ENVIRONMENTALLY FRIENDLY PROTECTION SYSTEMS OF Mg AND Al LIGHT ALLOYS

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Summary: Anodic coatings on light metals have a great potential to be an alternative to toxic chromium treatments. This electrochemical oxidation process is an effective method to improve the corrosion resistance of Mg, Al and their alloys by forming a protective, typically 1-150 μm-thick layer on their surface. It is possible to conduct anodizing process by two different approaches: below (typically in acidic solutions) and above breakdown potential (in basic solutions), the latter known as Plasma Electrolytic Oxidation (PEO) process. The different mechanisms of anodic layer formation lead to varied morphology of obtained coating. Both types of anodizing have a greater variety of factors that can be easily modified and affect the final composition and structure of the obtained coatings and their anticorrosive properties.

Keywords: anodizing, plasma electrolytic oxidation, corrosion protection, light alloys

1. INTRODUCTION.

Since fossil fuels energy sources are being fast depleted, the further reduction of their utilization in the transport and aeronautic industry is a burning topic. One of the strategies to achieve this goal is a reduction the weight of the vehicles through the use of light metal alloys such as aluminium and magnesium.

Al and Mg alloys are very commonly used lightweight materials because of their unique physical and chemical properties. Mg is the lightest of the metals that can be applied in the vehicles engineering, having a density of 1.74 g/cm^3. It is 35% lighter than aluminium (2.7 g/cm^3) and about four times lighter than steel (7.86 g/cm^3). Both metals are active elements with low corrosion resistance predetermined by its atomic properties and its standard potentials: $E° = -2.37$ V_{SHE} for Mg, and $E° = -1.66$ V_{SHE} for Al. This makes those metals highly susceptible to atmospheric and galvanic corrosion, the latter caused by presence of intermetallic particles in the alloys. In the presence of humidity and some ions like Cl$^-$ from sea-water, micro-galvanic couplings are formed between the metal matrix and intermetallic particles which fast leads to initiation of the corrosion process. The typical and the most effective way to prevent corrosion of metal surface is to isolate it from the corrosive environment by creating a barrier layer.

For a very long time, since 1920's, the majority of corrosion protection surface treatments for metals employed products containing hexavalent chromium as they possess high efficiency; unfortunately Cr(VI) it is very harmful for humans and environment. According to REACH (EC 1907/2006) regulation it is required to abandon using these compounds by September 2017. The urgency for their replacement is the main motivation for our studies. The challenge of such a replacement consists in meeting the combined requirements of excellent corrosion resistance, fatigue performance, adhesion to paints and primers and of being economically reasonable.

One of the approaches to provide the corrosion protection of metal surface consists in its electrochemical treatment in electrolyte, called anodizing. This electrochemical oxidation process is an effective method to improve the corrosion resistance of Mg, Al and their alloys by forming a protective, typically 1-150 μm-thick layer on their surface. The formed coating is characterized by good adhesion to the substrate and comprise a barrier layer that isolates the base material from aggressive environmental agents. In general, it is possible to conduct anodizing process by two different approaches: below (typically in acidic solutions) and above breakdown potential (in basic solutions). Classical method of anodizing in a low potentials region and acidic solution is well applicable for Al alloys but not very suitable for Mg alloy. It is because the value of Pilling-Bedworth ratio (molar V_{ox}/V_m) for MgO/Mg system is only 0.81 which leads to a strong cracking of the oxide coating. Therefore, it is necessary to introduce into Mg oxide layer other types of chemical species, preferably with big volume and corrosion resistance, which is possible only if anodizing is carried out above breakdown potential by plasma electrolytic oxidation process (PEO).

2. NEW TRENDS ON ANODIZING OF ALUMINIUM ALLOYS FOR CORROSION PROTECTION.

As an environmentally friendly alternative to chromic acid anodizing (CAA) different processes have been developed based on phosphoric acid anodizing (PAA), sulfuric acid anodizing (SAA) and mixed electrolytes such as boric-sulfuric acid anodizing (BSA), phosphoric-sulfuric anodizing (PSA), phosphoric-sulfuric-boric acid anodizing (PSB) or tartaric-sulfuric acid anodizing (TSA)[1-4].

The anodized film is normally characterized by a duplex structure, composed of an inner thin barrier layer and an outer thicker porous layer. The microstructure depends on the substrate composition and the anodizing conditions, ranging from linear porosity, typical of pure aluminium, to a sponge-like porosity on copper-containing alloys [5].
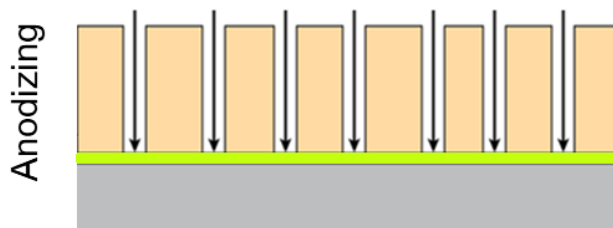

Figure 1. Schematic diagram of an anodized aluminium cross-section.

