

Metallurgy of Magnesium – a Problem in Surface Treatment?

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Magnesium is becoming a very interesting material for many industries. New alloys with attractive properties such as improved strength, better creep performance and good ductility have penetrated the market in recent years. These types of magnesium alloys contain zirconium, zinc, aluminum, manganese, silicon etc.. Surface treatment such as plating, anodizing and other types of conversion coatings can be strongly affected by metallurgical phases containing these alloying elements. In this work especially AZ91 and AM50/60 have been investigated.

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Introduction to Metallurgy of Magnesium:

Magnesium alloys are one of the lightest groups of construction metals used today. With a density of only 1.74 g/cm^3 for pure magnesium (aluminum: 2.70 g/cm^3), and a very high strength to weight ratio, magnesium alloys are very attractive materials for the aerospace and automotive industries.

There are numerous types of different magnesium alloys available for commercial applications, but two alloys, AZ91 and AM60 are predominantly used. The naming of magnesium alloys follows a simple system as described below.

Magnesium alloys are named after the alloying elements, and the quantity of the elements given in weight percent. The first letter indicates the element present in largest quantity and the second letter the element present in second largest quantity. The rest of the alloying elements present are not listed in the alloy designation, but can still affect the properties of the alloy. The numbers following the letters indicate the quantity of each alloying element present in the alloy (table 1).

Table 1
The Nomenclature for the Different Alloying Elements Used in Magnesium Alloys.

A	Aluminum
C	Copper
E	Rare earth metals
H	Thorium
K	Zirconium
L	Lithium
M	Manganese
Q	Silver
S	Silicon
W	Yttrium
Z	Zinc

As an example, AM60 alloy is a magnesium alloy containing about 6 wt. % aluminum and less than 1 wt. % manganese. AZ91 alloy contains about 9 wt. % aluminum and 1 wt. % zinc. The declaration of the alloying elements are often followed by a letter that indicates the technical state of the alloy. A declaration like AZ91D is the fourth registered composition of the AZ91 alloy, and it possesses the highest purity of the registered compositions. The exact composition of any given alloy is included in the supply from the manufacturer.

An X after the alloy declaration indicates that the composition of the alloy is still under development.

After the alloy declaration code the heat treatment can be stated and informs about the heat treatment of the present alloy. The codes for heat treatment of magnesium are similar to codes for aluminum.

As mentioned above, the two most frequently used alloys are AZ91 and AM60. Traditionally it is AZ91 that is used in largest quantities but AM60 alloy is gradually gaining a greater market share. The reason why AZ91 alloy is so frequently used is that it possesses good values in a broad spectrum of properties, such as strength, elasticity, elongation after fracture and ultimate tensile strength. The strength to weight ratio is especially high for magnesium alloys because of the light weight of the alloys. Magnesium alloys also possess shielding against electromagnetic radiation, and are used in laptop computers and cellular phones.

Nowadays the AM60 alloy is used more and more, and the most common process for manufacturing components is die casting. The AM60 alloy has become very popular especially because of its very high ductility (15%). Other properties such as impact strength and corrosion resistance are also better for the AM60 alloy than for the AZ91.

The manganese content is responsible for the improved corrosion resistance, because manganese forms inactive intermetallic compounds with iron and copper, that reduce the impurities in the alloy, and thereby reduce the galvanic activity within the alloy.

The Mechanism Behind Corrosion of an Untreated Surface of a Magnesium Alloy:

The corrosion resistance of a magnesium alloy strongly depends on the impurities in the alloy, the microstructure and the environment to which it is exposed.

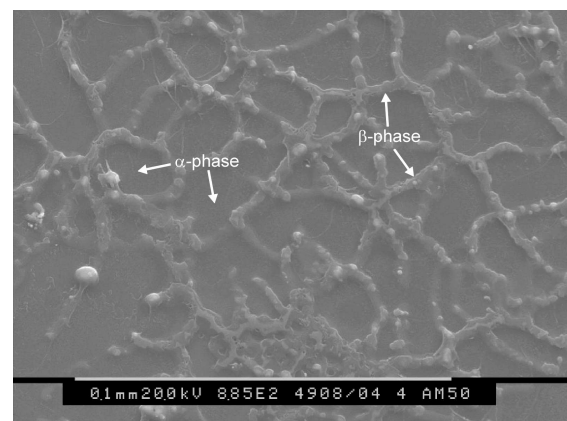


Figure 1 – Intermetallic Phases in a Magnesium Alloy

Traditional electrochemistry defines corrosion from the anodic and the cathodic reactions.

