

A Review of Magnesium/Magnesium Alloys Corrosion and its Protection

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Abstract: A review is provided about the current research on magnesium/magnesium alloys corrosion in the industry. Except for reviewing the kinds of corrosion on galvanic corrosion, stress corrosion, and corrosion fatigue, its corresponding mechanisms are also explained, such as the influence of metallurgical factors, and environmental factors. Furthermore, the protection of magnesium/magnesium alloys corrosion is presented, for instance, surface treatment/modification, coating and so on. Also, because the continuing challenges associated with the use of magnesium alloys, more considerations about future applications and research directions are given according to the properties improvement of magnesium alloys for the eco-friendly requirements.

Keywords: Magnesium, corrosion, surface treatment, coating, biomaterials, metallurgy.

1. INTRODUCTION

The current challenge involves the increasing use of light alloys in high-technology constructional materials, with the aim of both reducing mass and saving energy. The related typical application areas include vehicle construction, aeronautics and the space sector, along with the mechanical engineering and electrical industries. Moreover, the increasing concerns on environmental protection and sustainable economic development draw a great deal of attention in reducing greenhouse gas emissions [1-5].

Due to the low density, good heat dissipation, good damping, and good electro-magnetic shield, magnesium alloys have the extensive and increasing applications because of their lightest of all structural metallic materials [1-9]. For years, automobile makers have studied the relationship between vehicle mass and fuel economy for decades in order to meet the demands for more economic use of fuel and lower emissions in a time of growing environmental impact. As an interesting innovation, more and more parts, such as the crank case, camshaft sprocket, gearbox housing, several covers, and the arm of an electric generator, in automobiles have been replaced by magnesium and its alloys [2, 4, 6-9].

However, it is well known that magnesium and its alloys are of the hexagonal crystal structure. Hence, the multi-slip planes jeopardize their formability at ambient temperature because of the localized slip and build-up stresses at the deforming grain boundaries [10]. In moist air, magnesium and its alloys always form a thin surface film. This natural outer layer is not dense, because its corresponding Pilling-Bedworth ratio ≈ 0.81 , which indicates that the underlying metal can not be completely covered. As a result, magnesium and its alloys are highly susceptible to corrosion.

In the past, the corrosion behavior of magnesium alloys is the overriding factor to prevent their applications. However, a further attractive factor of magnesium alloys is they act as a substitute for polymers, which the satisfactory recycling solutions have not been found yet. Although the reduction of the critical contents of Ni, Fe, Cu etc. influenced the application of magnesium alloys, they still lack the self-healing layer for protecting effectively. In both alloying and manufacturing, efforts need to be directed towards composition and its corresponding microstructure involved the grain size and alloy temper/heat treatment to reduce the corrosion susceptibility. Also, according to the corrosion requirements, physical (such as grinding, abrading, particle blasting, polishing and brushing) and chemical (organic solvents/emulsions, alkaline, acid) treatment methods are generally taken. Furthermore, after appropriate preliminary treatment, a conversion layer should be formed with the appropriate organic or inorganic coatings [1-5, 9, 10]. The minimization of corrosion by surface conditioning or coating has given satisfactory results in some applications, but a systematic evaluation of the physical and chemical basis is still required for a full optimization.

In the meantime, with the requirements of a green environment for our quality of lives, recycling Mg alloys scrap is becoming more and more important. The rapidly growing market of magnesium die-castings increases steadily the magnesium scrap, typically due to end-of-life of vehicles and scrap from manufacturing processes. Properly recycling magnesium scraps from both die casting returns and post-consumer scrap in a closed loop manner ensures the environmentally sound and cost effective applications of magnesium alloys in automotive industry. Therefore, recycling processes for magnesium scraps need to be capable of regaining the original chemical composition and cleanliness of the magnesium alloys. Furthermore, industry also bears the objective to minimize the life cycle costs, the energy consumption and the emission of CO₂ of the magnesium products in mind [1-10]. It is thus important for the industry to improve continuously the friendliness of the

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process in recycling the magnesium scraps by establishing the recycled alloy specifications and by developing the efficient technologies for recycling die caster returns and post-consumer scrap.

