Corrosion and Protection of Magnesium Alloys - A Review of the Patent Literature

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Abstract: Magnesium (Mg) and its alloys posses low density, high specific stiffness and electromagnetic shielding property, which are attractive to the automobile industry, 3C (computer, communication, consumer electronics), military and aerospace industry. Mg alloys have relatively low open circuit potential and thus highly susceptible to galvanic corrosion when they are in touch with other metal materials. Mg can also easily be oxidized and form a thin layer of loose MgO when exposed to air or humid environment. These disadvantages limited its applications. Therefore, surface coating technologies have been developed to protect Mg and its alloys from corrosion. Patented state-of-the-art technologies for surface treatment of magnesium alloys including chemical conversion, electrochemical plating, surface coating, and multiple-step surface treatment technologies have been reviewed and analyzed. Some new techniques have been introduced in this paper. It was found that conversion coating technologies account for a large amount of proportion among the patents of surface treatment. These technologies are also the main technologies used in industry. Japanese inventions on conversion coating of Mg alloys were patented in multiple countries. As the structures and service conditions of Mg alloy parts are of variety, a single surface-treatment process might not satisfy all requirements. Combined surface-treatment techniques appeared to meet the needs in different applications. More and more new and environmental friendly techniques are invented. Factors such as capital investment, ease manufacturing, and coating performances have to be considered when develop a coating technology for an industrial applications. There are still many good patents have not been used in industry. Hopefully this review of the state-of-art technologies of Mg alloy corrosion and protection can be helpful to the fellows engaged in this area.

Keywords: Corrosion and protection, magnesium alloys, surface treatment, patents.

1. INTRODUCTION

The low density and high specific stiffness of magnesium-based alloys make them attractive for the aerospace and automobile industries, although they must be balanced by their susceptibility of corrosion in aqueous environment. A number of methods to prevent magnesium alloys from corrosion or delay the speed of corrosion are used. First, corrosion of magnesium alloys can be controlled by changing the environmental factors since it usually occurs in the pH<12 moist conditions. However, environmental factors cannot be controlled in most of the times. Consequently, numerous coating technologies have been used to protect the magnesium from corrosion.

As Mg alloy coating and corrosion protection attract the interest of researchers, B. Luan [1] reviewed the protection of magnesium alloys in 2001. The paper, cited 171 references including papers and patents, reported in details of electrochemical plating, conversion films, anodizing, gas-phase deposition, laser surface alloying /cladding and organic coatings. Eight year passed since then, the R&D on Mg alloys developed rapidly in the world, particular in China in recent years. It is beneficial to reveal the state of the art of corrosion and protection of magnesium alloys. Thus more than 350 patents in seven countries have been searched from espacenet data (http://v3.espacenet.com/), wanfang data (http://s.g.wanfangdata.com.cn/Patent. aspx) and other resources using key words "magnesium, protection, coating and surface". This paper mainly reviewed the patents on the protection of magnesium alloys. It was found that magnesium alloy-related patents have increased every year in the last twenty years. The first patent on Mg alloy in the world was granted in USA in 1928. The number of such patents in Japan and USA appeared a peak during 1990-2000 and began to reduce in 2001, and then keep in a relatively constant. But patents increased rapidly after 2001 in China and reached the peak in 2008, which is higher than the sum of Japan and USA peaks in the last 10 years. Chinese patents on corrosion and protection of Mg alloys published in recent 8 years account for the No.1 in quantity, which illustrates the prosperous R&D on Mg alloys in China.

2. OUTLINE OF MAGNESIUM ALLOY PATENTS

Magnesium and its alloys have been extensively studied, for their excellent physical and mechanical properties, in many countries such as USA, Japan, China, and Germany. A great number of techniques have been invented for corrosion protection and surface treatment of Mg alloys. The distribution of the patents in different countries is shown in Fig. (**1**). Based on the searched patents, we can see that 165 (42.1%) patents have been granted in China, followed by

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130 (33.1%) in Japan, 74 (18.8%) in USA, and 12 (3.1%) patents in Germany.

Fig. (**2**) shows the distribution of the number of patents versus years. In order to reveal the recent progress of the patent, the abscissa axis (year) is divided into three sections: before 1990, 1991-2000, and 2001 - October 2009. It is shown that there were only a few patents granted before 1990. The patents in USA and Japan concentrated in 1990s and kept the relatively constant numbers since then. Though the first Chinese patents was granted in 2001, 73 years behind the USA (first patent granted in 1928) and 21 years behind Japan (first patent granted in 1980), the quantity of patents in China increased tremendously since 2001. The number of patents has been increasing every year. Especially after 2004, the number of patents in China was much more than that of other countries. In additional, the number of patents in USA and Japan changes very little after 2001, indicating that the technology of magnesium protection has been mature compared to that in China. China is one of the most magnesium-resource rich countries, not only the quantity of its minerals, but also the quality. The R & D on magnesium alloys has received great attention from Chinese government since the end of 1990s. And more than 40,000 thousands RMB was distributed to Industry, Institutes and Universities. Therefore, the R & D developed very fast in China these years.