The corrosion of magnesium alloys normally takes place as a result of the difference in electrode potential between the different phases in the present magnesium alloy.

The magnesium rich α -phase will always be the less noble of the present phases in the alloys, and hence during galvanic corrosion it is the α -phase that corrodes as the first phase. See figure 1 for α - and β - phases. EMBED EMBED

Normally an increase of the anodic polarization will increase the rate of the anodic reaction, and reduce the rate of the cathodic reaction. In the case of zinc and iron an increase of the potential will increase the dissolution of the metal and reduce the hydrogen formation.

In the case of magnesium another phenomenon called NDE (negative difference effect) takes place. The NDE phenomenon is a unique property for magnesium.

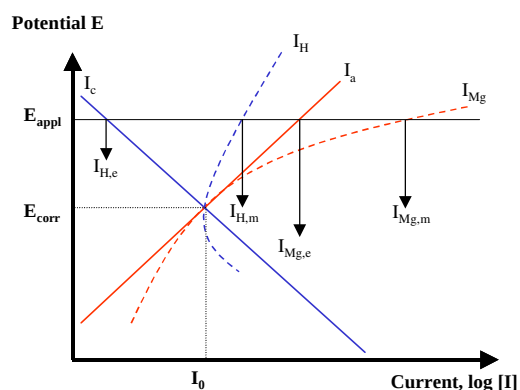


Figure 2 – Current – Potential Diagram to Illustrate the NDE Phenomenon

The NDE is outlined in the current – potential diagram shown in figure 2. In the figure the normal anode and cathode reactions are shown as the straight lines, I_a and I_c , according to the Tafel kinetics. At the corrosion potential E_{corr} , the figure shows a corrosion rate according to I_0 and applied potential E_{appl} . In theory, the Tafel kinetics gives rise to a corrosion rate indicated by the intercept $I_{Mg,e}$, and a hydrogen rate of formation $I_{H,e}$. However for magnesium the situation is totally different and unexpected. It is shown by experiments that an increase in the applied potential increases the corrosion rate of magnesium and at the same time increases the hydrogen formation. As mentioned before, this should actually have resulted in a decrease in the rate of formation for hydrogen.

The phenomenon is shown in figure 2 as the dotted lines I_{Mg} and I_H . The lines show that the hydrogen formation increases if an anodic polarisation is applied, and follows the line I_H . This indicates that at an applied potential, E_{appl} , the rate of hydrogen production is in fact $I_{H,m}$. It is also

noted that the actual rate $I_{H,m}$ is much higher than the theoretical $I_{H,e}$. Under these circumstances NDE takes place and is calculated as:

$$\Delta = I_0 - I_{H,m}$$

Δ is negative for magnesium as $I_{H,m}$ is bigger than I_0 . This phenomenon where $I_{H,m}$ deviates from the theoretical expected I_0 is called the negative difference effect. It is only called NDE when Δ is negative, as the electrode behaves according to theory when the values are positive.

Another experimental observation is that the dissolution of magnesium progresses faster than expected by the theoretical anode reaction, indicated by I_a . This is shown by the dotted line I_{Mg} , which is to the right of the I_a -line. As a result of this, the applied potential gives rise to an increased corrosion rate of magnesium according to $I_{Mg,m}$ instead of the expected $I_{Mg,e}$. As the figure shows, the corrosion rate is much higher than expected.