Nowadays, with the large number of bioanalytical assays implementation related to biocompatible/biodegradable properties of magnesium alloys in microfluidics, the fast degradation or decomposition rate of magnesium and its alloys in human bioenvironment is a new change, and the detailed mechanism of corresponding corrosions will be a more significant challenge. The kind of magnesium and its alloys corrosion and its related protections are expressed in detail as follows.

2. MAGNESIUM/MAGNESIUM ALLOYS CORROSION

Because of the effect of air pollutants and the existence of salts, there are various kinds of corrosion of the magnesium and its alloys.

2.1. Galvanic Corrosion (Contact Corrosion)

2.1.1. Conditions for Galvanic Corrosion

Galvanic corrosion is also known as contact corrosion. There are four basic conditions for active galvanic corrosion: (i) an anode (the magnesium); (ii) a cathode (a dissimilar metal); (iii) direct electrical contact and (iv) an electrolyte between the anode and cathode [1-5]. Magnesium alloys will lose as the sacrificial anode and wear away in such active environments. Fig. (1) shows the internal galvanic corrosion of the semi-solid processing (SSP) AZ91D [11].

2.1.2. General Solution

There are two ways to protect magnesium and its alloys from galvanic corrosion. (1). Minimize the chemical potential difference between the magnesium/magnesium alloys and the dissimilar materials; (2). Maximize the circuit resistance.

For minimizing the potential differences, a number of metals show significant cathodic polarization in couple with

magnesium and its alloys (do not have anodic tendency) in salt water environments – for example aluminum alloys such as 5056, 6061, 5052 and 6063. In addition to aluminum tin, cadmium and zinc also polarize, and show good compatibility [12]. These metals are commonly used coatings on steel fasteners to minimize the galvanic corrosion. Otherwise, magnesium and its alloys will be corroded if the steel fasteners were used in an uncoated state [13]. However, for the maximizing the resistance in the galvanic circuit, the options are relatively few [14, 15].

2.2. Stress Corrosion

2.2.1. Mechanisms and Types

For pure magnesium, it is immune to stress corrosion cracking (SCC) in atmospheric and aqueous environments [1, 4, 5, 16]. For magnesium alloys, two kinds of mechanisms have been mainly involved SCC: (i) discontinuous crack propagation at the crack tip under the effect of mechanical fractures; (ii) continuous crack propagation at the crack tip under the effect of anodic dissolution. According to the many mechanisms proposed in these years, hydrogen embrittlement (HE) is best supported by experimental evidence listed as follows: (1) crack initiation and propagation are accompanied by hydrogen evolution; (2) immersion in a cracking solution before the stress is applied produces a fracture similar to a SCC fracture; (3) the effect of pre-immersion in a cracking solutions is reversed by vacuum annealing or exposure to room temperature air; (4) testing in gaseous hydrogen results in the same crack characteristics produced in an aqueous solution test; (5) SCC occurs at crack velocities and only adsorbed hydrogen will be present at the crack tip [17-29]. The detailed stress corrosion cracking (SCC) of AZ91 in double distilled water at the strain rate $3 \times 10^{-7} \text{ s}^{-1}$ is shown in Fig. (2) [22].

Moreover, according to the crack propagation routine, SCC can be classified as two types: One is transgranular SCC (TGSCC), and the other is intergranular SCC (IGSCC). Both kinds of crack propagation have been reported for

