Noise problem.
Organic coating	Easy process; Low cost.	Only for short period protection; Poisonous.
Thermal spraying	Huge anchoring strength between coating and base metal.	Expensive equipment.
Physical Vapor Deposition (PVD)	Huge anchoring strength between coating and base metal; Quick process; PECVD particularly suit for Low melting point magnesium alloy.	Expensive equipment Small Working region Not suitable for mass production.

Table 1: Summary of conventional technologies for surface treatment of Mg alloys [2,5,8].

processing time, flexibility in operation, economy in time/energy/material consumption, shallow heat affected zone and precision are the important advantages of laser processing methods [10].

Laser shock processing (LSP) is a surface engineering process in which the base metal covered by an absorbing coating (aluminum foil) and transparent constrained layer (water), is hit by a high power density (GW/cm^2) short pulse (nanosecond) laser. After the coating absorbs laser energy rapidly, ultimately forms a large number of dense high-temperature (>10 K) high pressure (>1GPa) plasma. Correspondingly, it produces an explosive shock wave on the metal surface. When the peak pressure of the shock wave exceeds the dynamic yield strength of the material, it generates plastic deformations which finally impart beneficial residual stress within the material. Such deep high magnitude compressive residual stresses induced by LSP increase the resistance of materials to surface-related failures, such as fatigue, fretting fatigue and stress corrosion cracking [11] (Figure 2).

In 2008, Jiangsu University firstly conducted LSP on Mg alloys to form dense dislocations, vacancies and vacancy clusters, in turn changing microstructure and mechanical properties of Mg alloys [12]. After this, more researchers mainly examined mechanical properties of Mg alloys after LSP, and they found that surface micro-hardness was increased by more than 50%, surface residual stress up to hundreds of MPa, local plastic deformation within 1mm, and the enhanced fatigue properties [13-17]. Table 2 shows the residual stress of different magnesium alloys after LSP, indicating that the compressive residual stress up to hundreds MPa is achieved, which will be beneficial for surface properties enhancement including anti-corrosion.

Laser Shock Processing on Anti-corrosion

Effect of LSP on corrosion behavior of Mg alloy has not been widely studied. The first paper was published in 2008 [14], and only a few papers covering electrochemical corrosion, stress corrosion cracking, and hot corrosion exist can be found to the limit of our knowledge [15-18]. It has been claimed that LSP induces compressive residual stress on the surface of Mg alloys, resulting in grain refinement, a large number

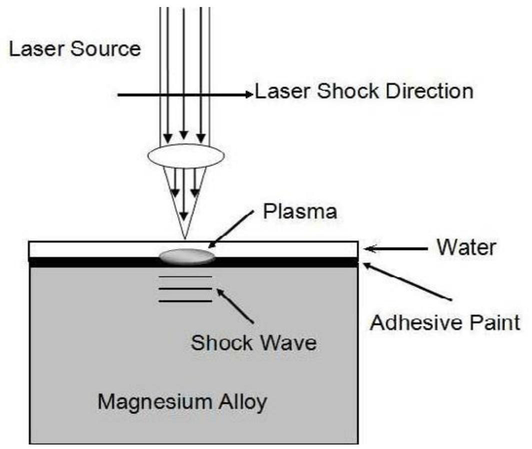

Figure 2: Schematic of laser shock processing on magnesium alloy [11].

Material	Power Density(GW/cm^2)	Residual Stress(MPa)
AZ31	2.5	-138
AM50	3.1	-146
AZ31B	3.86	-125
AZ91D-T6	1.5	-123
AZ91	1.2	-120

Table 2: Residual stress after LSP of Mg alloys [13-17].

of twins, and a high density of dislocation, thus improving the stability of passive film and the corrosion resistance [15-18].