An explanation of the NDE is that exposed surface area increases as the applied potential or current density increases. These surface areas are free of surface film, and are essential to the NDE. In the film-free areas, magnesium corrodes by formation of the monovalent ion Mg^+ and hydrogen. The proposed reactions are:

- (1) $Mg \rightarrow Mg^+ + e^-$
- (2) $Mg^+ + H_2O \rightarrow Mg^{2+} + OH^- + \frac{1}{2} H_2$

When the applied potential or current density is very negative, the surface film stays intact. There is thus little or no exposed film-free surface area, and the anodic dissolution of magnesium is therefore very little. Contrary to this, hydrogen production can occur on a film covered surface at a sufficient negative potential, but the reaction rate decreases until the pitting potential is reached.

During pitting the surface film is destroyed, and both magnesium dissolution and hydrogen production evolves easier on the film-free surface. With increasing potential or current density the expansion of the film free surface area increases, which gives rise to increased reaction rates of reaction (1) and (2).

Surface Treatment of Magnesium:

Magnesium has to be protected with a surface treatment because the material is very sensitive to corrosion.

To increase the corrosion resistance of magnesium alloys the alloys can be surface treated by chemical or electrochemical means. Examples of the best known surface treatment methods are:

- Electroplating (Cu, Ni etc.)
- Electroless plating with EN (Electroless Nickel)
- Anodizing
- Chemical conversion coatings (chromating, stannate treatment etc.)

Electroplating of magnesium:

When plating magnesium alloys it is important to clean and activate the surface properly before plating. The surface can be contaminated with both organic and inorganic compounds depending on the casting process and the post processing after casting (tooling, grinding etc.). Under the casting, process additives (for instance silicones) are applied to decrease the stick properties. These thermally decomposed compounds (MgO/SiO_2) formed under the casting process have to be carefully removed from the surface before starting the plating process. Otherwise insufficient adhesion or corrosion protection will be a result of bad preparation prior to surface treatment.

Organic contamination can normally be eliminated by an alkaline soak cleaner and/or electrolytic cleaning (cathodic). The compounds formed by the thermal processes (depending on the alloy composition of the metal) can be removed from the magnesium surface by activating or etching in an acidic solution based upon an carboxylic acid or fluoride containing mineral acid. After cleaning the surface of the material, it has to be "activated" so a chemical pretreatment before the real electroplating takes place.

A common way to electroplate upon a magnesium surface is to apply a thin layer of zinc by an ion exchange plating (zincating) based upon pyrophosphate. The zincate treatment upon the magnesium surface is applied to avoid the formation of magnesium oxides which form very quickly because of the thermodynamic conditions for the metal. A similarly method is also used before plating of aluminum.

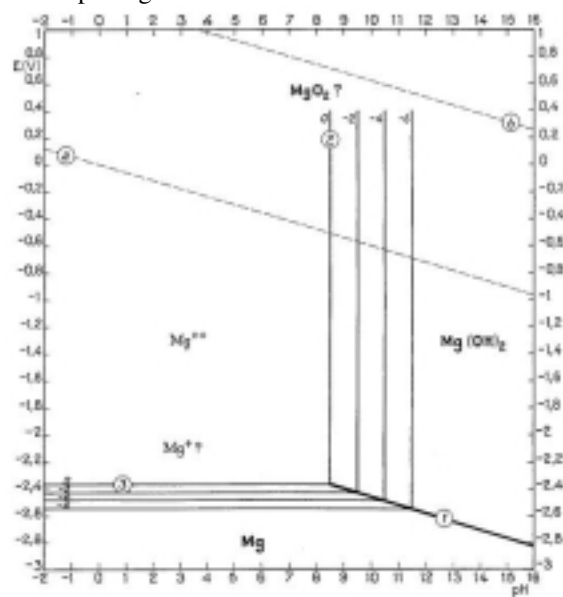


Figure 3 – Pourbaix Diagram for the Magnesium – Water System at 25 °C

It is important to obtain a dense zincating layer to avoid galvanic corrosion during the next process

steps, where an alkaline cyanide copper bath (Rochelle-bath) is the first step. This step is normally not critical because magnesium is passive at that pH and potential, according to the Pourbaix diagram for magnesium shown in figure 3.

The next step is much more critical, and is typically carried out in a Watts nickel bath with a pH of about 4.0 or an acid copper bath with an extremely low pH. These plating steps can cause severe problems because of a corrosion attack of the base metal through possible pores introduced by an insufficient zincate treatment. The corrosion attack will already take place under the plating process in the acid electrolytes.