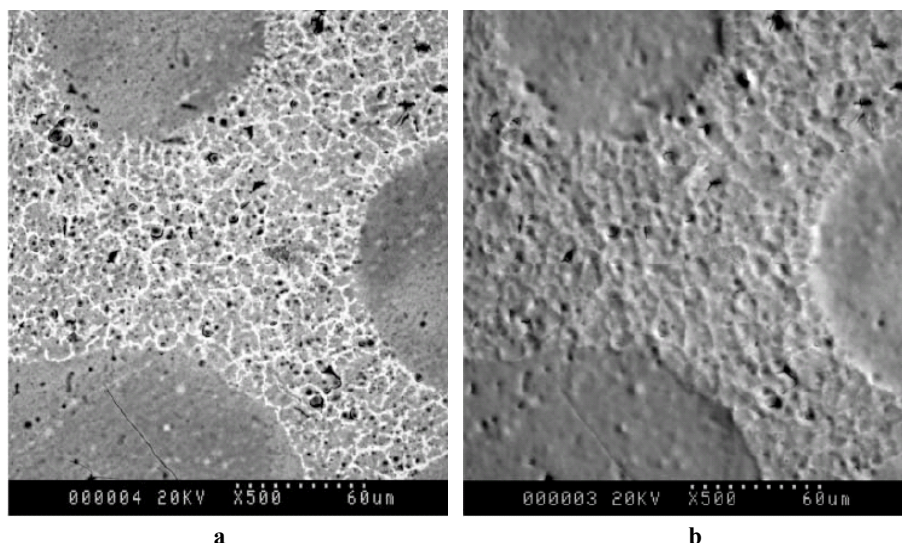


Fig. (1). SSP AZ91D-Galvanic corrosion after 72 h of immersion in ASTM D1384 water, pH=8.2: (a) composition mode and (b) topographic mode [11].

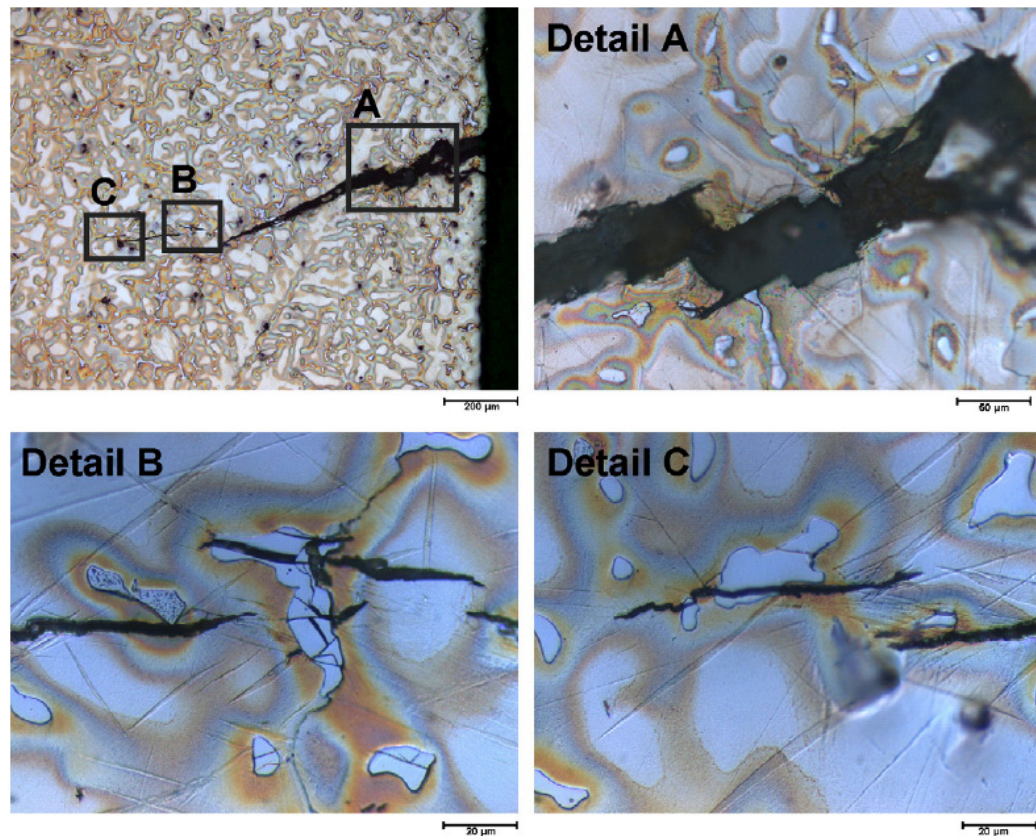


Fig. (2). Detailed SCC of AZ91 in double distilled water at the strain rate $3 \times 10^{-7} \text{ s}^{-1}$ [22].

magnesium alloys over years, however, transgranular failure with significant secondary cracking, or branching, is the most common mode of failure [21, 24, 25, 29].