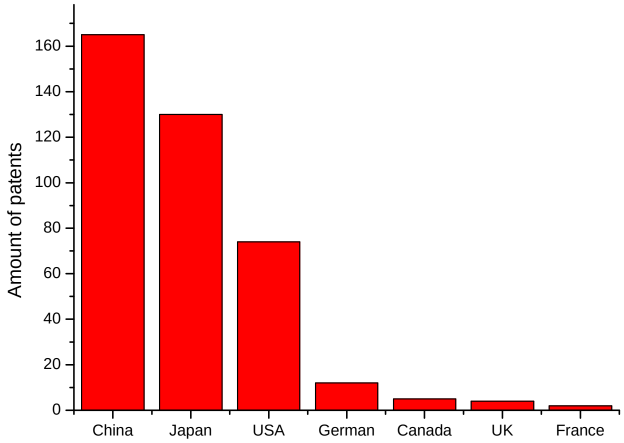

Fig. (1). Distribution of the patent number in different countries.

There are a number of coating technologies related to the corrosion protection of magnesium and its alloys. These include conversion films [2-5], electrochemical plating [6], surface coatings [7-9] and multiple surface treatments [10, 11]. Fig. (**3**) shows the distribution of the numbers of patents for different coating technologies. It is shown that there are 145 (41%) conversion coating technique patents, the largest share of the technologies. It is the hotspot due to its excellent binding strength and low cost. The organic coating and anodizing account for 65 (18%), followed by multiple surface treatment technique for 60(17%), and plating for 53 (15%). There are only 14 (4%) vapor deposition patents since the cost and sample size restrictions hamper its development. Each of these will be described in the following sections.

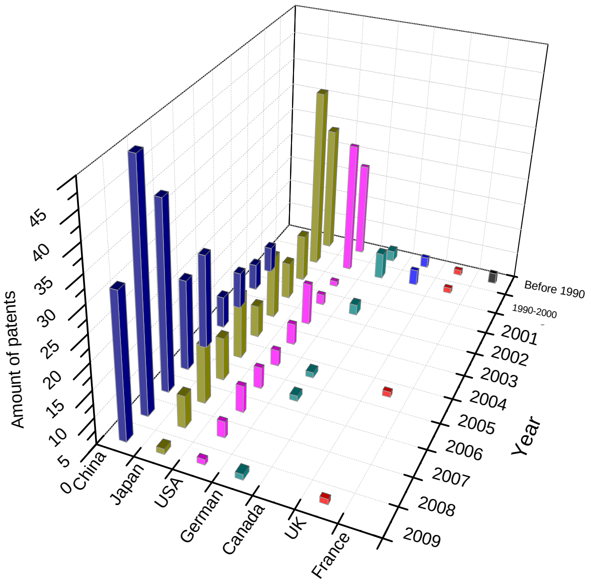

Fig. (2). Distribution of the patent number in different years.

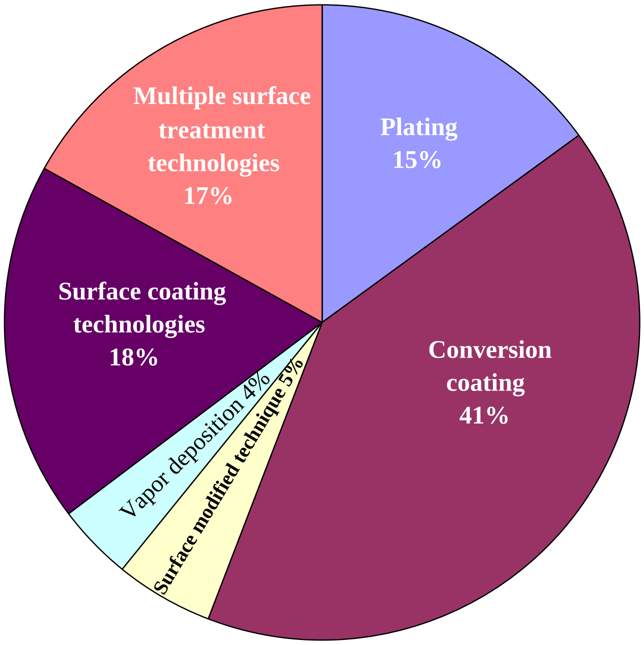

Fig. (3). Distribution of the patent number for different coating technologies.

3. STATE-OF-THE-ART COATING TECHNOLOGIES

3.1. Chemical Conversion Coating

Conversion coatings are superficial films of substrate metal oxides [5, 12, 13], chromates [14], phosphates [15, 16] or other compounds [17-19] produced by chemical or electrochemical treating of a metal surface. The superficial films are chemically bonded to the metal surfaces. The films provide to magnesium alloys not only corrosion protection but also good paint-base properties.

