

Research Paper

The study of Design Surface Treatment Obtained Metal Color in Magnesium Alloy

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Received February 2, 2017; revised February 27, 2017; accepted February 27, 2017

Abstract The shape of the reflection spectrum is complex and appears to overlap with several signals, because the surface state is uneven due to the natural oxide film, so that the spectrum becomes a complicated signal shape divided into regions 1 and 2 due to diffuse reflection. On the other hand, it is seen that the reflection spectrum after PEO surface treatment is overlapped with several signals. In addition, the reflectance of the energy band varies from 1.32 to 1.46 eV. Usually, the MgO-type oxide film was observed at an energy band of ~4.2 eV. The thickness of the oxide film was increased as the DC voltage was increased by the thin film thickness meter (QuaNix; 7500M) after Plasma Electrolytic Oxidation (PEO) surface treatment. This is because the higher the DC voltage, the easier the binding of the OH⁻ ions in the solution solution and the Mg⁺ ions of the magnesium alloy. An important part of the bonding of ordinary ions is the energy source (plasma) which can promote bonding. However, when a certain threshold voltage or more is applied, the material is adversely affected. The oxide film of the surface may be destroyed without increasing the thickness of the oxide film, that is, whitening of the material may occur.

Keywords: Magnesium, Surface Treatment, Industrial Design

I. Introduction

Surface treatment technology is a technique to improve the durability and functionality of materials and components by physically, chemically or electrochemically treating the surface of the material and to enhance the added value of the product by improving the appearance. Which is different from the Bulk characteristic of the material. There are two methods of surface treatment: wet process and anodizing process, electroplating process, electro less process, and coating / electrodeposition process. Dry process includes vapor deposition process, chemical vapor deposition process, And a plasma deposition equation. Wet surface treatment technology is mainly used as a final finishing process in the production process of products, and it is predominant in production of small quantity of various products due to pollution, technological diversity, closeness and expertise [1]. In addition, since the facility investment cost is lower than other industries and the factories can be operated on a small scale, there is a phenomenon of excessive competition in the order process, Technology development has become more stagnant. However, the wet surface treatment technology is widely applied to major and core parts ranging from general decorative accessories to the

automobile, semiconductor, and electronics industries, which are the major export industries of the current countries, to the aerospace industry, Which is a field where innovation of technology is required [2].

Dry surface treatment technology has been developed and applied recently as a process to improve the performance of products and to increase the added value by applying corrosion or abrasion resistance, lubricity and ornamentation to the material through vacuum deposition or plasma treatment. Especially, recently, the problem of polluting wastewater, which is a problem in the wet surface treatment process, can be completely solved by a vacuum process, and a new functional film can be created, and thus it is attracting attention as a new advanced technology field. This dry surface treatment technology is widely used as a technique for improving wear resistance and corrosion resistance in tools, molds, automobile parts, electric / electronic parts and other industrial fields, and is applied to high value-added decorative coatings of various ornaments. Dry surface treatment techniques result in new functional hard coatings, corrosion resistant coatings, lubricating coatings and plasma surfaces that are not obtainable through wet surface treatment and heat treatment techniques. Therefore, in this study, oxide film was formed by plasma electrode oxidation (PEO) surface treatment using AZ91D material for die casting in Mg alloys. The characteristics were studied by reflectance, metallographic

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microscope, scanning electronic microscopy and X-ray diffraction measurement. Usually design requires a lot of emotion. However, technology is more important for companies manufacturing goods first. Among the technical properties, design through surface treatment is important. Based on this analysis, we surveyed the technical requirements of customers in terms of industrial design.

II. Theory

(H_3PO_4), sodium silicate ($NaSi$), and potassium permanganate ($KMnO_4$) electrolytes from the conventional chromium / fluoride-based electrolytes even in the case of anodic oxidation. When ammonium phosphate is used, $Mg_3(PO_4)_2$ detected in the anode coating contributes to the improvement of corrosion resistance, and addition of ammonia, alcohols, amines, etc. contributes to flattening and densification of the film by discharge spark. In the case of the phosphate electrolytic solution, since a low-melting-point complex compound coating of MgO , $MgAl_2O_4$, and $Mg_3(PO_4)_2$ is formed in the magnesium alloy containing Al, gas discharge is facilitated during the solidification process. In the phosphate solution containing aluminate ions, a coating layer similar to an alumite coating observed in the anodic oxidation of aluminum is formed, and the addition of a trace amount of silicate greatly improves the corrosion resistance [3].

