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Surface Modification of AZ91 Magnesium Alloy

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Abstract

Magnesium is the lightest structural metal with the highest specific strength. It is therefore considered as a solution for vehicular mass reduction so as to reduce the fuel consumption and greenhouse gas emission. Unfortunately, magnesium and its alloys are highly susceptible to corrosion, particularly in salt-spray conditions. This has limited its use in the automotive and aerospace industries, where exposure to harsh service conditions is unavoidable. To improve its corrosion resistance it is viable to apply a desirable engineering coating on the magnesium surface.

This communication discusses the practical aspects of magnesium surface modification based on our review. A novel immersion coating process is also discussed along with the corrosion behavior of coated and uncoated AZ91 magnesium alloy.

1. Introduction – summary of a review on the state-of-the-art

Prior to starting the design of a novel deposition process for coating of AZ91 magnesium alloy, an extensive review was conducted [1]. Summarized below are the conclusions from the review that describes various processes for the modification of magnesium surface. It is our opinion that no single coating technology had been developed which functions to adequately protect magnesium from corrosion in harsh service conditions, though it is possible to develop appropriate coating schemes for the protection of magnesium for use in automotive components.

There are a number of patents that claim to have coating processes for magnesium and its alloys. While some of these have direct evidence to support the use of these technologies on magnesium, there are a large number of claims that only provide direct evidence that the coating technology works on aluminum and its alloys. The chemistry of aluminum is quite different from that of magnesium and it is therefore possible that these coatings may not perform as well on magnesium.

There are a number of factors to be considered when developing a coating process for an industrial application. These include capital investment, ease of manufacturing, coating performance and environmental issues.

In the case of electrochemical plating, the capital investment is relatively small. However, there are some serious concerns over waste disposal. The most successful example of electroless plating technology for magnesium has a maximum turnover rate of 6, when a strict replenishment schedule is followed. Further research is required to enhance the longevity of plating baths and to decrease waste generation. Another challenge associated with electroless plating on magnesium is the narrow window for operating conditions in order to obtain optimum coatings. Despite these challenges, this technology does have the potential to produce uniform, corrosion and wear resistant coatings with good electrical conductivity and solderability, at a low cost.

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Conversion coatings also represent a minimum capital investment, however the most widely used type of conversion coatings are chromate conversion coatings. These represent a serious environmental risk due to the presence of leachable hexavalent chromium in the coatings. A number of chromate free conversion coatings are under development but this technology is still in its infancy. Conversion coatings do not provide adequate corrosion and wear protection from harsh service conditions when used alone. However, they can act as a good base for producing adherent organic coatings and act to enhance corrosion resistance of a combined coating system by protecting the substrate at defect sites in overlying layers.

Anodizing is the most widely commercially used coating technology for magnesium and its alloys. This process is technologically more complex than electroplating or conversion coating but is less sensitive to the type of alloy being coated. It does involve more capital investment due to the need for cooling systems and/or high power consumption but this may be balanced by the decreased cost of waste disposal.

The use of gas-phase coating processes and laser surface melting/ alloying/cladding to modify the surface or create coatings on magnesium is an excellent alternative with respect to its environmental impact. These techniques produce very little and in some cases no hazardous waste. However, the capital cost associated with these techniques is much higher than solution phase coating technologies.

Organic coatings are extremely versatile and can be applied to many metals provided an appropriate pretreatment can be developed for the substrate. The adhesion and corrosion resistance of these coatings are inadequate without pretreatment . Organic coatings are typically the last step(s) in a coating system. They may be applied for a purely decorative effect or to enhance the corrosion resistance of the overall coating system. There are some environmental concerns with the use of solvent borne organic coatings but the development of water-borne and powder coating technologies has led to a decrease in the use of these chemicals.

There are a large number of coating technologies available for protecting magnesium and its alloys. However, the widespread use of magnesium in the automotive industry is still deterred by the lack of appropriate protective coatings that can withstand harsh service conditions. A great deal of research is still required to develop better, simpler, cheaper coating technologies so we can take advantage of the lower weight and excellent mechanical properties of this material.

2. Development of immersion coating on AZ91 magnesium alloy

In order to achieve a quality coating on magnesium substrate, a process was designed that includes a chemical etching step to pre-treat the magnesium surface, and an immersion coating process to form an underlayer for protecting the Mg surface for the subsequent electroless / electro-depositions. While each step in the procedure is essential, the immersion coating process is critical. For this reason, copper immersion coating processes have been developed in our labs. This communication focuses on copper immersion coating (CIC) in acidic and alkaline bath. In the acidic bath that contains hydrofluoric acid, the role of HF concentration and the effect of sonication were investigated. In the alkaline bath, the effect of fluoride content and pH were studied.