The copper or nickel process can be followed by all types of plating processes to obtain decorative or technical surfaces.

Depending on the alloy composition there are large differences in the activation before the zincating process.

For instance the activation method used on the AM60 alloy will cause severe corrosion on the AZ91 alloy. It is therefore not easy to apply a single process method for plating various magnesium alloys, but the series of steps in the plating process must be carefully selected to suit the different alloys.

Figure 5 demonstrates these problems in a series of pictures from the plating process of a cast AM60 alloy. Picture (a) shows the untreated surface before the plating process. The picture illustrates the as cast surface with grains and thermal decomposed anti stick compounds on the surface. In picture (b) and (c) the surface is shown after two different acidic treatments. In picture (b) the α -grains remain. Picture (c) illustrates the surface after pickling in an acidic solution. In the picture the α -grains are removed and the grain boundaries prevail. The grain boundaries mainly consists of the β -phase with the composition $\text{Mg}_{17}\text{Al}_{12}$. The β -phase is located in the middle of the phase diagram in figure 4.

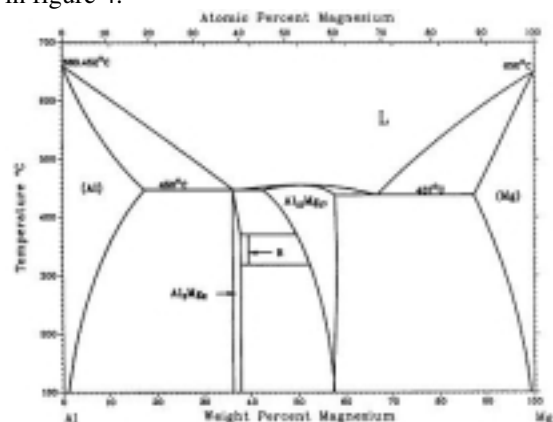
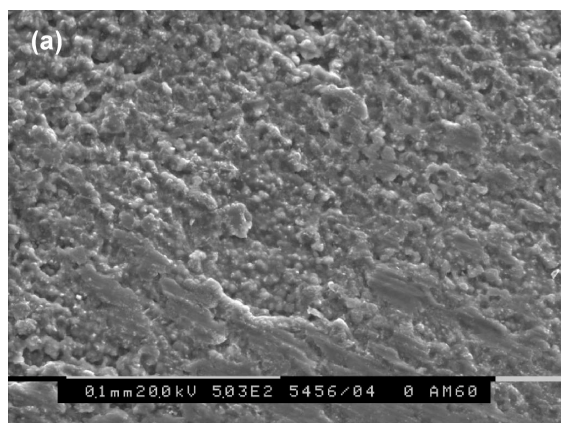
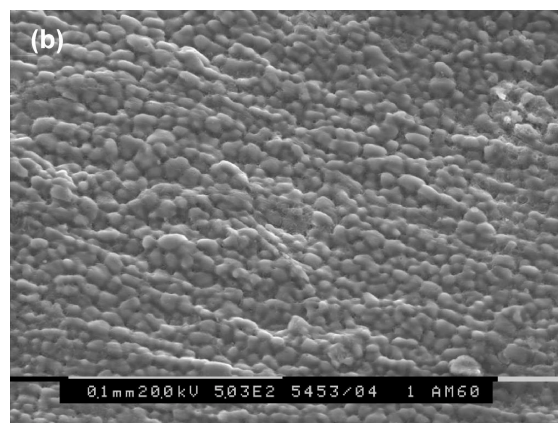