There are many different types of conversion films, mainly including chromate [14, 20-24], phosphate, anodizing films. The chromate conversion technique, described in details by B. Luan [1], is the most effective and mature process. It has been widely exploited in industry due to its excellent adhesion and corrosion resistance. After immersion in chromate solution, a protective coating can be obtained with uniform iridescent brassy color and free of any gray powdery material. Besides, there is no sparking when the work piece is subjected to wire brushing grinding operation [20]. However, the Cr^{6+} in chromate bath is highly toxic carcinogens and is gradually facing compulsory forbidden. The development of an environmental friendly process [25] is necessary due to the more and more stringent environment protection laws currently in effect or being proposed.

Phosphate treatments [15, 25-27] are being explored as an alternative to conventional chromate conversion films. Phosphate films are formed when Mg substrates react with dihydrogen phosphates ($M(H_2PO_4)_2$, where M represents metal elements or chemical groups such as Mn, Fe, K, Zn, Na, and NH_4. The process is generally expressed by the following reaction

$$Mg - 2e = Mg^{2+}$$

$$(x + y + 3z)Mg^{2+} + (2x + 2y + 6z)H_2PO_4^-$$
$$= xMg(H_2PO_4)_2 + yMgHPO_4 + zMg_3(PO_4)_2 \downarrow + (y + 4z)H_3PO_4$$

Meanwhile,

$$M(H_2PO_4)_2 = MHPO_4 + H_3PO_4$$
$$3MHPO_4 = M_3(PO_4)_2 \downarrow + H_3PO_4$$

Therefore, phosphate films are formed by crystallization of $M_3(PO_4)_2$ and $Mg_3(PO_4)_2$.

Table **1** lists the typical magnesium patents for phosphate treatments. The earliest patent was granted in 1928 [3]. It shows that the phosphate solution has been changed from the simple salt of phosphate to more complicated solution consisting manganese ions, phosphate ions [28] and permanganate ions [29]. The uniform phosphate films [30] of deeper colors formed in the manganese phosphate solutions can improve the wear resistance, corrosion resistance of Mg alloys. A phosphate-fluoride conversion coating [16, 31] based on chromate-free vanadates and was invented to improve the conversion rate and compactness of phosphate films. An active corrosion inhibitor consisting of organophosphonic acids was added in the conversion solution. The phosphoric acid group reacts with the magnesium metal substrate to form an insoluble salt. Later, nitric acid and tannin [32] were added respectively in the phosphate-permanganate solutions to improve the corrosion resistance and bonding strength. The results [32] showed that corrosion resistances of the treated magnesium alloys were all above grade 9 after 8 h 5% NaCl salt spray test, the surface electrical resistance of the samples were all less than 2Ω, and bonding strength were all above 3B.

Although the phosphate treatment has been used in industry to magnesium alloy parts such as 3C products, there are also many challenges for this technology. Firstly, the grains of phosphating film are coarse and crack occurs in the grains due to the high activity of magnesium alloys. The composition of phosphate solution, therefore, should be improved to obtain fine grains. Secondly, heavy metal ions in phosphate solution can cause environmental pollution and thus increases the cost of waste treatment.

Anodizing technology [39-44], an electrolytic process producing a thick and stable oxide film on metal and alloys, is another widely used technique in industry. The anodic oxide coating can be used to improve paint adhesion to metals [45, 46], as a key for dyeing [5, 47, 48] or as a passivity treatment.

Generally, there are two basic processes for anodizing i.e. oxygen precipitation and film forming. The reaction at anode and cathode is shown in the following equation.

Table 1. The Typical Phosphate Treatments Patents on Magnesium

Patent Numbers	Years	System of Phosphate Solution	Comments
US1677667 [3]	1928	Phosphoric acid, manganese dioxide.	First magnesium patents on phosphate treatment.
JP09183547 [33]	1999	Diammonium hydrogenphosphate.	Containing magnesium phosphate on the surface, which has good adhesion with the following coating.
US19970822444 [15]	1999	Phosphoric acid, manganese dihydrogen phosphate, triethylamine.	Form a conversion coating that contains P-Mn and Mn-N., The breadth of scratch after 120 h Salt Spray Test is 1.0~1.5 mm
JP9901275W [34], JP11024956 [35], DE19996002151 [36]	1999	Alkaline metal ions, phosphate ions, borate ions.	Containing magnesium condensed phosphate and magnesium phosphate.
JP10288094 [37]	2000	Sodium hydroxide, sodium pyrophosphate, triethanolamine.	Provide a low pollution surface treatment method for imparting corrosion resistance and painting adhesion
JP11302499 [38]	2001	Sodium pyrophosphate, acetic acid, sodium acetate, salt of permanganic.	Using a nonchromate treating solution capable of attaining corrosion resistance equal to or above that by chemical conversion treatment using a chromate.
US20020106098 [30]	2002	Manganese phosphate, permanganate ion.	Impart coating film adhesion, corrosion resistance and rust prevention.
US20080168054 [32]	2009	Phosphoric acid, carbamide, nitric acid, manganese dihydrogen phosphate, tannin.	Bonding well with the paint coating.