2.2.2. Conditions for Stress Corrosion Cracking

There are three conditions for SCC: (i) long-term tensile stress above a critical level; (ii) a susceptible alloy; and (iii) in a SCC inducing environment.

2.2.3. Environments of Stress Corrosion Cracking

In atmospheric exposures rainfall, dew, high humidity, deionized water, NaCl + K₂CrO₄, H₂SO₄, HNO₃, NaOH, NaCl, NaNO₃, Na₂CO₃, KF, KCl etc., SCC of Mg alloys will be occurred [29].

2.2.4. Elements Susceptive to Stress Corrosion Cracking

Magnesium alloys containing Al are considered the most susceptible to SCC in air, distilled water and chloride-containing solutions. With the increment of aluminum content, the tendency to SCC is increased correspondingly. Therefore, magnesium alloys such as AZ61, AZ80, and AZ91 with 6, 8, and 9% aluminum, respectively, show higher susceptibility to SCC, while AZ31, a 3% aluminum alloy used in wrought product applications, is considered to show good resistance [17-24].

Zirconium and rare earth elements are considered only mildly susceptible, while magnesium alloys without aluminum or zinc, are the most SCC-resistant, such as ZK60, ZE41. Whereas, magnesium alloys with manganese addition show good resistance to SCC [30, 31].

2.2.5. General Solution

In accordance with the SCC occurrence conditions, to prevent SCC in practical application, it is necessary to design continuous loads of 30–50% of the yield stress and employ the effective corrosion barrier finishes, combine with the less susceptible alloys. Design precautions should also include limiting the stresses in bolting and riveting components together, and the use of heat treatments to relieve the stresses induced by welding [29].

2.3. Corrosion Fatigue

Corrosion fatigue is the combined action of an aggressive environment and a cyclic stress leading to premature failure of metals by cracking [32, 33]. Several surveys of corrosion failures in different industries have shown that 20–40% of the failures experienced have been due to corrosion fatigue [34-36]. Since many mechanically loaded parts are often subjected to prolonged cyclic stresses in an active medium, it is of significant importance to prevent the corrosion fatigue of magnesium alloys.

2.3.1. Corrosion Fatigue Conditions

Same as other materials, fatigue properties of magnesium alloys are depended on a number of factors such as the mechanical process induced roughness, surface defects, residual compressive stresses, as well as the environmental exposures [37-39]. Moreover, the fatigue life of magnesium alloys in corrosive solutions such as NaCl, CaCl₂ is always less than that in air [40-47]. Also, the degradation in fatigue strength for high-strength extruded AZ80 and die-cast AZ91D alloys in NaCl solution is more distinct than that of

AZ31 and AM20-AM40 alloys because of a higher percentage of the second phase ($Mg_{17}Al_{12}$) in AZ80 and AZ91D alloys [40, 41, 45, 46]. In the meantime, the NaCl environment enhances pit formation and growth resulted in the drastic reduction in fatigue limit more than in the $CaCl_2$ environment, due to the high Cl concentration and low pH value [46]. Literature [47] studied the corrosion fatigue behavior under different oil environmental exposure. It shows that the mineral oil environment causes an increase in the lifetime of AZ91 and AM51 in comparison with the gear oil. As above-mentioned, the corrosive environment results in a significant reduction in the fatigue performance of similar samples. However, many years ago, literature [48] shows the effect on fatigue performance does not seem to correlate consistently with the severity of the environment in some cases. For example, the bending fatigue limit for AM50 die cast samples tested in air and seawater was repeatedly found to be 105 MPa, but when tested in deionized water the endurance limit was reached at stress amplitudes as low as 70 MPa. Earlier studies [49] present AZ61A and AZ31A sheet bending at 1500 cycles per min in both a dry air exposure and in a 0.01% sodium chloride spray. It shows that in air at 107 cycles the observed fatigue strength was 103 MPa and 117 MPa and in the salt spray the corresponding data was 34 MPa and 40 MPa respectively. Fig. (3) shows the fracture surface of extruded AZ31 alloy after a corrosion fatigue test in 3.5% NaCl solution in the crack origin area with pitting (a) and in the area of dimpled fracture (b) [41].