Figure 4 – Phasediagram for the Al-Mg system

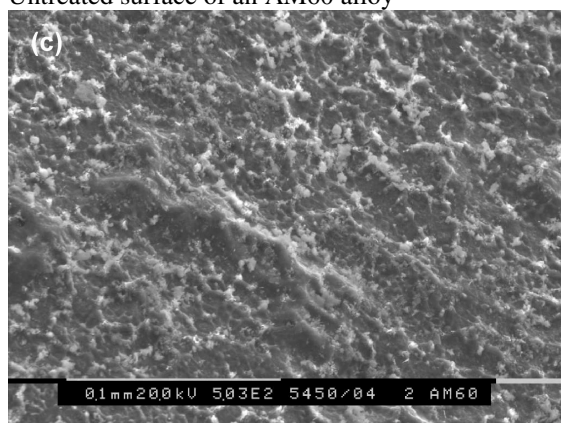
Picture (d) shows the surface after it has been activated in a basic NH_4HF_2 -solution. The surface



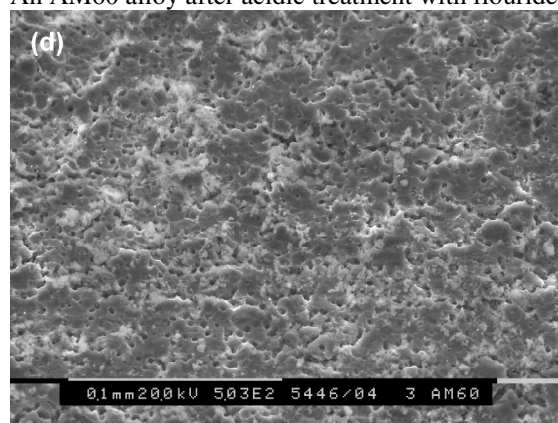
Untreated surface of an AM60 alloy



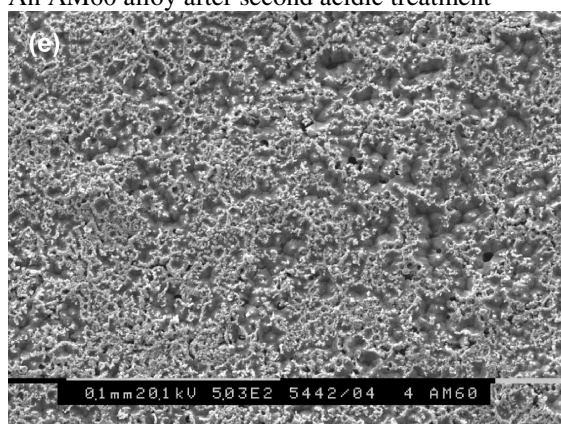
An AM60 alloy after acidic treatment with fluoride



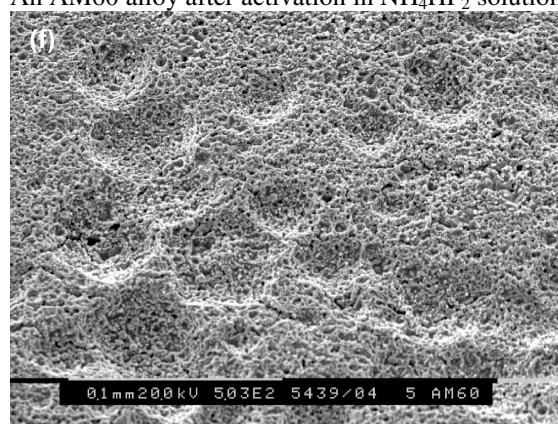
An AM60 alloy after second acidic treatment



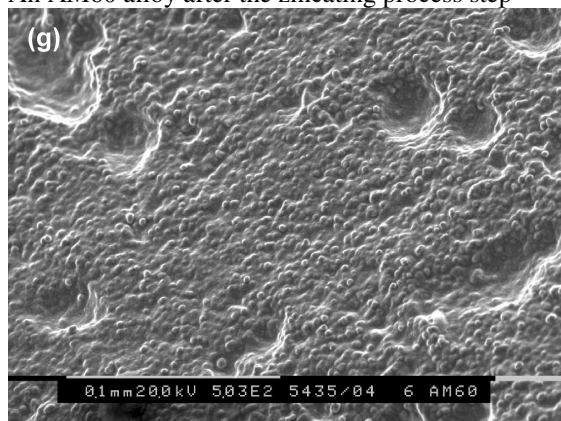
An AM60 alloy after activation in NH_4HF_2 solution



