

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)**ScienceDirect**

Journal of Magnesium and Alloys 3 (2015) 253–257

[www.elsevier.com/journals/journal-of-magnesium-and-alloys/2213-9567](http://www.elsevier.com/journals/journal-of-magnesium-and-alloys/2213-9567)

Review

# Research of growth mechanism of ceramic coatings fabricated by micro-arc oxidation on magnesium alloys at high current mode

Wei-wei Chen, Ze-xin Wang, Lei Sun, Sheng Lu \*

*School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, 212003 Jiangsu, China*

Received 27 May 2015; revised 4 July 2015; accepted 20 July 2015

## Abstract

Micro-arc oxidation (MAO) coatings of ZK60 magnesium alloys were formed in a self-developed dual electrolyte composed of sodium silicate and phosphate at the high constant current of 1.8 A (15 A/dm<sup>2</sup>). The MAO process and growth mechanism were investigated by scanning electron microscopy (SEM) coupled with an energy dispersive spectrometer (EDS), confocal laser scanning microscopy and X-ray diffraction (XRD). The results indicate that the growth process of MAO coating mainly goes through “forming → puncturing → rapid growth of micro-arc oxidation → large arc discharge → self-repairing”. The coating grows inward and outward at the same time in the initial stage, but outward growth of the coating is dominant later. Mg, Mg<sub>2</sub>SiO<sub>4</sub> and MgO are the main phases of ceramic coating.

© 2015 Production and hosting by Elsevier B.V. on behalf of Chongqing University.

*Keywords:* ZK60 magnesium alloys; Micro-arc oxidation; High current; Growth mechanism

## 1. Introduction

Magnesium alloys have been paid enough attention to for many years due to the resource, performance, and price advantage, called as “the green structural materials in the 21st century”. However, the application potential and range are both limited by their susceptibility to corrosion and inferior wear performance. Therefore, the proper surface modification treatment can enhance the corrosion resistance of the existing magnesium alloy which has important practical significance [1,2].

Micro-arc oxidization (MAO) is a simple, friendly, efficient surface treatment method of forming ceramic coatings on Al, Ti, Mg and their alloys. The surface properties, such as wear and corrosion resistance, electrical insulation, adhesion to substrate, can be considerably improved by MAO [3–5]. It is an incontrovertible fact that the growth mechanism of MAO process is extremely complex, including chemical, electrochemical, high temperature plasma reaction, etc. And no reasonable model can fully and precisely describe the theory at home and abroad. Chen et al. [6,7] thought the process is a submonolayer growth, which is a cyclic process experiencing

the repeated course of “forming → breakdown → melting → liquating → sintering → reforming”. Cellular structure composed of nanoparticles is growing layer-by-layer, whose dense layer is made up of MgO mainly. Ge et al. [8] studied the MAO process of wrought magnesium alloy in the silicate system. They found that dense layer is formed in the preliminary stage, and loose layer appears later, accounting for a large percentage of the total film thickness. They also carried out quantitative analysis and measurement of the energy loss and impedance change of membrane layer in reaction. The researchers of Northwestern Polytechnical University [9–11] studied the effect from rare earth elements on the growth of membrane layer. They thought the MAO film is a double-layer structure in silicate system. The dense layer is mainly composed of MgO, and the loose layer is mainly composed of MgSiO<sub>3</sub>.

Our group has completed the research on growth mechanism at low-current earlier [12]. In this paper, combined with the testing results, the authors aim to make a further exploration at the high current in order to form a complete system on MAO process and growth mechanism at constant current mode.

## 2. Experimental

The substrate material used for investigation was wrought ZK60 magnesium alloy with a chemical composition (Zn 4.8–6.2%, Zr > 0.45%, impurities ≤ 0.30%, Mg balance). The samples with a size of 20 mm × 20 mm × 5 mm were successively ground to 1600 grit silicon carbide papers, cleaned

\* Corresponding author. School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang, 212003 Jiangsu, China. Tel.: +86 15751012979.

E-mail address: [lusheng88168@qq.com](mailto:lusheng88168@qq.com) (S. Lu).

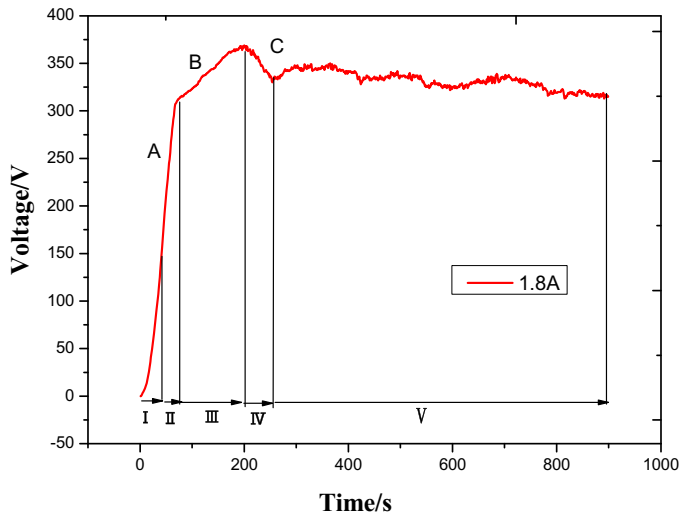


Fig. 1. Voltage-time curve at the current of 1.8 A.

by alcohol, and then dried in cold air. WHD-20 MAO system was employed for MAO treatment. The samples acted as anodes and a stainless steel container acted as cathode. The experiments were carried out in an optimized dual electrolyte composed of sodium silicate and phosphate under constant current. The temperature was kept in electrolyte under 40°C through circulating water cooling system.