2.3.2. General Solution

To protect magnesium alloys from the corrosion fatigue effectively, a suitable coating is always adopted [29, 48-50].

Simultaneously, it should be noted that other types of magnesium alloys corrosion such as pitting corrosion, filiform corrosion, and crevice corrosion similar to aluminum corrosion will be occurred during the processing.

3. INFLUENCES OF METALLURGICAL FACTORS ON MAGNESIUM ALLOYS AND PROTECTIONS

The metallurgical factors affected the corrosion performance of a magnesium part are composition and its

corresponding microstructure involved the grain size and alloy temper/heat treatment [51, 52].

3.1. Composition

According to reference [53], aluminum, manganese, sodium, silicon, lead and tin do not have the detrimental effect on the basic corrosion resistance of primary magnesium at levels up to 5% by weight. Furthermore, beryllium, cerium, praseodymium, thorium, yttrium and zirconium can be applied to resist the salt-water corrosion at levels exceeding their solid solubility or up to a maximum of 5%. However, calcium, cadmium, silver, and zinc have the moderate accelerating effects on the corrosion rate, while cobalt, copper, iron, and nickel have extremely severe accelerating effects. In order to achieve good corrosion performance from a magnesium alloy, only compatible elements are accepted and contaminant elements such as iron, nickel, and copper must be controlled to low levels. Recent research [54] shows magnesium alloys AM70 with Sn addition (which had been immersed in 5 wt.% NaCl solution for 70 h) has a faster corrosion rate after long term immersion in terms of the weight loss or anodic dissolution rate. Nevertheless, it is interesting that the modified AM70 is less susceptible to localized corrosion attack. It should be noted that with the development of magnesium and its alloys application, the zirconium family of alloys is normally used in low-pressure sand cast or permanent mold cast applications. However, the Mg alloys based on neodymium, yttrium [55], terbium [56], gadolinium and rare earths with zirconium [57-64], WE43, WE54 etc., have shown higher properties of the corrosion resistance. Fig. (4) shows the surface features of the corroded specimens after the immersion test in 5% NaCl solution and removal of the corrosion products. It shows that specimen with 0.42 % Zr addition has almost no corroded area, with only some small corrosion pits [57]. Due to the cost of these elements, its corresponding magnesium alloys have been limited to premium aerospace applications and other weight critical applications, where good mechanical properties at elevated temperatures are required.

Moreover, related references [64-67] show because of Si and Ca addition, new phases are found, i.e. intermetallics

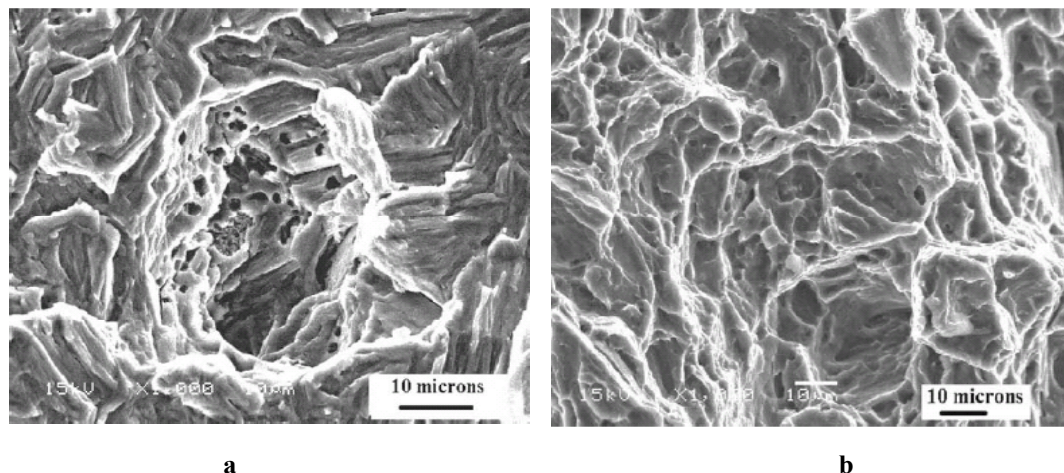


Fig. (3). Fracture surface of extruded AZ31 alloy in the crack origin area with pitting (a) and in the area of dimpled fracture (b) in 3.5% NaCl solution [41].