Electrochemical Behavior

The capability of corrosion resistance of Mg alloys depends on the surface passive film, $Mg(OH)_2$, which determines the properties of the effect of corrosion control [17]. Good passive film should be able to prevent the outflow of metal ions from the metal surface, while also preventing the inflow of harmful ions from the external film [18]. At the same time, the impedance is significantly increased due to uneven surface because of plastic deformation generated by LSP, while corrosion current density reduced tremendously and improved the corrosion resistance of the base material effectively. Zhang and his co-workers measured the polarization and EIS curves under different power density by LSP, showing that Tafel curve of the metal moves towards positive direction and EIS increases at lower laser density, and EIS begins to decrease when laser density reaches 0.7 GW/cm^2, as shown in Figure 3a and 3b. Moreover, Figures 3c and 3d indicates that subtle shifts causes change of Tafel curve and EIS curve when laser density is more than 1GW/cm^2 [18]. Guo and his co-workers studied biodegradable Mg alloy by LSP, and indicated that LSP slowed down corrosion rate to a large extent in Figure 4a, and laser-peened surface had less potential to initiate corrosion in Figure 4b [19] (Figures 3 and 4).

Stress Corrosion Cracking (SCC)

LSP induces plastic deformation on the surface and elastic deformation on the sub-surface. At the end of the shock, the surface layer material is compressed, material particles away from the equilibrium position. In the mean time, the plastic layer blocks the elastic deformation layer from returning to the equilibrium position,

Citation: Rujian S, Yingchun G, Ying Z (2015) Development of Anti-Corrosion Processing on Magnesium Alloys. Mod Chem appl 3: 153. doi:10.4172/2329-6798.1000153

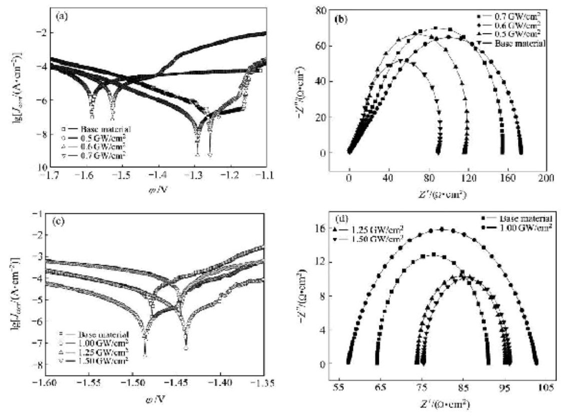

Figure 3: Polarization and EIS curves of hot rolled sheet of AZ31 alloy by LSP in 3.5% NaCl solution: (a) and (c) for Tafel curves; (b) and (d) EIS curves [18].

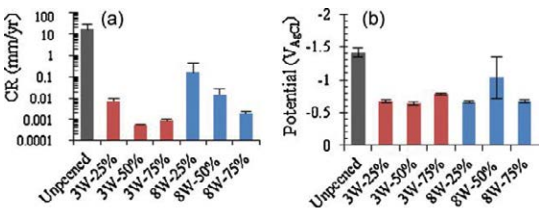

Figure 4: (a) Corrosion rate (CR) and (b) potential of laser-peened MgCa surfaces [19].

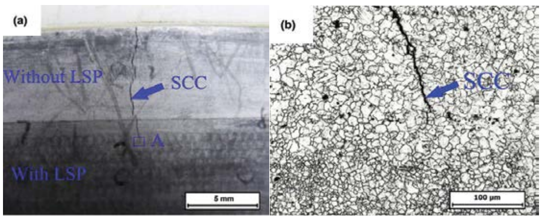

Figure 5: (a) SCC in the sample with and without LSP (b) Micrograph showing crack-free and refined grain within treated region, and region without LSP treatment [20].

so that compressive residual stress is formed on the surface layer of the material, which can then be used to balance tensile stresses when it is in working condition, thereby preventing the generation of stress corrosion cracking, and preventing the growth of stress corrosion cracks, as shown in Figure 5 [20].

Hot Corrosion

It has been found that LSP can improve the hot corrosion resistance by improving its oxidation film composition in titanium alloy [21]. The hardened layer formed with high level of compressive residual stress enables it to endure larger stresses, and prevents the penetration of salts into the scale. Thereby, the layer has excellent resistance for hot corrosion. On basis of previous study, refinement of coarse grains occurs in the plastic deformation layer during LSP of Mg alloy [20]. Accordingly, a large amount of twins and highly tangled dense dislocation arrangements will be formed in the microstructure, which can delay crack initiation. Therefore, it is suggested that LSP can also be applied to Mg alloy for preventing hot corrosion.

