

Ceramic coated Y1 magnesium alloy surfaces by microarc oxidation process for marine applications

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Abstract. The magnesium alloys occupy an important place in marine applications, but their poor corrosion resistance, wear resistance, hardness and so on, have limited their application. To meet these defects, some techniques are developed. Microarc oxidation is a one such recently developed surface treatment technology under anodic oxidation in which ceramic coating is directly formed on the surface of magnesium alloy, by which its surface property is greatly improved. In this paper, a dense ceramic oxide coating, ~20 µm thick, was prepared on an Y1 magnesium alloy through microarc oxidation in a Na₃SiO₃–Na₂WO₄–KOH–Na₂EDTA electrolytic solution. The property of corrosion resistance of ceramic coating was studied by CS300P electro-chemistry–corrosion workstation, and the main impact factor of the corrosion resistance was also analysed. Microstructure and phase composition were analysed by SEM and XRD. The microhardness of the coating was also measured. The basic mechanism of microarc coating formation is explained in brief.

The results show that the corrosion resistance property of microarc oxidation coating on the Y1 magnesium surface is superior to the original samples in the 3.5 wt% NaCl solutions. The microarc oxidation coating is relatively dense and uniform, mainly composed of MgO, MgAl₂O₄ and MgSiO₃. The microhardness of the Y1 magnesium alloy surface attained 410 HV, which was much larger than that of the original Y1 magnesium alloy without microarc oxidation.

Keywords. Magnesium alloy; ceramic composite coatings; microarc oxidation; corrosion resistance.

1. Introduction

Magnesium is a metal with the lightest weight among all the structural materials. It and its alloy have many traits in application, including high specific strength and stiffness, low elastic modulus, excellent damping capacity, stronger vibration load resistance, fine processing or machinability, little dimensional change, etc. Its highest advantage is sought in marine applications (Jiang *et al* 2004). Magnesium alloy Y1 contains Al and Zn as alloying elements. Due to these elements, Y1 finds marine applications like side panels, floor plates, moldings, ship structures, etc. But in marine environment, its corrosion is fast and also pitting of surface further degrades its properties. The major techniques for solving these problems include electroplating, chemical plating, anodic oxidation, chemical conversion coatings, physical vapour deposition, surface coating and laser surface treatment and so on, but all of them have certain limitations (Robert and Alivait 1977; Dittrich *et al* 1984; Kurze and Krysmann 1986).

Microarc oxidation is also called microplasma oxidation or anodic spark deposition, a new surface treatment technology developed recently, which has become a hot-

spot of international researches (Wirta and Brown 1991; Kurze 1994; Zozulin and Bartak 1994). It breaks the limitations of traditional anodic oxidation operating voltage. By introducing the work zone into the high-voltage discharge zone, ceramic coating is directly formed on the surface of nonferrous metals (also called valve metals) such as Al, Ti or Mg, etc with the high instant temperature in the microarc zone. Ceramic has become the third generation of engineering materials to follow steel and aluminum for its special physical and chemical features, but its poor properties in machinability limit its application. Through microarc oxidation, *in situ* grown ceramic coating is directly formed on the surface of magnesium alloy, which makes the perfect combination of the second or third generation of engineering materials possible (Wenbin *et al* 1998; Gnedkov *et al* 2001).

2. Experimental

2.1 Materials and methods

Experimental material adopts Y1 magnesium alloy which is an Mg–Al wrought magnesium alloy with chemical components (wt %) including Al 3.2–3.5%, Zn 0.7–1%, Mn 0.2–1.0%, Si ~0.05%, Cu ~0.01% and remaining contents

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of Mg. A specially created marine environment is used for testing this sample. As a device used for surface treatment, self-designed 30 kW pulse microarc oxidation device consists of pulsed ionizing power supply, electrolytic bath, rabbling system, cooling system, equal-electrode workpieces and copper plate. The samples are $\varnothing 20 \times 5$ mm round cakes. The electrolytic solution is mainly composed of Na_2SiO_3 (10 g/L) prepared with deionized water and some additional additives such as Na_2WO_4 , KOH and Na_2EDTA .