Anode:

$$2OH^{-} \rightarrow H_2O + O + 2e$$

$$O + Mg \rightarrow MgO$$

$$Mg \rightarrow Mg^{2+} + 2e$$

$$2OH^{-} + Mg^{2+} \rightarrow Mg(OH)_2$$

Cathode:

$$2H^{+} + 2e \rightarrow H_2$$

The growth of anodizing coatings can be divided into three stages i.e. forming of compact layer, forming of porous layer, and growth of the porous layer, as shown in Fig. (**4**). The properties of the coatings depend on various parameters such as electrolyte compositions, voltage and time. Chemical treatment Dow 17, invented by Dow Chemicals [49], and HAE process can be applied to all magnesium alloys. The treatment process is:

Degrease→ Acid Pickle→ Electrobrightening or polishing→ Anodizing→Sealing

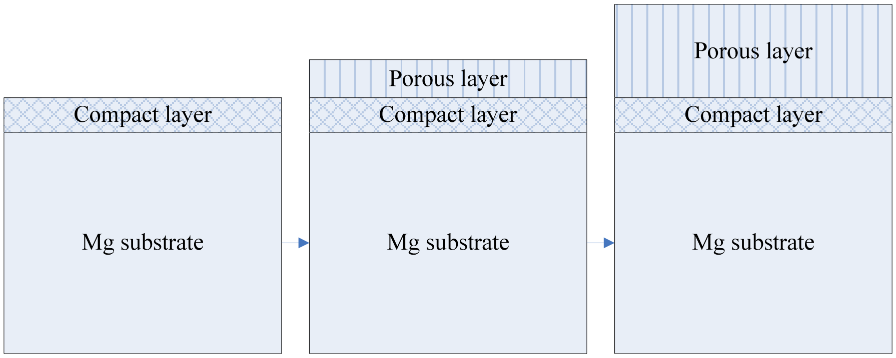

Fig. (4). Schematic of the growth of anodizing coating.

Table 2. Typical Processes of Dow 17 and HAE [49]

Processes	Solution	Technological Conditions	
Dow 17	NH_4HF_2 240~300 g/L	Temperature (℃)	70~80
	$Na_2Cr_2O_7{\cdot}2H_2O$ 100 g/L	Voltage (V)	60~90
	H_3PO_4 86 g/L	Current density (mA/cm^2)	5~50
		Time (min)	5~25
HAE	KOH 135~165 g/L	Temperature (℃)	15~30
	$Al(OH)_3$ 34g/L	Voltage (V)	70~90
	KF 34g/L	Current density (mA/cm^2)	5~50
	Na_3PO_4 34g/L	Time (min)	8~60
	$KMnO_4$ 20g/L		

The chemicals solutions and process parameters are listed in Table **2**. As we can see, the Dow 17 solution contains toxic chromate. Therefore, the application of this technique has been limited. The improvement of this technique was mostly on the power supply and electrolytes. Table **3** lists the typical patents covering anodizing technology. It is shown that power supply of anodizing technology has been gradually changed from DC to Pulsed DC power, which can effectively control and maintain the appropriate cation-anion ratio near the anode. The anodizing coating becomes more colorful and protective. Meanwhile, the development of power supply is towards low-voltage. One of the main challenges for anodic coatings on magnesium results from the electrochemical inhomogeneity due to the phase separation in alloys. Another disadvantage of this technique is that the coatings constitutes of a brittle ceramic material prone to cracking or shedding after collision.

To further improve the corrosion resistance and abrasion resistance of anodizing coatings, a technology called micro-arc oxidation (MAO) [44, 50-53] or plasma electrolytic oxidation (PEO) is invented base on the anodizing technology. It is similar to anodizing, but it employs higher voltage, so that discharges occur and the resulting plasma modifies (and enhances) the structure of the oxide layer. This process can be used to grow thick (tens or hundreds of micrometers), largely crystalline, oxide coatings that can offer protection against wear, corrosion and heat, as well as electrical insulation. The reference [51] has reported the patent progress on MAO before 2008. There are about ten new patents appeared in recent two years, which mainly dedicated to reduce the voltage to save energy [54, 55] and equipment costs. The trend of MAO development is to improve the coating appearance, adhesion strength, corrosion resistance and hydrophobic properties [56-58]. A micro-arc oxidation process for forming a coating with excellent corrosion resistance on magnesium surfaces has been disclosed [55]. TiO_2 nanoparticles are added into the electrolyte using sol-gel method. In addition, a superhydrophobic coating [56, 57] can be prepared by adding the polytetrafluor ethylene (PTFE) into the electrolyte; a self-lubricating surface can also be obtained.