2.1. Experimental

All the substrates used were AZ91D magnesium alloy coupons cut into $1.5 \times 10 \times 10$ mm^3 specimens. The pretreatment of substrates started with glass-beading for 10 seconds at a pressure of 450 kPa, followed by a sonication cleaning in iso-propanol for 3-6 minutes. An alkaline degreasing process was subsequently performed in a solution containing 60g/L NaOH + 10g/L Na$_3$PO$_4$ at 75°C for 3-6 minutes. After thoroughly rinsed in deionized water, the substrates were immediately transferred into a solution for copper immersion coating.

The CIC processes were performed in either acidic or alkaline bath. The acidic bath contains 0.67M CuSO$_4$.5H$_2$O + xM HF in various concentrations, while the alkaline bath consists of 100g/L K$_4$P$_2$O$_7$, 30g/L Na$_2$CO$_3$, 12.5g/L CuSO$_4$.5H$_2$O + x g/L NaF. All CIC processes were performed at room temperature.

The immersion coating obtained from the CICs were examined by SEM using back scattered electron (BSE) mode. The resultant BSE images were processed with an Image – Pro plus Software (Media Cyberhetics Inc.) to obtain surface coverage.

2.2 Result and discussion
2.2.1. Theoretical consideration of CIC

Fig. 1 shows the microstructure of the AZ91D magnesium alloy. It consists of matrix α-phase and intermetallic β-phase with a stoichiometric composition of Mg$_{17}$Al$_{12}$. The Mg$_{17}$Al$_{12}$ particles are distributed at boundaries of small, cored grains of α matrix. It is generally known that β-phase serves as a galvanic cathode and accelerates the corrosion process of the α matrix. Furthermore, the matrix α-phase, in turn, consists of primary α and eutectic α, which also possess different electrochemical behavior [2-4]. This microstructural heterogeneity on the surface of magnesium alloy substrate complicates the process of copper immersion coating.
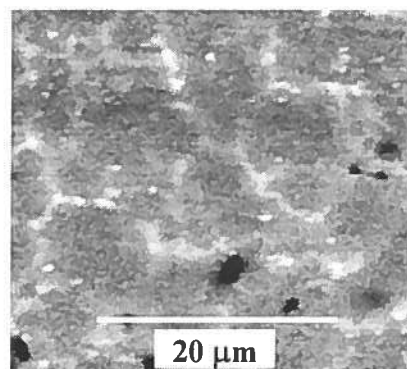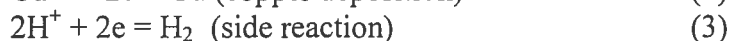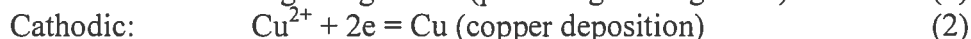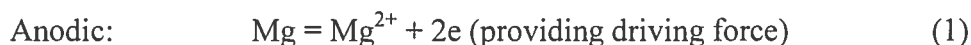

Fig. 1 Microstructure of AZ91D

The CIC on AZ91D magnesium alloy is a process involving several reactions taking place simultaneously, namely, Mg dissolution as an anodic reaction and, hydrogen evolution and copper deposition as cathodic reactions:

Anodic:	$Mg = Mg^{2+} + 2e$ (providing driving force)	(1)
Cathodic:	$Cu^{2+} + 2e = Cu$ (copper deposition)	(2)
	$2H^+ + 2e = H_2$ (side reaction)	(3)

For copper deposition to take place, the potential of magnesium substrate must be maintained in the region where metallic copper is stable, and the dissolution of magnesium is continuous thereby providing driving force for copper reduction.

The potential – pH diagrams can be used to thermodynamically determine the condition of CIC. According to the diagrams of copper-water and magnesium-water [5], there is a broad pH region (between 2 to 9) within which the theoretical conditions for CIC are satisfied. However, a quality coating can not be achieved by a simple immersion of magnesium substrate into a copper ions containing solution within the pH range. It was observed that during a simple immersion coating process, violent reactions of magnesium

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dissolution, copper reduction and hydrogen evolution occurred and the resulted copper deposits were spongy and non-adhesive.

The following discussion is therefore focused on the practical aspects of CIC for achieving a quality coating on AZ91D magnesium alloy.