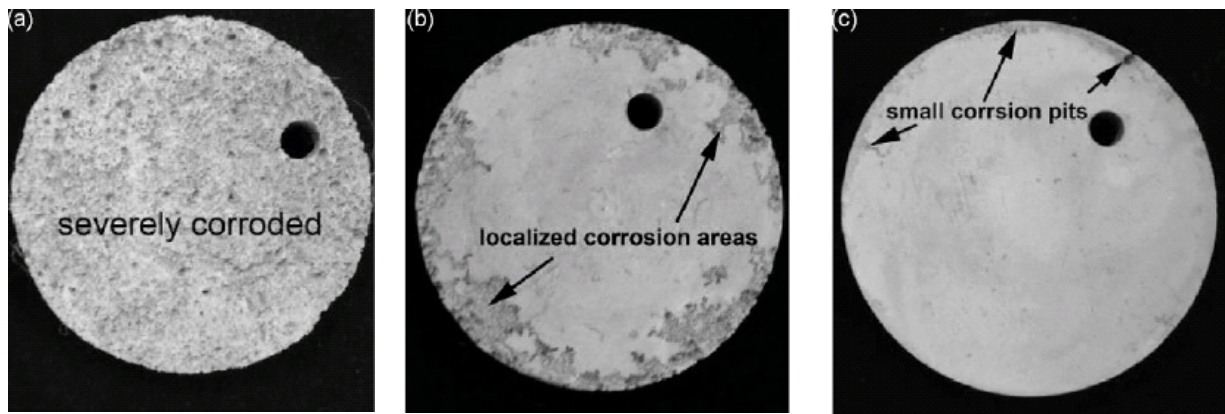


Fig. (4). Corroded surface photographs of magnesium alloys with various Zr addition after immersion in the 5% NaCl solution for 72 h and removal of the corrosion products: (a) 0 % Zr; (b) 0.33 % Zr; (c) 0.42 % Zr [57].

containing Si-Mn, Mg-Si, Mg-Zn and Mg-Si-Ca phase. At the same time, all phases exhibited higher potential differences relative to magnesium matrix indicating a cathodic behavior. Results show the additions to Mg-Zn-Mn wrought alloys can significantly improve SCC resistance to some extent, which also depends on the other critical alloying elements such as zinc and the microstructure.

3.2. Grain Size

The rapid solidification process can refine the microstructure to improve the materials corrosion properties. Reference [68] expressed the relationship between corrosion behavior and microstructure of Mg-Zn-Y alloys prepared by rapid solidification at various cooling rates. It shows that variation in the cooling rate has strong influences on the corrosion behavior of Mg-Zn-Y alloys. An increase in the cooling rate delays the occurrence of filiform corrosion, owe to grain refinement and formation of a supersaturated single α -Mg phase solid solution in the mg alloys. Moreover, by the rapid solidification, the mechanism of corrosion can be changed essentially; from pitting corrosion of Mg-Al magnesium alloys into overall corrosion [69]. As the traditional method, aluminum and zirconium, these two elements play the critical role of nucleating the formation of magnesium grains during solidification resulted in reasonably finer grain structures, higher mechanical properties, and superior the corrosion resistance. Contrarily, in literature [70] for comparison and more fully understand the behavior of die cast AZ91D authors studied the corrosion to its microstructure using slowly solidified high purity AZ91, Mg-2%Al, Mg-9%Al, low purity magnesium and high purity magnesium in 1 N NaCl at pH11 at the same time. Results show that the skin of die cast AZ91D has better corrosion resistance than the interior. This is attributed to a combination of (1) a higher volume fraction of the β phase; (2) a more continuous β phase distribution around finer α grains, and (3) lower porosity in the skin layer than in the interior of the die cast.