Conclusion

LSP has been regarded as a useful method to improve mechanical properties of materials. Little work has been conducted for corrosion behavior. On basis of current analysis, LSP can play a significant role in improving surface anti-corrosion; therefore there is far more necessary research space to be filled. It is proposed that LSP is a promising technique for enhancing corrosion resistance of Mg alloys, especially for stress corrosion cracking, which will be very useful for practical applications in industries.

References

1. Huang YC, Zhang JQ (2012) Modern Materials Corrosion and Protection, Shanghai: Shanghai Jiaotong University Press.
2. Hou B (2008) The progress of magnesium alloy corrosion surface treatment. Electro-Mechanical Engineering 24: 42-44. (In Chinese)
3. Song GL, Atrens A (1999) Corrosion Mechanisms of Magnesium Alloys. Adv Eng Mater 1: 11-33.
4. Guan YC, Zhou W (2008) Calorimetric analysis of AZ91D magnesium alloy. Mater Lett 62: 4494-4496.
5. Zeng R, Dietzel W, Witte F, Hort N, Blawert C (2008) Progress and Challenge for Magnesium Alloys as Biomaterials. Adv Eng Mater 10: B3-B14.
6. Singh A, Harimkar SP (2012) Laser Surface Engineering of Magnesium Alloys: A Review. JOM 64: 716-733.
7. Gray JE, Luan B (2002) Protective coatings on magnesium and its alloys-a critical review. J Alloys Compd 336: 88-113.
8. Li JG (2013) Microarc Oxidation Coating on Mg-7Li Alloy and Its Corrosive and Tribological Properties. Published thesis (PhD), Harbin Institute of Technology.
9. Guan YC, Zhou W, Zheng HY (2009) Effect of laser surface melting on corrosion behaviour of AZ91D Mg alloy in simulated-modified body fluid. J Appl Electrochem 39: 1457-1464.
10. Lawrence J, Pou J, Low DKY, Toyserkani E (eds.) (2010) Laser industry: an Introduction to laser processing and its industrial application. Advances in laser materials processing.Wood head Publishing limited, CRC Press, USA.
11. Li YH (2013) Laser Shock Processing Theory and Technology. Science Press, Beijing, China.
12. Xu RJ (2008) Experimental Study of Laser Melting and Laser Shock on Magnesium Alloys. Zhenjiang, Jiangsu University.
13. Zhang LQ, Wu TD, Qian Y (2014) The research on laser shock processing and high cycle fatigue properties of cast AZ91D-T6 magnesium alloy. Chinese Journal of Lasers 41: 1-7.
14. Zhang YK, Chen JF, Xu RJ (2008) Experimental Research of Laser Shock Strengthening AM50 Magnesium Alloy. Chinese Journal of Lasers 35: 1068-1072.
15. Li XC, Zhang YK, Chen JF (2013) Effect of laser shock processing on stress corrosion cracking behaviour of AZ31 magnesium alloy at slow strain rate. Mater Sci Eng A Struct Mater 29: 626-630.
16. Ge MZ, Xiang JY, Zhang YK (2012) Effect of laser shock processing on stress corrosion cracking of AZ31B magnesium alloy. Chinese Journal of Lasers 39: 1-7.
17. Li SZ, Zhang LF, Xing QP (2013) Laser shock processing on the electro-chemical corrosion behavior of AZ91 magnesium alloy. Chinese Journal of Lasers 40: 1-5.
18. Zhang LQ, Bao SX, Wang R, Yang Q, Zhang Y, et al. (2014) Effect of laser shock processing on surface morphology and electrochemical corrosion resistance of AZ31 and AZ91 alloys. The Chinese Journal of Nonferrous Metals 10: 2465-2473.
19. Guo Y, Sealy MP, Guo C (2012) Significant improvement of corrosion resistance of biodegradable metallic implants processed by laser shock peening. CIRP Annals-Manufacturing Technology 61: 583-586.
20. Zhang Y, You J, Lu J, Cui C, Jiang Y, et al. (2010) Effects of laser shock processing on stress corrosion cracking susceptibility of AZ31B magnesium alloy. Surf Coat Technol 204: 3947-3953.
21. Hua Y, Bai Y, Ye Y, Xue Q, Liu H, et al. (2013) Hot corrosion behavior of TC11 titanium alloy treated by laser shock processing. Appl Surf Sci 283: 775-780.