2.2.2. CIC in acidic bath

Fig. 2 shows the effect of HF concentration on surface coverage. It reveals that surface coverage first increases with increasing HF concentration and then decreases after reaching a maximum at 2.2M HF. In the lower HF containing bath, the surface film formed on magnesium possessed a loose and discontinuous feature with poor protection (Fig. 3a). The dissolution of magnesium is therefore violent, resulting in non-adherent and spongy copper deposits that were subsequently partially removed from the substrate surface by violent hydrogen evolution. With an increase of HF concentration, the surface film formed became

Fig. 2 Effect of HF concentration on the surface coverage of (CIC) on AZ91 magnesium alloy in a bath containing 0.67M $CuSO_4$ + HF (coating time: 10 min)

increasingly dense and stable as observed on SEM images (Fig. 3b). Such a compact film, simultaneously formed during copper deposition, not only prevented violent magnesium dissolution but also enabled copper to deposit as fine and adhesive crystallites. With the further increase in HF concentration, however, copper deposition was only able to take place at a very early stage because the rapid film formation limited the available anodic sites on the surface. As a result, a decrease in copper coverage starts when the HF concentration is higher than 2.2 M (Fig. 2).
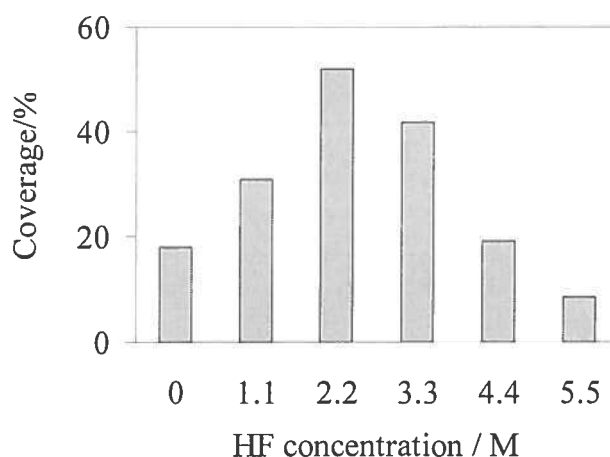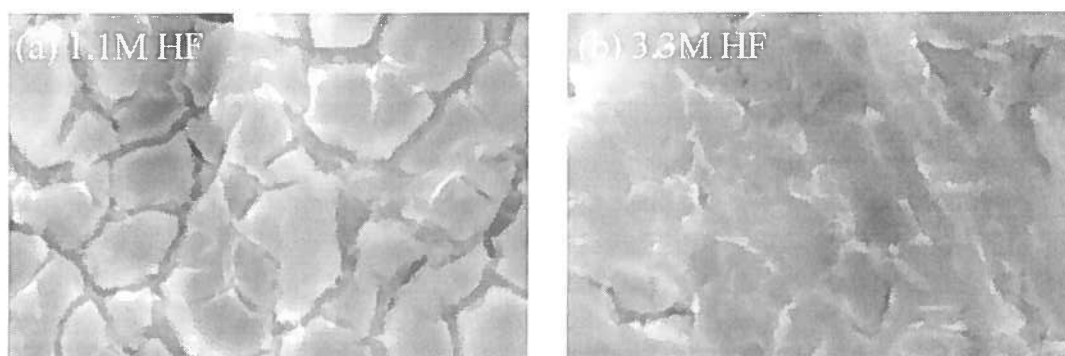

Fig. 3 Secondary electron (SE) images for AZ91 magnesium alloy after etching in 1.1 M and 3.3M HF solution respectively (etching time 10 min).