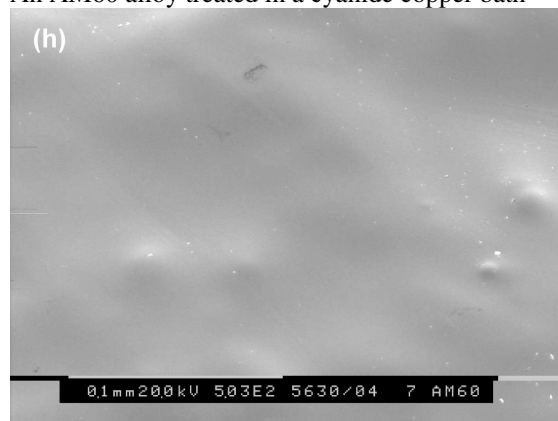
An AM60 alloy after the zincating process step



An AM60 alloy treated in a cyanide copper bath



An AM60 alloy treated in an acid bright copper bath



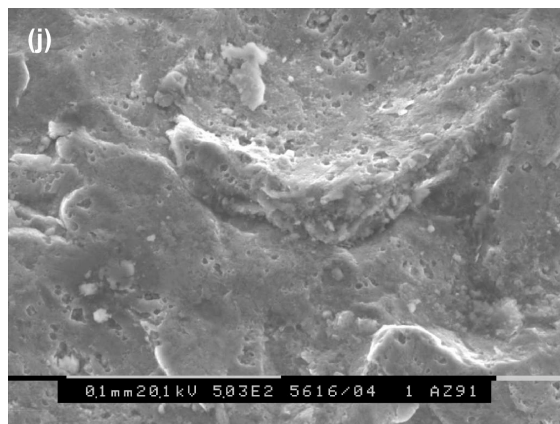
An AM60 alloy electroplated in a bright nickel bath

Figure 5 – Pictures of the AM60 Surface After Different Steps in the Plating Process

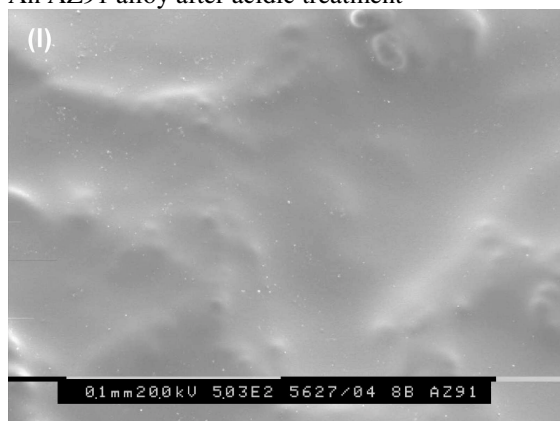
is now more homogenous and the α -grains are distributed on the surface. The surface is now sufficiently receptive for the zincating process. This step is shown in picture (e) where the zinc phases are the light phases. The zinc crystals have grown dendritically from the alloy surface. Picture (f) shows the AM60 surface after plating in a cyanide copper electrolyte. The picture illustrates that the surface layer is not dense (i.e. porous) and that the copper layer is mainly deposited on the top of the zinc dendrites. The final picture (g) shows the surface after treatment in an acid bright copper electrolyte. The surface is now very dense and smooth because of the levelling effect. The treatment in an acid bright copper electrolyte shows that the surface is durable because the electrolyte is very acidic and will cause severe corrosion of the magnesium surface if the underlying zincate and copper layer processed in the preceding alkaline processes contains defects and pores. A good levelling electrolyte is able to eliminate mechanical defect in the surface and improve the corrosion protection of the base metal. Picture (h) illustrates the surface after electroplating in a bright nickel bath.

Direct plating of magnesium without zincating is possible when applying a specially formulated electroless nickel based upon fluoride. The function of the fluoride is to form a coating on the surface to prevent uncontrollable ion exchange plating of nickel upon the magnesium surface. The process is seldom used in practice.