Recent advances in anodizing of aluminium and its alloys for corrosion protection involve different strategies that can be summarized as follows [6-9]:

i)   **In situ doping**: allows the incorporation of compounds into the anodic oxide film during the treatment, improving the coating properties. Different additives have been used for this purpose including: $Ce(SO_4)_2$, Na_2MoO_4, $KMnO_4$ and adipic acid, Na_2MoO_4, $KMnO_4$ and $LiNO_3$.

ii)   **Pulse anodizing:** non-constant voltage regimes influence the final oxide morphology and therefore its properties. Optimization of pulse voltage/current has been reported to improve significantly the corrosion properties.

iii)   **Post-treatments with inhibitors:** this strategy combines the anodic film passive protection with active protection provided by the corrosion inhibitors. In contrasts to base coatings which isolate the whole metal surface from corrosive media, inhibitors are able to target specific regions of the metal surface, interact with metal surface in corrosive media and precipitate in form of an insoluble compound in the place of coating damage. The porous structure of the anodic films can be used as reservoir for the corrosion inhibitors and can be an excellent base for adhesion of paint and primers which is a crucial parameter for industrial applications.

3. ADVANCED ANODIZING FOR Mg AND Al: PLASMA ELECTROLYTIC OXIDATION.

Plasma electrolytic oxidation (PEO), also known as micro-arc oxidation or spark anodizing, is a surface modification technique used to produce ceramic-like coatings on aluminium, magnesium, titanium and other valve metals. The technique involves the polarization of the alloy under high voltage causing the dielectric breakdown, which generates short-lived plasma microdischarges across the growing oxide. Different electrical regimes can be used for PEO processes including DC, AC, unipolar or bipolar pulsed regimes

(Figure 2). It is important to notice that microdischarges can be better controlled using alternating current and complex waveform designs [10].
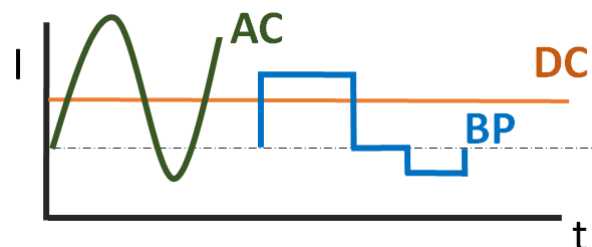

Figure 2. Modes of PEO processing.

The mechanism of formation of PEO coatings is a complex process including chemical, electrochemical, thermodynamic and plasma-chemical reactions that has been described using different models, e.g. dielectric breakdown, discharge-in-pore, and contact glow electrolysis [11].

The most common electrolytes are based on silicate, phosphate, aluminate and fluoride compounds, or mixtures of thereof and their composition is important for tailoring the final coating in terms of composition and morphology [12].

Oxide layers can be developed in a range of 5-150 µm-thick and usually contain crystalline and amorphous phases with species originating from the substrate and the electrolyte [10,12]. The coatings generally show 2-3 different layers that can be divided into a dense barrier layer in the interface substrate/coating, followed by a intermediate layer with low porosity and a more porous outer layer (Figure 3 and 4).
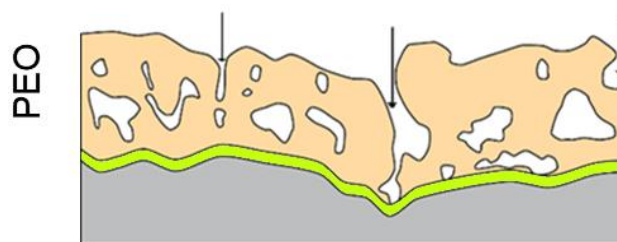

Figure 3. Schematic diagram of a 2-layer PEO cross-section.

It is well known that PEO coatings improve the corrosion and wear behavior of the Mg and Al based materials acting as a passive barrier. Novel trends for corrosion protection are focused on the possibility to grow PEO coatings with a <5 µm thickness fast (so-called "flash-PEO") and offer a "self-healing" functionality to defects arising during service. Up to day this is still a challenge, but promising results have been recently reported. In particular, it is worth to notice the improved corrosion properties obtained for PEO coatings on Al alloys with nanocontainers based on Layered Double Hydroxides (LDHs). LDHs consist of layers of mixed metal hydroxides separated by layers of anions

and water and their protective mechanism involves both the absorption of chloride anions from the corrosive environment by ion-exchange mechanism and release of incorporated ionic inhibitors triggered by this process [14-17].
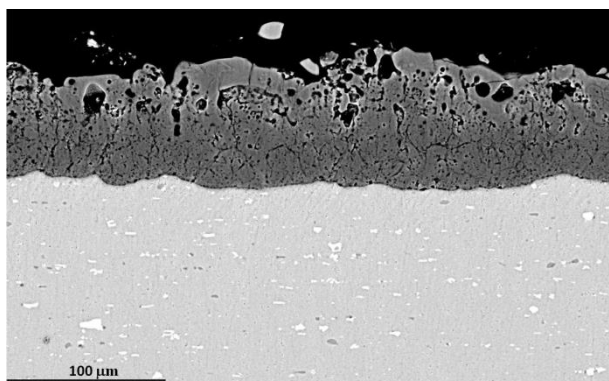

Figure 4: SEM cross-section of a 3-layer PEO coating on AA6082 developed in silicate electrolyte

4. OUTLOOK.

Literature analysis shows wide interest in anodic and/or plasma electrolytic oxidation coatings on Mg and Al as an alternative to toxic chromium (VI)-based treatments. Different approaches to improve the performance of anodic/PEO coatings are currently under investigation and the most novel trends are focused on the functionalization of surfaces using inhibitors.

5. ACKNOWLEDGNENTS.

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