3.3. Alloy Temper/Heat Treatment

The common alloy tempers include F, T4, T5 and T6. It is clearly evident that the F and T4 corrosion rates are significantly greater relative to the standard high purity die cast performance depended on grain size, refining process, and considerable variations related to each result. However,

in the T5 and T6 tempers, the variations are much reduced and the corrosion rates are nearly same as high pressure die cast material.

4. PROTECTIONS

4.1. Preliminary Surface Treatment

4.1.1. Types

In accordance with the corrosion requirements, physical (such as grinding, abrading, particle blasting, polishing and brushing) and chemical (organic solvents/emulsions, alkaline, acid) treatment methods are generally taken. For physical treatments, it should be carried out immediately before the surface treatment itself is applied except for die cast with great precision.

4.1.2. Attention Items for the Initial Surface Treatment

For initial surface treatment, items listed as follows should be noticed.

- (1) Detrimental elements (Ni, Cu, Fe, etc.) and some remain emulsified salts (Cl⁻) should be avoided, which will make serious corrosion under the protective coating and form the hydrogen;
- (2) Removal of functional cast crust is should be avoided;
- (3) Impurity of blasting particles should be avoided;

4.2. Senior Surface Treatment

4.2.1. Surface Conversion Coatings

After appropriate preliminary treatment, a conversion layer will be formed by (1) *electroless electrochemical treatments such as in chromate or free chrome* (Mn, V, Mo and W) solutions [1-5]. Where, reference [71] describes the conversion coating treatment on pure commercial Mg, AZ61A, AZ80A and AZ91D formed by a permanganate-phosphate solution. Results show that the conversion coating has an equivalent or slightly better passive capability than the conventional Cr⁶⁺ based conversion treatment of AZ series alloys, but an inferior capability for the pure Mg specimen; (2) *Anodic oxidation* [72-74]. Anodic oxide coatings, a conventional method for aluminum protection applied to magnesium, are porous and rough with a coarse surface structure. Because of its Pilling-Bedworth ratio, the anodic finish must be sealed. Furthermore, the anodic oxide

coatings are lack of hardness resulted in the lower wear resistance. Also, its cost is almost twice as high as those for conversion coatings provided by electroless electrochemical surface treatment due to the time-consuming handling, the consumption of electrical energy and a prolonged coating time; (3) *Anodic plasma-chemical reaction in the electrolyte*, such as anodic spark deposition (ASD), anodic spark discharge, microarc oxidation (MO), electrical breakdown and plasmachemical oxidation [75-80]. By this type of methods, with suitable electrolytes and aqueous solutions (the anions fluoride, phosphate, borate, silicate etc.), it offers a coating of a crystalline ceramic nature, the thickness and hardness suitable for protection against both corrosion and wear without any need for further treatment. Moreover, besides the excellent corrosion and wear-prevention properties, coatings also display a high amount of resistance to heat and radiation exposure [81]. (4) *Galvanic-deposit coatings*. Because the slightest imperfection in a metallic coating of this type can lead to serious galvanic corrosion, the visible pitting of the underlying magnesium alloy will appear and spread drastically, as a result, the metallic coating will be peeled off. However, there is a tendency to use galvanically deposited coatings in applications in the electronics industry, such as on the casings of laptop computers and mobile telephones. Reference [82] describes the electroless nickel-phosphor coatings to pure Mg, AZ31 and AZ91 Mg alloys. After studying the deposition rate, nucleation process, chemical composition and microstructure of the electroless Ni coatings, it is found that Ni deposition is initiated on the phase or grain boundary areas due to the galvanic coupling effect. Also, the mechanism of Ni deposition on Mg alloys has been put forward, i.e. chemical replacement and subsequent autocatalytic reactions. (5) *Physical methods* such as PVD (Physical Vapour Deposition), arc-PVD, plasma-oxidation and arc-PVD ion implantation etc. [83-91]. By these methods, additional alloyed boundary layers, containing highly stable chemical compounds such as spinel $MgAl_2O_4$ are introduced. However, as an object of the current research, there is not actual application procedure available for magnesium alloys. (6) *Organic coating treatment* [92-98]. In literature [94] authors describe the utilization of thin film deposited in Plasmas fed with hexamethyldisiloxane-oxygen (HMDSO-O₂) mixture for the corrosion protection of Mg alloys. Results show that by plasma enhanced chemical vapor deposition, the corrosion resistance of Mg alloy (94.16% Mg, 3.42% Y, 2.41% Nd) has been improved significantly. (7) *Other methods*. The methods mentioned above cannot cover the entire surface treatment methods for magnesium protection. Attempts are currently being made to coat magnesium alloys by other methods, such as laser treatment [99-101], thermal spray coating [102], etc.