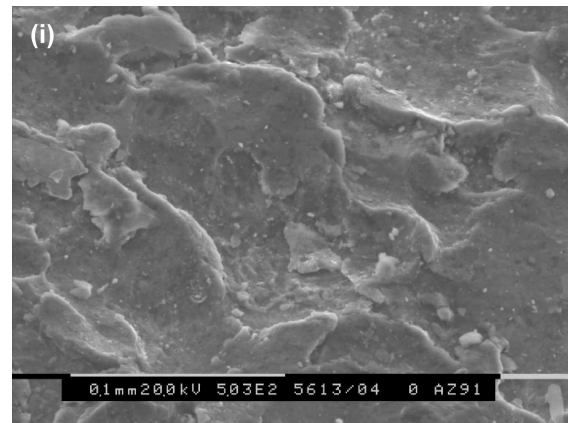
In figure 6 pictures from a plating process of an AZ91 alloy is shown. Picture (i) illustrates the untreated as cast surface. Release agents and other



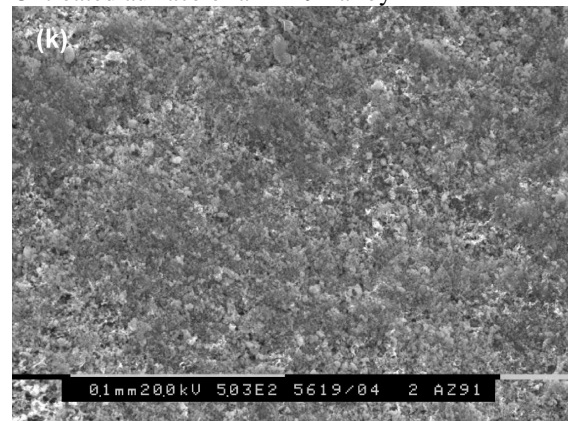
An AZ91 alloy after acidic treatment



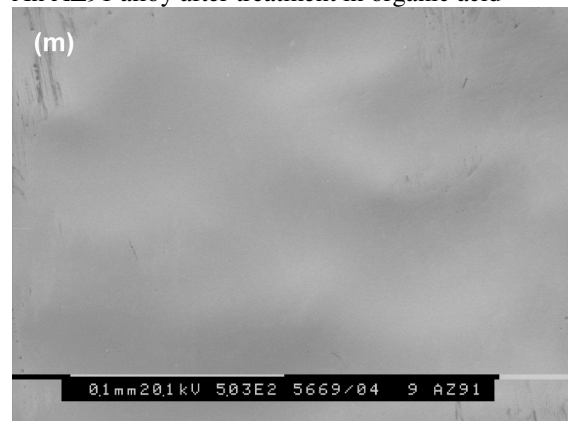
An AZ91 alloy treated with acid bright copper



Untreated surface of an AZ91 alloy



An AZ91 alloy after treatment in organic acid



An AZ91 alloy electroplated with bright nickel

Figure 6 – Pictures of the AZ91 Surface After Different Steps in the Plating Process

impurities can be seen. In picture (j) the surface after acidic treatment is illustrated. Impurities are removed leaving small indentations where the release agents and impurities were situated. If the AZ91 alloy is exposed to an organic acidic pickling, the surface corrodes as illustrated in picture (k). The formed corrosion products results in very poor adhesion of the next surface layer. This shows the different approaches that have to be taken in working with different alloys. Picture (l) illustrates the surface post treatment in an acid bright copper electrolyte. The surface is all most fully levelled and free of surface defects. The surface post treatment in a bright nickel bath is illustrated in picture (m).

Anodizing of Magnesium:

Electroplating of magnesium is a good method for obtaining many different technical properties upon the surface, but application of conversion processes is another viable method especially if corrosion protection is important.

Among the most popular processes are anodizing and chromating, where especially anodizing is able to improve both corrosion and wear protection.

Anodized coatings on magnesium range from thin clear to light gray-green, to thick dark green or brown coatings. The clear coatings are used as a base for subsequent clear lacquers or paints to produce a final appearance similar to clear anodizing on aluminum.

The Dow 17 anodic finish results in a light gray-green to dark green coating and are used in most applications which are to be painted. The thick, dark green coating offers best combination of abrasion resistance, protective value and paint base characteristics. The thin coating is light gray to pale green in color and about 5.0 microns in thickness. The thicker dark green layer can be as thick as 30 microns. See table 2 for composition.