In order to achieve higher surface coverage the effect of sonication HF concentration are studied.
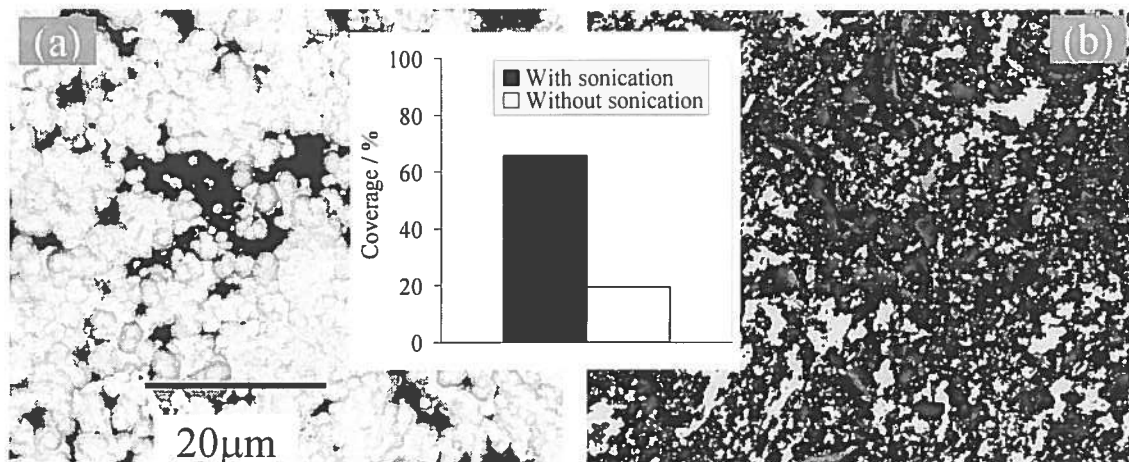

Fig. 4 Surface morphologies of CIC on AZ91D in a bath containing 4.4MM HF + 0.67M $CuSO_4$ (room temperature, coating time 10 min), (a) sonicated bath and (b) non-sonicated.

Fig. 4 shows the surface morphologies obtained with or without sonication. It clearly shows a significantly higher surface coverage with the application of sonication, by comparing Figures 4(a) and (b).

It was suggested that in an F^- containing aqueous solution, surface film containing $Mg(OH)_nF_{2-n}$ [6] may form and suppress anodic dissolution [7], thereby preventing the increase of copper coating coverage. Sonication is known for its capacity to erode/clean substrate surface mainly through asymmetric cavitation [8-9]. With the application of sonication to the immersion coating bath, the fluoride film formed on magnesium substrate is possibly erased/abraded by the asymmetric cavitations. Furthermore, the reformation of the surface film during coating process is also hindered/limited by vigorous local fluid motion (micro-jet effect) that removes the intermediate species, MgF^+, away from the electrode surface, thus preventing its conversion to, and the subsequent precipitation of, MgF_2 as a protective film. As a result, the anodic reaction (magnesium dissolution) could be maintained to continuously provide a driving force for the cathodic reduction.

2.2.3. CIC in an alkaline bath

It is of note that with the increase of pH value to beyond 9, the thermodynamically stable region of $Mg(OH)_2$ in the potential-pH diagram of magnesium-water [5] is gradually entered. Accordingly, the dissolution of magnesium may be decreased, which may render CIC in an alkaline bath possible.

Fig. 5 shows the effect of pH on the CIC. With increasing pH, copper coverage first increases then decreases after a peak point at approximately pH = 10.3. To investigate the immersion coating mechanism, EIS measurements in a three electrode cell (Ag/AgCl/KCl as the reference, Pt the counter and AZ91D Mg the working electrode) were conducted in a bath with the same components as the copper immersion coating bath without copper sulfate.

A typical Nyquist spectrum obtained is shown in Fig. 6. The charge transfer resistance (R_{ct}, derived from Nyquist spectra) vs. pH is depicted in Fig. 7. It shows that with an increasing pH, the charge transfer resistance, R_{ct}, is significantly increased, suggesting a decrease of magnesium dissolution, in which event a high copper coverage should be observed at a lower pH. However, this is not the case since an even lower Cu coverage is observed at pH 9.3 than those at higher pH (e.g. pH 10.3). This may be due to the violent dissolution of magnesium which results in non-adherent and spongy deposits that might be partially removed from the substrate surface due to vigorous hydrogen gas evolution. With increasing pH, a possible film formation on the magnesium surface mediated the magnesium dissolution, which not only prevented the magnesium substrate from violent dissolution but also resulted in a uniform coating (Fig. 5, pH = 10.6). With the further increase in pH, however, Mg enters into its stable region and the dissolution was further slowed down therefore leading to a decrease in copper coverage (e.g. Fig. 5, pH =11.2).
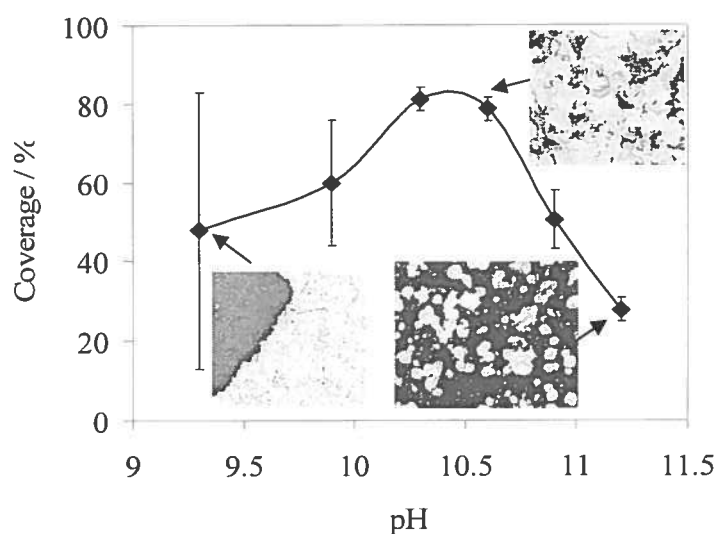