The sample is kept in an electrolytic solution of Na_2SiO_3 (10 g/l) and a current of 300V/3 A is passed for some time (usually in minutes). This will cause oxidation of surface under maintained conditions and a dense thick oxide layer would be formed on the surface. Thickness, cross-sectional microstructure, surface morphology and phase structure of the sample are measured using S250MK3 English scanning electron microscope (SEM) and Rigaku D/max 2500 X-ray diffractometer (XRD). The corrosion resistances of magnesium alloy before and after microarc oxidation are tested through CS300P electrochemical corrosion testing system. The samples are cleaned in acetone, alcohol and distilled water. At room temperature of $20 \pm 2^\circ\text{C}$, the corrosive medium is 3-5 wt% NaCl solution, reference electrode is saturated calomel electrode (SCE), auxiliary electrode is Pt electrode, and corrosion time is 2 h.

3. Results and discussion

3.1 Microstructure of microarc oxidation ceramic coating

Figure 1 is a cross-sectional microstructure of microarc oxidation ceramic coating of Y1 magnesium alloy at 300 V/3 A/40 min. The thickness of the oxidized ceramic coating is about 20 μm . The microarc oxidization coating consists of three layers including loose layer (I), compact layer (II) and contact layer (III). The loose layer takes up 30% or so of the total thickness, compact layer, 40-50%, and contact layer between dense layer and metal surface. Oxide and basal body form a typical alloy by penetrating and joining to each other.

3.2 Analysis of microhardness of microarc oxidation ceramic coating

Microhardness curve of microarc oxidation ceramic coating over a treatment time of Y1 magnesium alloy at 300 V, 3A is shown in figure 2. A load of 15 kg was used for testing. The microhardness of magnesium alloy surface obviously increased after microarc oxidation, but change of the hardness is not always proportional to time. At the initial stage of microarc oxidation, the microhardness increased over passing of treatment time.

However, it reached 410 Hv, three times the original material microhardness after 40 min, and then the microhardness reduced over treatment time passing afterwards. The thickness of oxide film formed on the sample surface increased over a treatment time at the initial stage, which made its hardness to increase continuously. After its thickness reached the maximum value, the oxide film formed for the first time was broken through and big holes appeared on the sample surfaces, which resulted in reduction in thickness and hardness. If the treatment time continued to extend, the oxide film formed on the sample surfaces for the second time, and then its thickness and hardness continually increased. Further increase in holding time caused oxide layer to form but due to improper bonding between layers, these films broke into small chips and also resulted in very brittle oxide coating (Apelfeld *et al* 2000).

3.3 Surface morphology of microarc oxidation ceramic coating and XRD phase analysis

The surface morphology of microarc oxidation ceramic coating is shown in figure 3. Many chimbs and holes can be seen on the surface of magnesium alloy oxide film. All of them are bigger than those on the magnesium alloy surface. The film surface is on the surface. The whole surface of microarc oxide film is a porous surface, which is loose and rough due to uneven melt solids. In addition, obvious extended cracks can be seen on the surface. These cracks are caused by overlage thermal stress in fast composed grains with different diameters, which are

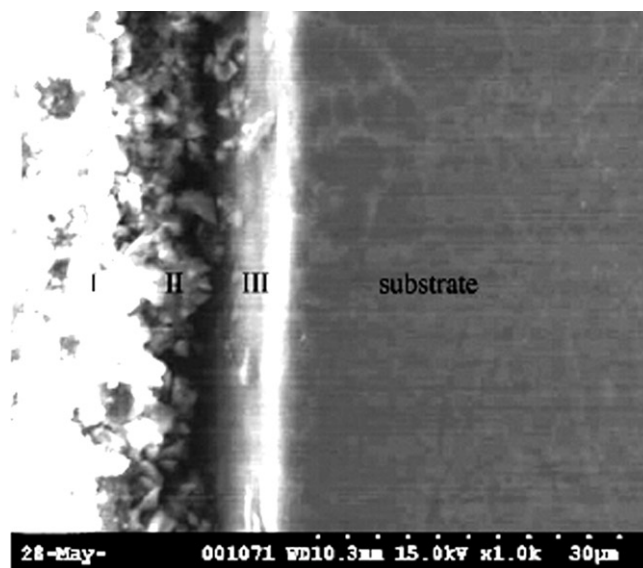


Figure 1. Microstructure of microarc oxidation ceramic coating (300 V, 3A, 40 min). Here I, II and III indicate the layer of coatings formed subsequently.

melt and unevenly distributed solidification of melts when the film surface comes into contact with the solution (Wenbin *et al* 1997, 1999; Wenbin and Zhiwei 2000; Bailing *et al* 2003).