In addition to the traditional chemical conversion treatment, molybdate conversion technology [65], vanadate conversion technology [17], and tartrate chemical conversion technology [66] have been invented for corrosion protection of magnesium alloys due to their friendly environmental. A method [17] improving corrosion

Table 3. Typical Magnesium Patents Covering Anodizing Technology

Patent Numbers	Year	Power Supply	Electrolyte	Comments
JP56096562 [59]	1983	DC	Alkali metal silicate, alkali metal hydroxide.	The voltage is further boosted by spark discharge.
JP56096564 [47]	1983	DC	Alkali metal silicate, alkali metal hydroxide, soluble salt such as copper, iron, Ni, Co, silver, Cr, Mn, Al and Ca.	Obtain an excellent colored protective film having various color tones
US19840631577 [48]	1985	AC	Aluminate, alkali hydroxide, boron compound, phenol, sulfate, iodine compound.	Obtain a colored coating.
JP59154069 [60], JP60077724 [61]	1986	AC	An aluminate and a compound selected among the oxides, hydroxides and salts of amphoteric metals.	A hard and dense film having superior corrosion resistance and uniform white color
US19870030941 [13]	1988	AC	Aluminum hydroxide, potassium hydroxide, potassium fluoride, trisodium phosphate, potassium permanganate.	A novel solution by dissolving silicate, carboxylate and alkali hydroxide in water.
US5470664 [62]	1995	Pulsed DC	Hydroxide, fluoride, silicate	Obtain a hard anodic coating
CN02816684.1 [63]	2004	Pulsed DC	Nickelous, pyrophosphoric, sodium hypophosphite, ammonium rhodanate.	Obtain a conductive coating.
JP2005112939 [64]	2006	Pulsed DC	Fluoride, permanganate, silicate, sulfate, nitrate, addtive.	A porous anodized coating with a thickness of 1 to 80 μm having many pores with the mean pore size of 50 nm to 25 μm.
CN200810226985.4 [55]	2009	AC	Silicate, borate.	In a low voltage (5V~20V).

resistance and paint adhesion of magnesium alloys has been invented by adding silane in vanadate solution. The result [17] showed that the sample surface with silane was still intact after 300 h 5% NaCl salt-spray test and the paint adhesion was excellent.

3.2. Plating

The plating process can be subdivided into two categories: electroplating and electroless plating. In both cases a metal salt in solution is reduced to its metallic form and deposited on the surface of a work piece. In electroplating, the electrons are supplied by an external power source. In electroless plating, the electrons are supplied by a chemical reducing agent in the solution.

There are three major steps in a plating process, as shown in Fig. (**5**). Firstly, the cations are gathered at the cathode surface by concentration diffusion. Secondly, the displacement reaction occurs at the cathode and the cations are consumed in the meantime. The general formula is shown as $Me^{n+} + ne \rightarrow Me$. Finally, a film is formed by the deposition of metal crystal from displacement reaction at the substrate surface.

Plating on magnesium and alloy surfaces has shown to be useful in applications. However, due to the high chemical activity of magnesium, a strong replacement reaction occurs in plating process accompanied by a large number of hydrogen evolution. The plating films, therefore, have weak adhesion to magnesium alloys. Generally, the pretreatment is complicated for plating on magnesium alloys. Thus, standard ASTM B 480-1988 [67] was established for preparation of magnesium alloys in electroplating. Improved methods have been proposed to make the process more simple and lower the cost. Table **4** lists typical magnesium patents covering electrochemical plating. Ni, Cu or Au plating with dry Al pretreatment has shown excellent electrical conductivity and heat radiation characteristics of the surface of a Mg or Mg alloy material [68]. To improve the adhesion of the film to the substrate material by prescribed surface treatment, a pretreatment of Cr plating has been invented [69]. The Cr plating solution, however, contains toxic substances. A solution containing fluoride, iron compounds and complex agents has been invented as an alternative to toxic cyanide solutions [70]. A simplified process in reference [64] has been shown capable to make the coating integrity after 1000 h salt spray test [71]. A method has been invented for plating Zn-Ni alloys [72] on magnesium and alloys. The plated films

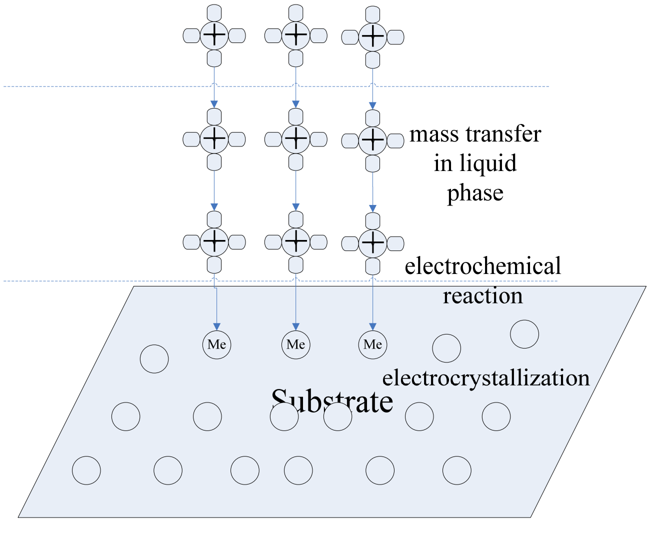

Fig. (5). Schematic of electroplating process.