Also, by repeating the waveform for one minute after electrolysis using $KOH + Al(OH)_3$ mixed solution for 5 minutes, corrosion resistance is greatly improved even at low voltage. In addition, forsterite (Mg_2SiO_4) is formed by a multistage process which is anodizing with phosphoric acid solution ($K_2SiO_3 + KOH + KF$) and anodic oxidation after $100^\circ C$ H_2O . A method of obtaining a conductive film of 0.4Ω or less by anodic oxidation using a mixed solution of an aqueous solution of phosphoric acid and aqueous ammonia has been developed in order to shield electromagnetic waves from electronic devices and prevent electrification of electronic circuits [4].

Plasma electrolytic oxidation (PEO) using a discontinuous oxidation reaction accompanied by a spark discharge at a high voltage of several hundreds of volts exceeding the range of anodic oxidation has recently been noted. When a high voltage is applied between two electrodes, the voltage rises linearly in the anodic oxidation region and reaches the micro arc oxidation (MAO) region where the dielectric breakdown vibration occurs due to a minute discharge in the material immersed in the electrolyte. In the MAO region, a relatively thick porous film is formed and expected to be used as a surface treatment method for abrasion resistance, corrosion resistance and heat resistance. AZ91D alloy was formed by applying a voltage of 300 V for 5 minutes in an electrolyte (pH 12.86) of K_2ZrF_6 (10 g / l) - Na_2SiO_3 (10 g / l) - KOH (4 g/l) Show the film. The oxide layer grows to $12.9 \mu m$ in only 5

minutes to form a porous layer near the surface and a dense inner layer. The composite coating consisting of Mg_2SiO_4 , ZrO_2 , MgF_2 , and SiO_2 components has corrosion resistance even at $60^\circ C$ great. A PEO method has also been reported in which polytetrafluoroethylene (PTFE) nanoparticles are dispersed in a solution of a surfactant-added alkaline phosphate electrolyte to form a film on a pulsed power source, by filling the pores of the porous PEO film with a refractory material.

The PTFE nanoparticles contained in the electrolyte easily permeate into the micropores of the coating layer, so that a dense coating is formed as compared with the coating made only of PEO, and the corrosion resistance is improved [5]. In addition, hydrophobicity and lubrication effect of the PTFE component acts to improve abrasion resistance and to improve the corrosion resistance of magnesium which is vulnerable to moisture. A PEO coating method using CeO_2 particles using a Na_2SiO_3 -based electrolyte and a PEO + SNAP coating method using a self-assembled nanophase particle (SNAP) solution have been reported in a similar manner. In addition, recent studies on the PEO method have shown that the effect of various additives ($NaAlO_2$, $Na_2B_4O_7$, Na_3PO_4 , K_2TiF_6 , $CO(NH_2)_2$, etc.) on the corrosion resistance of PEO coatings in KOH -containing alkaline silicate electrolytes, The effect of current mode and discharge type on the corrosion resistance of PEO film, the effect of formation of nanocrystal sol gel layer for pore filling of PEO film, microstructure and corrosion resistance of pre-treated PEO film by laser Verification results are being published. Coating technology by PEO method has been actively researched in domestic universities and companies, and it is published as a thesis or patented technology [6].

III. Experiment

The surface treatment method used in this study is the PEO method and burning method using plasma. Fig. 1 is a general PEO process diagram. And Fig. 2 is a burning schematic. The burning method is a method of forming an oxide film by applying a volatile solution on a magnesium alloy surface and annealing. The experiment was carried out in a 1: 3 mixture of methanol (CH_3OH): acetone (CH_3COCH_3): chloroethyl ether (ClC_2H_4) 40: diacetone alcohol (CH_3COCH_2COH (CH₃) 2: dimethylglyoxime (CH_3)₂C₂ : 5: 8: 9 ratio and burned in the chamber to perform surface treatment.



Figure 1. Normal process of PEO method.

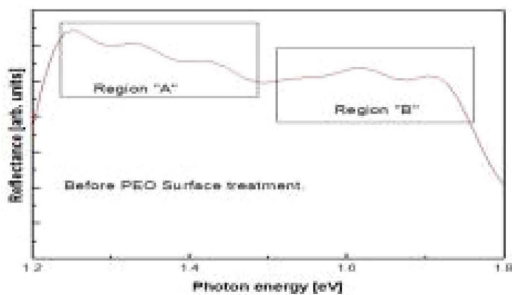


Figure 2. The photography of burning device.