Figure 4 shows the diagram of XRD of microarc oxidation ceramic coating. The microarc oxidation ceramic coating is mainly composed of cubic MgO, and MgAl₂O₄ sharp spinels as well as a little amount of MgSiO₃, which di-

ffers from amorphous film phase structure after the anodic oxidation of magnesium alloy in principle. Microarc oxidation makes oxidized amorphous MgO into cubic through high-temperature and -pressure instant sintering. Such structures can make the dense layer denser to increase the hardness and corrosion resistance of magnesium alloy. The formation of MgSiO₃ phase indicates that ions in the solution have directly engaged in chemical reactions near the microarc zone (Rama *et al* 2003).

3.4 Electrochemical corrosion experiment

Figure 5 shows polarization curves of original sample and testing samples treated through microarc ceramic coating oxidation in 3.5% NaCl solution. It can be seen from the results that the anodic polarization curve of original Y1 sample enters into active dissolution zone when the potential reaches -1588 mV.

The anodic current density increases with the potential increasing within this zone. When the potential reaches -1420 mV, the curve goes into the passivation zone or stable passivation zone. When the potential reaches -1360 mV, the curve goes into the over passivation zone, in which the anodic current density increases with potential increasing at this time. The anodic polarization curve of testing samples treated through microarc oxidation goes into the active dissolution zone when the potential reaches -1532 mV, in which the anodic current density of metal electrode increases with the potential increasing; it goes into the passivation zone or stable passivation zone on reaching -1400 mV, in which the current density is independent of the potential, i.e. the dissolution speed of metal anode remains unchanged within a wide potential range, and it goes into the over passivation zone when reaching -916 mV, in which the anodic current density increases with potential increasing at this time.

The Tafel extension method (Weifang *et al* 1985) is used to measure corrosion current densities and corrosion

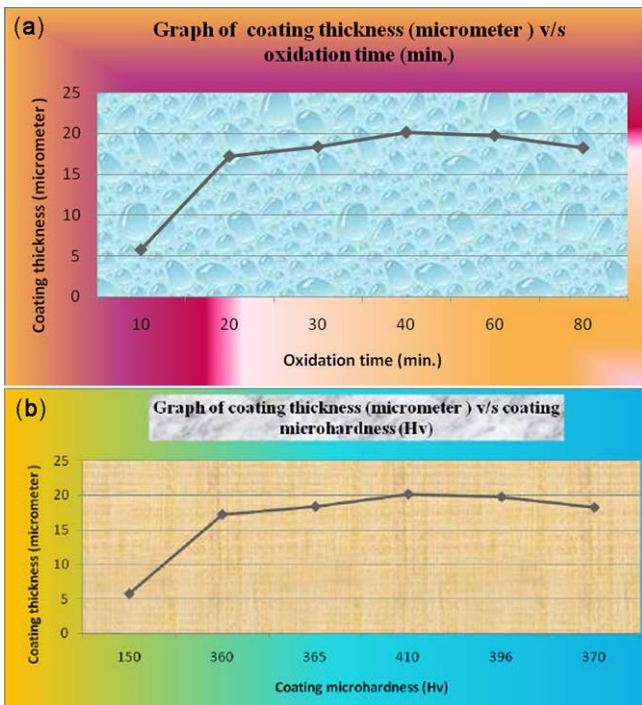


Figure 2. (a) Graph of coating thickness (μm) vs oxidation time (min) and (b) microhardness curve of microarc oxidation ceramic coating over a coating thickness.

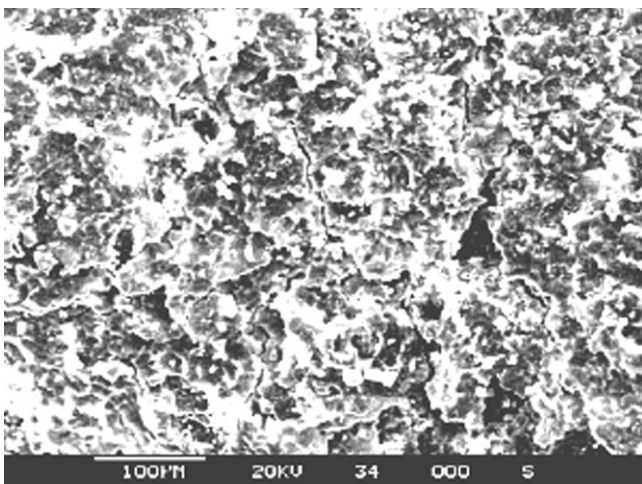


Figure 3. Surface morphology of microarc oxidation ceramic coating (300 V, 3A, 70 min).