Table 4. Typical Magnesium Patents Covering Electrochemical Plating

Patent Numbers	Year	Coatings	Comments
JP60117921 [68]	1986	Plating dry Al, then further Cu, Ni and Au	The surface treated layer having the stable quality and the electrically good conductivity or heat resistance and heat radiation characteristic.
JP62223239 [69]	1989	Plating dry Cr, then further Cu, Ni and Au	Chromate is used for improving the adhesion of a film to the base material by prescribed surface treatment.
JP63304542 [80]	1990	Plating the material with Zn, Cu and Au.	Having excellent electric conductivity and corrosion resistance.
JP03075111 [81]	1992	Plating Zn, and then plating further Cu for double times.	With a required metal film having satisfactory adhesion and superior electrical conductivity and capable of improving weather resistance.
CN02144834.5 [70]	2004	Plating Fe, and then Ni.	Use the pre-plating Fe to replace the plating Zn or Cu for decreasing pollution.
CN200510070949.X [73]	2005	Plating Zn, and further Zn and Sn.	Zn-Sn coating combined with good mechanical impact.
CN200510136764.4 [82]	2006	Organic coating, and then plating further Cu.	Combine the organic silicon heat-resistant coating with plating Cu for improving heat, wear and corrosion resistance.
US20070750949 [83]	2007	Plating Ni, and then plating further Zn and C_o.	Form a transition layer containing Ni, Zn or C_o crystals.
US20060646971 [84]	2008	Plating Cu, and then thickening the copper coating layer.	The pre-treating solution contains no cyanide and thus is low toxic and safe to operator during electroplating
CN200710158234.9 [85]	2009	Plating Zn-Al, and then plating further Zn.	The pre-treating solution contains no cyanide and thus is low toxic.

have smooth surfaces, striking-free, and good bonding to the substrates. Additionally, electroplating or electroless plating of alloys such as Zn-Sn [73], Ni-P [74-76], Ni-Cu-P [77], Ni-W-P [78], Ni-P-V [79] can produce surface films to increase the corrosion resistance, surface hardness and thermal conductivity.

As we known, magnesium and its alloys are prone to have galvanic corrosion while they are in touch with other metals due to their high reactivity and low open circuit potentials. General corrosion rate can be accelerated by galvanic corrosion once the plated films rupture. The existence of Ni as an impurity in Mg alloys can reduce corrosion resistance severely. Hence, Ni is a disastrous element to the corrosion resistance of Mg alloys. However, most coatings contain Ni, which has to be carefully removed when Mg alloys are recycled. In addition, the electrolytes have a limited life, which is a serious limitation from both coating and environmental perspectives. There are many challenges to be overcome in order to develop a versatile plating process.

3.3. Surface Coating

Surface coating technologies have been used to form protective layers on substrates *via* thermal spraying [86], overlaying welding [87, 88] and hot-dipping [89]. Coating layers can be metal alloys [90, 91], ceramics [92], paints [93] etc.

In a thermal spraying process, the coating materials, which can be metal, ceramic, cement or polymeric, are fed to a torch or a gun and heated to above or near its melting point. The resulting droplets are accelerated by a gas stream and sprayed into thin lamellar particles, which adhere to a substrate. An Al or Al/Zn thermal spraying coating has been invented for improving the corrosion resistance of Mg alloys [91, 94]. The elements of Al, Zn are the main constitution of Mg alloys. They make the recycling of Mg alloys with these coatings much easier, compared to metal plating such as Ni and Cr plating. However, spray coatings are porous and need to be sealed or reheated before the parts expose to humid environment. The coating quality can be improved by further heating at 380-420oC to enable atom inter-diffusion at the coating and substrate interface. The coating-substrate adhesion can be improved by forming new Al-Mg or Mg-Zn phases. The coating is of good impact resistance and corrosion resistance (Figs. **6**, **7**) [95]. As the creep of magnesium occurs at elevated temperature, surface nanocrystallization process has been invented to reduce the diffusion temperature [90, 91]. Additionally, thermal spraying of ceramics [92] such as Al_2O_3, Cr_2O_3, TiC, Si_3N_4, ZrO_2, SiC, TiO_2, Cr_3C_2, MgO has also been invented to improve the surface hardness, abrasion resistance and thermal resistance of magnesium alloys for applications such as motorcycle and motor spare parts.