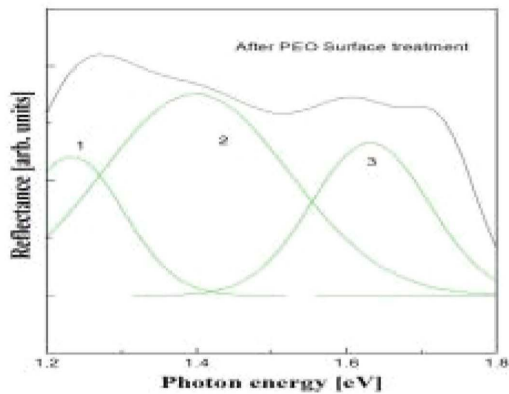
III. Results

1. Reflectance

Fig. 3(a) is the reflection spectrum before and after plasma electrolytic oxidation (PEO) surface treatment. As shown in the figure, the shape of the reflection spectrum is complex and overlaps with several signals. However, since the surface state is uneven due to the natural oxide film, the spectrum is divided into regions 1 and 2 by the influence



(a) Before PEO surface treatment



(b) After PEO surface treatment

Figure 3. The Reflectance spectrum in after PEO surface treatment and bulk.

of diffuse reflection, Because. On the other hand, Fig. 3(b) shows the reflection spectrum after PEO surface treatment. It is not a complicated form of the spectrum, but it can be seen that several signals are superimposed. Also, as shown in the figure, the reflectance changes greatly between 1.32 and 1.46 eV. In general, an oxide film of MgO type is observed at an energy band of ~4.2 eV. In particular, the reflectance intensity is dominantly observed between 1.2 and 1.5 eV. Therefore, it can be seen that the oxide film formed on the surface of AZ91D material is MgO type. And we observed that the observed signals were superimposed with three signals as a result of fitting using the Gaussian function. That is, spectra 1 and 2 are shapes due to the difference in reflectance due to porous pores present on the surface, and the actual spectrum of



(a) Before PEO surface treatment



(b) After PEO surface treatment



(c) PEO + Burning surface treatment

Figure 4. The photograph of metallography microscope in sample (a), (b) and (c).

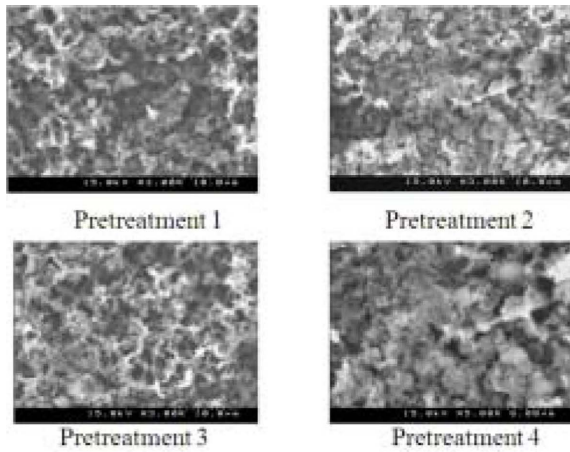
Mg(OH)₂ is spectrum 3. Usually, the surface of the PEO is an electrochemical reaction, and a MgO or Mg(OH)₂ type film is formed on the surface of the magnesium alloy [7].

2. Metallic microscope characteristics

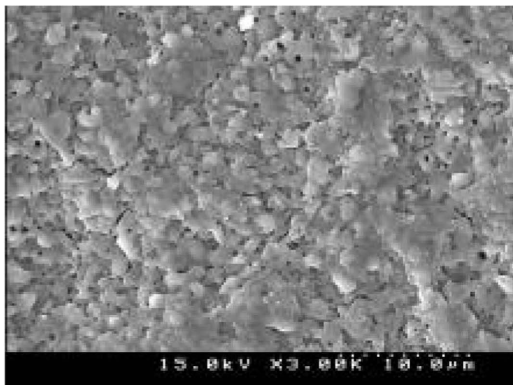
Fig. 4 is a photograph of a magnesium alloy PEO taken before and after surface treatment with a metallurgical microscope (500 X). As shown in the figure, the surface of the magnesium surface is markedly treated before (a), but after the PEO surface treatment (b), the oxide film is formed on the surface and the roughness of the surface state is much improved. (C) is a photograph of a PEO surface treated and then a burning surface treated again. As can be seen from the photograph, the surface condition is improved much more than PEO [8].