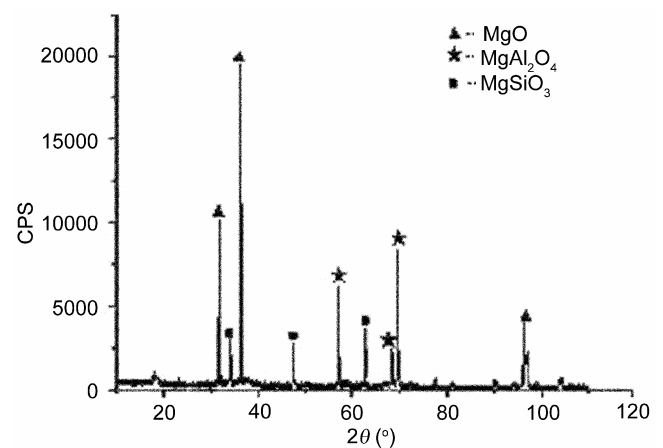
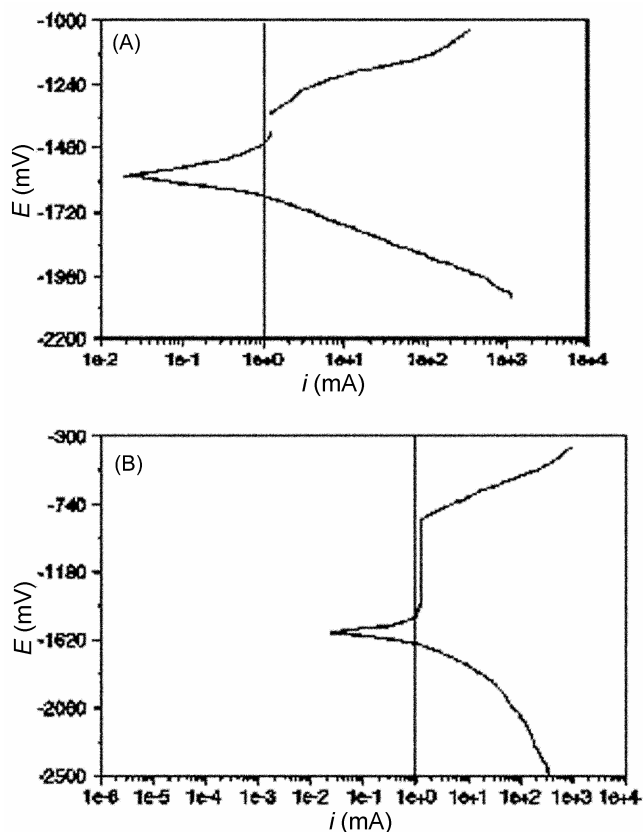


Figure 4. Diagram showing XRD of microarc oxidation.

Table 1. Results of electrochemistry corrosion.

Samples	Over passivated potential (mV)	Corrosion potential (mV)	Corrosion current density (mA/cm ²)	Corrosion speed (μm/s)
Y1	-1360	-1420	0.452	10.193
Coating	-916	-1400	0.152	3.428

**Figure 5.** Polarization curves of samples: (A) polarization curve of Y1 and (B) polarization curve of the ceramic coating.

speeds. Results are shown in table 1. Data shown in the table indicate that the corrosion speed of Y1 magnesium alloy surface treated through microarc oxidation is 3 times as slow as that of the original material and its corrosion resistance is greatly improved.

4. Conclusions

(I) Through microarc oxidation, *in situ* grown ceramic coating composed of loose, dense and contact layers is directly formed on the surface of magnesium alloy by which its surface property greatly improved.

(II) The corrosion resistance of Y1 magnesium alloy surface obviously improved in comparison with one of the original material after microarc oxidation. The electrochemical corrosion experiment shows that the corrosion resistance of microarc oxidation ceramic coating improved three times compared to that of the original material.

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