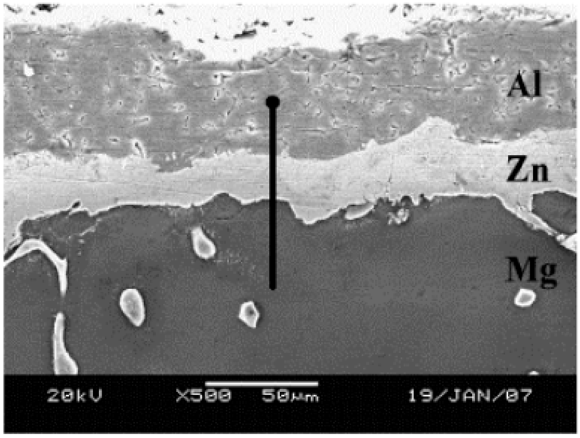

Fig. (6). The cross-section morphologies of as- Al sprayed specimen.

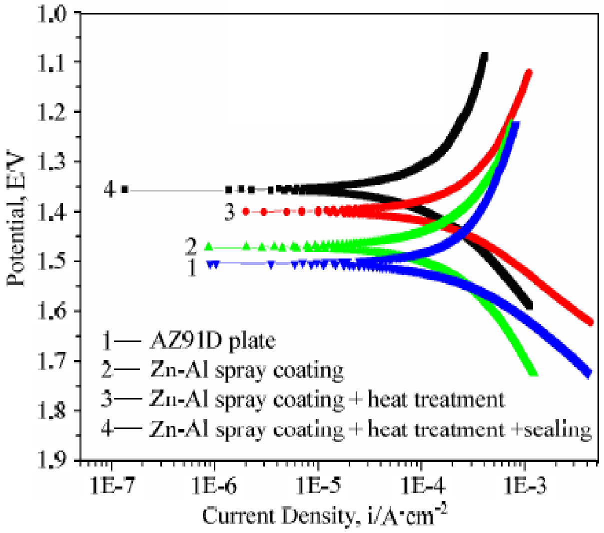

Fig. (7). Polarization curve of thermal spray Zn-Al coatings with different post-treatment.

3.4. Organic Coatings

An organic coating is typically used in the final stage of a coating process. It can enhance corrosion resistance or specific decoration [1]. Organic coating involves a variety of processes such as painting, powder coating, cathodic electrocoating (E-coating) and the application of lacquers, enamels and varnishes. Table **5** lists the typical magnesium patents covering organic coating technologies. It can be seen that silane plays an important role in organic coatings. Silane treatment is a class of environmentally-benign organic-inorganic hybrids, which has shown a great potential to replace toxic chromates in industries. Silane is a hydrolysable alkoxy group such as methoxy(OCH_3), ethoxy(OC_2H_5), acetoxy($OCOCH_3$). It has a general formula of $R'(CH_2)nSi(OR)_3$, where R' represents an organofunctional group, which bonds well with paint. OR has good adhesion with metal substrates. An independent silane film [8-9] without top coating has been initially used to improve the corrosion resistance of magnesium and its alloys. However, the silane film is too thin to protect the magnesium alloys for long time. Therefore, as a paint primer, the silane film provides excellent paint adhesion between metal and painting (see Fig. **8**) [96, 97].

3.5. Multiple Surface Coatings

A single surface treating might not meet the requirements of magnesium alloys in some working conditions. Therefore, surface treatment technologies [102] that combining two or more kinds of surface treatment together to form multi-layer surface coating have been developed rapidly in recent years.

The benefits of this type of technologies are not a simple addition of the properties of multiple layers but the synergistic effects. An example is: an insoluble fluoromagnesium film is formed on the surface of magnesium alloy, followed by immersing the coated metal in a metallic container comprising an aqueous solution of alkali metal silicate and an aqueous solution of alkali metal hydroxide [103]. Corrosion and abrasion resistance of magnesium alloys has been improved by fluoromagnesium film and top anodizing coating respectively. Additionally, this invention exhibited greater resistance to strong acids and alkali. Another example: an oxide film is formed by anodic oxidation; a thermosetting resin film is then formed on top of it; and finally a metallic conductive film is formed on the surface by a vapor deposition method [104-106]. This can enhance surface characteristics such as corrosion resistance and conductivity. Hoshi *et al.* invented a three-layer [107] structure - nickel/copper/aluminum were plated successively on magnesium alloy and then an anodized aluminum coating was formed on the out surface. The internal stress generated in the nickel plating film and the aluminum plating film is relaxed by forming a copper plating film between them. This, therefore, improves the adhesion of the films over the entire part.