3. Scanning electronics microscopy(SEM)

Fig. 5(a) shows that the applied DC voltage is 50 V (pretreatment 1), 55 V (pre-treatment 2), 60 V (pre-

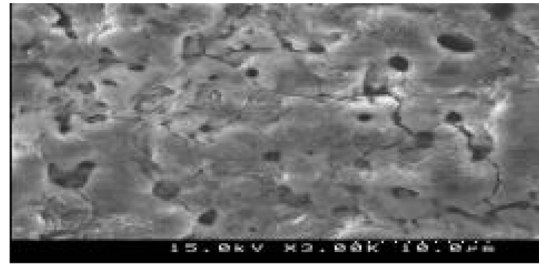


(a) pretreatment

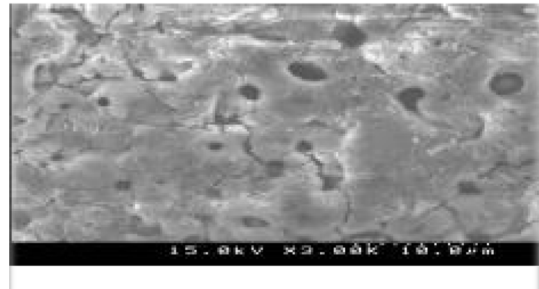


(b) Completion treatment

Figure 5. The Scanning electronics microscopy of pre-treatment(a) and finish treatment(b).(a) 1; 50 V, 2; 55 V, 3; 60 V, 4; 65 V, (b)70 V).



(a)After PEO surface treatment



(b)PEO + Burning surface treatment

Figure 6. The SEM of PEO, PEO + Burning treatments.

treatment 3) and 65 V And scanning electron microscopy (SEM) images showing the results. As the DC voltage increases, the bonding force of the oxide film on the surface becomes better. IV-3(b) is a SEM photograph of the experiment at 70 V for 30 sec. As can be seen, the shape of the surface oxide film is completely formed. Generally, when the PEO surface treatment increases the initial voltage and oxygen is generated on the surface, when the voltage reaches the breakdown voltage, the small flame travels rapidly over the surface of the sample for about 1 second to form a thin film, and then a film is formed on the entire surface of the sample, A small flame is generated in several places for about 4 to 5 seconds to grow the film and form a complete film as the PEO surface treatment proceeds. As the voltage increases, the flame movement becomes faster, which causes a thick, uniform film on the surface.

Fig. 6 is a SEM image of the surface after PEO surface treatment, followed by a burning process. As can be seen from the figure, it can be seen that the porosity number of the porous material is considerably reduced as compared with the result of the general PEO surface treatment. This is because the sizes of the pores generated during the surface treatment of PEO are different from each other because the chemicals are introduced into the pores relatively more than the surface while the burning process is performed to form more oxide films [9].

IV. Conclusions

In this study, for the development of high corrosion

resistance surface treatment process, AZ91D magnesium alloy is oxidized by DC voltage to 50~70 V during surface treatment of PEO, and the oxide is formed on the surface of material, and the reflection method, SEM, XRD, tensile stress test and Vickers The hardness test was carried out to investigate the properties of the magnesium alloy and the following conclusions were obtained.

1. The shape of the reflection spectrum is complex and appears to overlap with several signals, because the surface state is uneven due to the natural oxide film, so that the spectrum becomes a complicated signal shape divided into regions 1 and 2 by the influence of diffuse reflection. On the other hand, it is seen that the reflection spectrum after PEO surface treatment is overlapped with several signals. In addition, the reflectance of the energy band varies from 1.32 to 1.46 eV. Usually, the MgO-type oxide film was observed at an energy band of ~4.2 eV.

2. The thickness of the oxide film was increased as the DC voltage was increased by the thin film thickness gauge (QuaNix; 7500 M) after PEO surface treatment by voltage. This is because the higher the DC voltage, the easier the binding of the OH⁻ ions in the solution solution and the Mg⁺ ions of the magnesium alloy. An important part of the

bonding of ordinary ions is the energy source (plasma) which can promote bonding. However, when a certain threshold voltage or more is applied, the material is adversely affected. The oxide film of the surface may be destroyed without increasing the thickness of the oxide film, that is, whitening of the material may occur. In this experiment, the increase of the oxide film was not observed above 85 V, and whitening phenomenon was observed.

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