Fig. 5 Effect of pH on the surface coverage of CIC for AZ91D in a bath of 100g/l $K_4P_2O_7$ + 30g/l Na_2CO_3 + 5g/l NaF+12.5g/l $CuSO_4.5H_2O$ (coating time: 15 min).
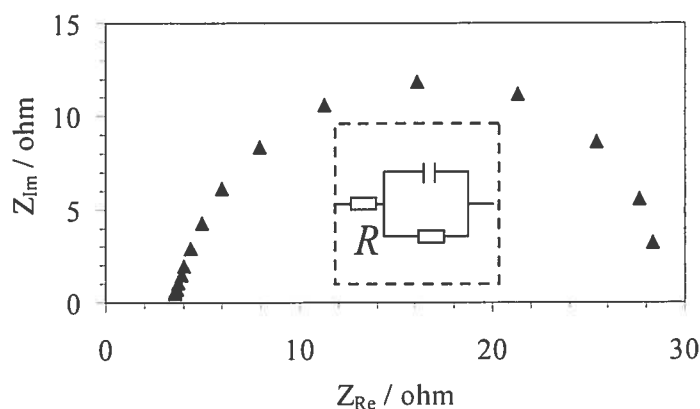

Fig. 6. Nyquist plot recorded for AZ91D in a bath containing $K_4P_2O_7$ 100g/l + Na_2CO_3 30g/l + NaF 5g/l (pH 10.3, immersion time 8 min). The insert is the equivalent circuit (Bias potential was 0.0V vs. OCP with a 5mV ac perturbation).
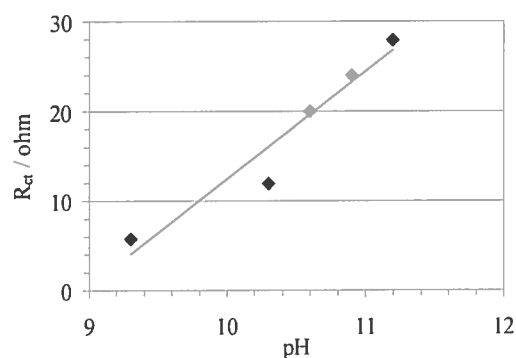

Fig. 7 Effect of pH on the charge transfer resistance (R_{ct}) derived from Nyquist plots in the same experimental conditions as in Fig. 5.

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It ought to be mentioned that the EIS was conducted in a bath containing NaF., without which a quality coating would not be achieved. Fig. 8 shows the effect of fluoride content in the coating bath on the surface coverage. Similar to the observation in the acidic bath, the surface coverage varies with fluoride concentration, with the maximum coverage obtained at an optimal range of fluoride concentration. This phenomenon might be related to the surface fluoride film formation similar to that discussed for acidic bath [6, 10]. According to Fig 8, this optimal range is from 5g/L to 10g/L, with a pH range of 10.3 – 10.6.

Fig. 8 Effect of fluoride concentration on the surface coverage of (CIC) for AZ91D in a bath containing $K_4P_2O_7$ 100g/l + Na_2CO_3 30g/l + 12.5 g/l $CuSO_4.5H_2O$ + NaF in various concentrations (pH = 10.6, coating time: 15 min).