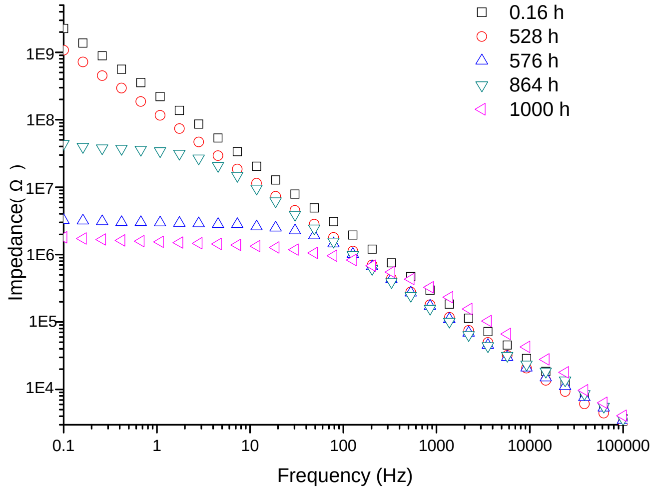

Fig. (8). Bode plots of Mg/silane/E-coating in 3.5 wt.% NaCl after different time immersion.

However, a typical multi-layer surface treatment technology involves chemical conversion or anodizing and paint coating to the conversion or anodizing film on magnesium alloys [29, 108, 109]. The chemical conversion or anodizing film can improve not only the adhesion between Mg substrate and paint coating, but also the corrosion resistance.

3.6. Other Technologies

Many other protective technologies such as surface heat treatment [110], vapor deposition [111-113], ion implantation [114, 115] have been invented. They are excellent alternatives with respect to environmental impact. However, these technologies usually involve more capital investment and power consumption. The corrosion and adhesion properties of these coatings on magnesium are not satisfactory yet.

4. SUMMARY

The technologies mentioned above reveal that almost all surface technique including pretreatment can be used for the corrosion protection of Mg alloys. It seems that the corrosion protection to Mg alloys is not a key point for their applications. However, up to now, no single technique or a multi-layer coating technique can meet the industry requirements for Mg alloys in different service conditions. As Mg alloys have low open circuit potential and negative differential effect, coating techniques suitable for Al or Fe or

Table 5. The Typical Magnesium Patents Covering Organic Coating Technologies

Patent Numbers	Year	Coatings	Comments
JP2000275616 [98], JP2000127827 [99]	2002	Synthetic resin coating	The curing of coating is used by ultraviolet-curable.
US20050099483 [9], US20050214810 [100], US2007069999 [8]	2005-2007	Organopolysiloxane film	Provide an organopolysiloxane composition for bonding to magnesium alloys which has good self-adhesiveness to magnesium alloys.
JP2004329050 [101]	2006	Silane and Al coating	Obtain an anticorrosive coating material composition for Mg alloys, a colorless and transparent coating film that is excellent in adhesion to the magnesium alloy.
US 20070166467 [7]	2007	Water dispersible silane coating	The coating forms a cross-linked and typically hydrophobic film, which exhibits excellent corrosion resistance, high thermal stability, and strong adhesion to the metal and to paint top coatings.
CN200510057166.8 [96] CN200610095111.0 [97]	2005-2006	Silane and electrodeposition coatings	Enhance the adhesion of magnesium alloys and electrodeposition coatings by silane treatment.

their alloys can not be applied directly to Mg alloys. Some corrosion protection techniques for materials other than Mg alloys may be useful for Mg alloy corrosion protection. However, the process parameters and/or solution compositions may have to be modified before they can be used to treat the components of Mg alloys. Meanwhile, recycling of Mg alloys should get rid of Ni, Fe, Cr, Cu coatings.

Of all the coating techniques, we can divide them into two types: dry and wet methods. Thermal spray, laser surface alloy or cladding, physical or chemical deposition, and solid diffusion are dry methods. Conversion coating, electrochemical plating, anodizing or plasma oxidizing, painting or organic/polymer coating, and sol-gel belong to wet method. Dry methods are usually environmental friendly and are suitable for treating precision or decorating parts with simple shape and small size and free of holes or grooves. Special apparatuses, which are usually very expensive, are needed for dry techniques. Wet methods, on the other hand, are easy to be realized with little investment and have good throughput. Wet methods are suitable for the complex and large components used in automobiles and bicycle industries. However, great efforts are needed for waste disposal especially for solutions consisting toxic and carcinogen components such as chromium and cyanide. Some new patents have shown techniques of chromium-free or cyanide-free coating, and lower power cost apparatus. Coating techniques for strong adhesion, corrosion- and wear-resistance, and high impact-resistance are the future R&D interest.

Magnesium alloys, known as "the green engineering materials with the greatest potential of development in the 21st century", has been paid more and more attention by the majority of researchers. The numbers of Mg alloy related patents has been increasing every year. However, only a small amount of these patents are really applied in industries. There are a number of factors including capital investment, ease of manufacturing, coating performances and environment issues need to be considered when develop a coating process for industrial application. Therefore, future trends for patents of magnesium alloys are predicted to be towards low cost, pollution-free, and easy to recycle.

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