The HAE anodic finish is probably the hardest coating available for magnesium and is available in different chemical variations. They exhibit stability at high temperatures and good dielectric strength. They are excellent as paint base. The HAE coating requires resin seal or paint for maximum corrosion protection. When using the HAE anodic finishing a surface layer varies from a light tan sub coating about 5.0 microns thick to a thicker phase formed at higher voltage. The latter is normally dark brown and usually about 30 microns thick. See table 2 for composition.

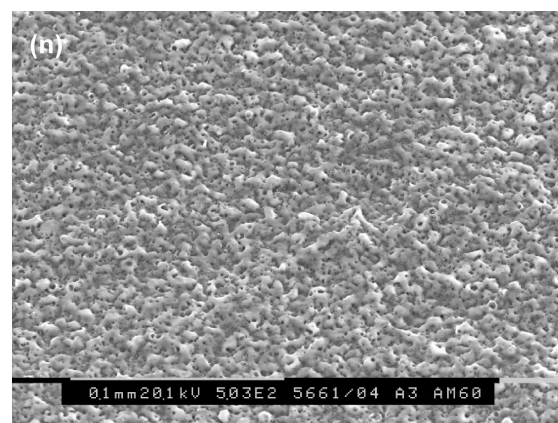
In figure 7 picture (n) is shown an anodized surface of an AM60 alloy. The sample has been anodized in a Dow 17 solution for approximately five minutes. This kind of treatment does not have a levelling effect as the plating processes. The picture

Table 2
Composition of the Dow 17 and HAE Anodizing Solutions.

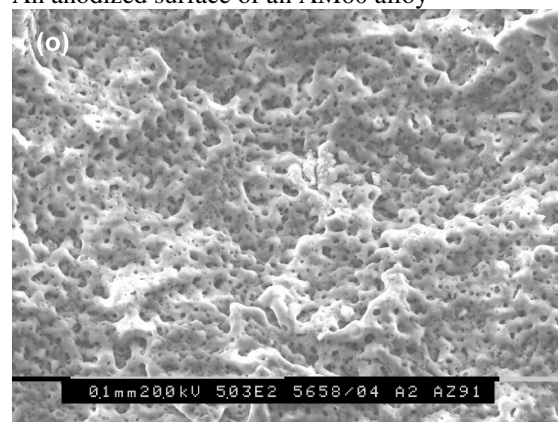
Name	Composition
Dow 17	240 g/L NH_4HF_2 100 g/L $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ 90 g/L 85 % H_3PO_4
HAE	165 g/L KOH 34 g/L $\text{Al}(\text{OH})_3$ 34 g/L K_2F_2 34 g/L Na_3PO_4 19 g/L K_2MnO_4

illustrates that anodizing is a conversion coating and the surface does not appear to be smoothed. Prior to the anodizing the material was given a similar treatment as shown in picture (c) in figure 5. The two pictures have similar surface roughness.

The similar effect is observed on the surface of an anodized AZ91 alloy sample. This is illustrated in picture (o) in figure 7. In comparison to the anodized surface, picture (j) in figure 6 illustrates the surface prior to anodizing.



An anodized surface of an AM60 alloy



An anodized surface of an AZ91 alloy.

Figure 7 – Pictures of Anodized Surfaces of AM60 and AZ91 Alloys.

Summary

Nowadays magnesium alloys are gaining more market shares. This is mainly due to their high strength to weight ratio. When using magnesium alloys commercially it is important to improve the corrosion resistance to give them better resistance to corrosion and longer lifetime.

When it is desired to improve the durability and performance of magnesium alloys, surface treatment can give a good and reliable solution. Prior to surface treatment it is important to possess the necessary knowledge about intermetallic phases and their interactions, and also the corrosion properties of the specific alloy. These issues are important to the result of the surface treatment, and have to be considered carefully to achieve a useful result.

When surface treating magnesium alloys it is important to clean and activate the surface before beginning the actual plating or conversion coating. The cleaning and activating steps are crucial to a successful result. Therefore it is necessary to adjust the pretreatment to the desired alloy.

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