2.2.4. Summary

It has been demonstrated that in an acidic bath, hydrofluoric acid can be employed to control the magnesium dissolution, and application of sonication could be used to modify the kinetic process. In the alkaline bath both pH and the fluoride concentration play an important role in controlling the copper immersion coating process. In both the acidic and the alkaline baths investigated, uniform and fine grained copper immersion coatings were achieved.
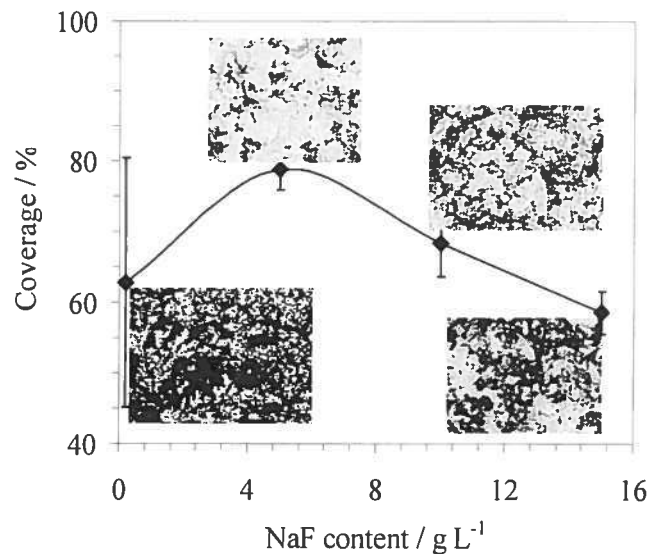
3. Application of electroless Ni-P on Cu immersion coated Mg AZ91 alloy

An acceptable coating on Mg alloy (i.e. AZ91D) requires the following characteristics. The coating needs to be corrosion and wear resistant, free of defects, and cost effective, and be simply produced by a safe procedure. Electroless Ni-P deposition meets most of these expectations. While the autocatalytic nature of the process provides a uniform coating even on complex shapes, challenge exists in its short bath life due to sudden bath decomposition. This is further aggravated when plating Mg alloys due to the dissolution of active Mg nuclei. The inherent problem of the electroless deposition process is overcome by applying a layer of Ni-P alloys on the immersion coated copper describe above.

The electroless Ni-P deposition was carried out in a bath containing: 30 g/L $NiSO_46H_2O$, 20 g/L CH_3COONa, 20 g/L $NaH_2PO_2•xH_2O$, and 0.1-5.0 mg/L $(H_2N)_2CS$ (or 0-3.0 g/L $C_4H_2O_3$). pH was adjusted with HCl to 4.5.

The electrochemical corrosion performance was investigated in the neutral 5 % (wt.) NaCl solution.

EDX analysis confirmed that no Mg or Cu dissolution was detected (Fig. 9), indicating that the Ni-P coating successfully protected the inner layer from the long period of corrosion in 5 % NaCl solution.

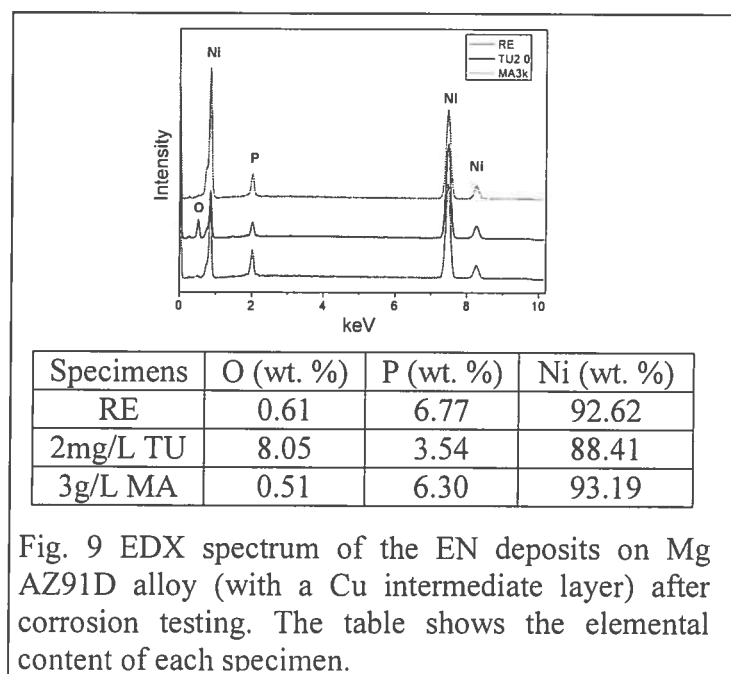| Specimens	O (wt. %)	P (wt. %)	Ni (wt. %)
RE	0.61	6.77	92.62
2mg/L TU	8.05	3.54	88.41
3g/L MA	0.51	6.30	93.19

Fig. 9 EDX spectrum of the EN deposits on Mg AZ91D alloy (with a Cu intermediate layer) after corrosion testing. The table shows the elemental content of each specimen.

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