4.2.2. *Welding and its Treatment*

For magnesium alloys welding such as laser welding, gas tungsten arc welding, stirring friction welding etc. [29, 79, 103-106], it should be carefully selected because the high temperatures during the processing can burn cathodic contaminants into the surface. The practical usages should be carefully evaluated, included both the mechanical strength and the impact on the internal and surface quality of the affected area. Surface contaminants can be dealt with, but

cathodic contamination within the weld will be a much more severe problem. Furthermore, all welds should be stress relieved to avoid the SCC failures.

5. NEW CHALLENGES

5.1. Biocorrosion

Magnesium alloys have the good biocompatibility and potential biodegradable materials in hard tissue implants, because they have lighter weight, greater fracture toughness than ceramic biomaterials such as hydroxyapatite, closer elastic modulus and compressive yield strength to the natural bone. Moreover, magnesium is essential to human metabolism included bone tissues. Therefore, with the Mg alloys applications *in vitro* and *in vivo* assessments, the major drawback of magnesium, the low corrosion resistance in human body becomes an urgent issue on biomaterial applications [107-115]. Although some promising techniques such as additional elements, coating etc. have been studied in recent years [112-117], the systemic researches are still needed imperatively.

5.2. Corrosion of Recycling Scraps

Due to the distinguished characteristics of magnesium alloys, the average annual growth rate of Mg alloys die cast is 15% in automotive industry since the early 1990s [1-10]. The usage of magnesium alloys in cars will continue to rise at an even faster pace in the next decade. This implies that the scrap of Mg alloys from both manufacturing stage (new scraps) and end of servicing life of vehicles (old scraps) will grow very fast. As a result, it is crucial to develop the recycling friendly alloy specifications or use more efficient technologies for protecting die cast returns and post-consumer scraps from corrosion to improve continuously the recycling friendliness of magnesium.

6. Future Prospects

6.1. Traditional Methods Improvement and New Techniques

New Mg alloys or improved alloys including cast and wrought alloys with better properties such as finer grain, new phases should be developed. Also, more feasible, reliable, maintainable and cheaper protection systems and higher techniques should be investigated and developed on the basis of the methods primarily for the surface treatment of aluminum.

6.2. New Chance

Since the first Lab-on-a-Chip systems, requiring the interplay of a number of different disciplines such as microfluidics, bioanalytics, or microfabrication, appeared in 1990s, the progress in microfabrication has reached a certain level. Nowadays, with the large number of bioanalytical assays implementation closely related to progress in microfluidics, being the art of handling fluids and controlling flow in microscale geometries according to the biocompatible/biodegradable properties of magnesium alloys, the fast degradation or decomposition rate of magnesium in human bioenvironment should be taken into consideration, and the corresponding systems should be designed effectively and studied in detail.

CONCLUSIONS

A review of the current research on magnesium/magnesium alloys corrosion its corresponding mechanisms in the industry such as galvanic corrosion, stress corrosion, and corrosion fatigue has been expressed. At the same time, the protection of magnesium/magnesium alloys corrosion (surface treatment/modification, coating, etc.) is also presented. Because of the well-known characteristics of magnesium and its alloys (highly susceptible to corrosion) and the continuing challenges, therefore new Mg alloys or improved alloys including cast and wrought alloys with better properties such as finer grain, new phases should be developed, more feasible, reliable, maintainable and cheaper protection systems and higher techniques must be investigated to match with the practical applications. Moreover, according to the eco-friendly requirements, more considerations on recycling should be given both in industrial environment and bioenvironment.

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