The micro-structural characteristics of coating, coating elements and phase constituent were investigated by scanning electron microscopy (SEM, JSM-6480), X-ray diffraction (XRD, Shimadzu XRD-6000) and Olympus confocal laser scanning microscopy (OLS4000). The micrometer was used to measure the thickness of the specimen before and after the MAO process. The MAO film thickness was measured by the coating thickness measurement equipment (OXFORD CMI233).

### 3. Results and discussion

#### 3.1. Analysis of voltage-time curve and MAO spark discharge phenomenon

The MAO coating growth process is monitored by the voltage-time curve, which can be divided into five distinguishing stages as shown in Fig. 1. At the first stage, within 0–40 s, the substrate surface quickly formed a very thin layer, named anodic oxidation stage. The substrate surface appeared the first spark (Fig. 2(a)), which meant that the MAO process reached the striking voltage about 140 V at around 40 s. The second stage lasted from 40 s to 70 s; the anodic oxidation coating got punctured and MAO coating was formed. The third stage (70 s–200 s) corresponded to the main period of rapid growth of MAO, involving large numbers of white and bright sparks (Fig. 2(b)), as a result of highlight plasma micro-arc discharge. The value of voltage reached a maximum of 370 V at about 200 s. In this stage, the porous film solidified rapidly because of the effect of high-temperature micro zone and “quenching” in the electrolyte. The thickness of coating increased by 25  $\mu\text{m}$  and the value of growth rate got to a maximum of 13.15  $\mu\text{m}/$

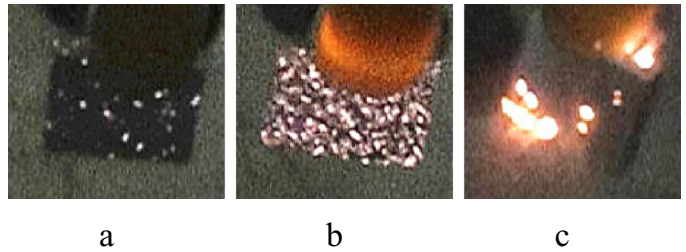


Fig. 2. Spark discharge characteristics at different time points.

min. After 200 s, plasma point discharge concentrated upon the places of edges or corners by the effects of high voltage and strong electric field, which led to the breakdown, and even dissolution and desquamation of part of the membrane layer. Compared with the second stage and third stage, the growth rate decreases significantly after 200 s. The voltage curve of the fourth stage (200–250 s) presents a brief drop; the voltage value drops slightly. Through macroscopic observation, the number of sparks reduced, but single spark became larger. So this stage can be named local large arc discharge (Fig. 2(c)). The last stage was characterized by a voltage plateau from 250 s to the end in which many micro-cracks and micro-pores were disappeared gradually and the surface also became smooth. According to the macroscopic experimental phenomena and microstructure, this stage played a key role to control the quality of the film through self-repairing.

#### 3.2. Analysis of microstructure

The surface and cross-section micro-morphologies of MAO coating at different stage are shown in Fig. 3. At the time of 60 s, passive film was punctured and large numbers of micro discharge channels appeared on the surface (Fig. 3(a)). When oxidation time lasted for 180 s, the variations of surface morphologies show normal regularity that the quantity of the micro discharge channels decreased but the size of micro-pores increased sharply. Most of the pore diameters are in the range of 10 to 15  $\mu\text{m}$ . In addition, continuous micro-cracks and loose micro-pores both existed in the surface and cross-section of coating due to the effect of quenching stress (Fig. 3(b) and Fig. 3(e)). At the low-voltage self-repairing stage of 480 s, the number of micro-pores decreased to some degree because plenty of melt accumulated on the surface and covered parts of discharge channels as seen in Fig. 3(c). The average pore diameter decreased to 4.3  $\mu\text{m}$ . At last, continuous micro-cracks of the coating disappeared gradually or transformed into discontinuous micro-cracks, and cross-section morphologies of the coating became smooth and dense (Fig. 3(d) and (g)). The average thickness of the coating reached 65  $\mu\text{m}$ .

#### 3.3. Analysis of growth characteristic

For growth characteristic of MAO coating by high-current mode, Fig. 4 shows the dynamic changing process of coating thickness in two sides. It can be found that the growth rate of the two sides is basically synchronous without huge difference. The growth rate is nearly close to 0 before 70 s, namely, only an

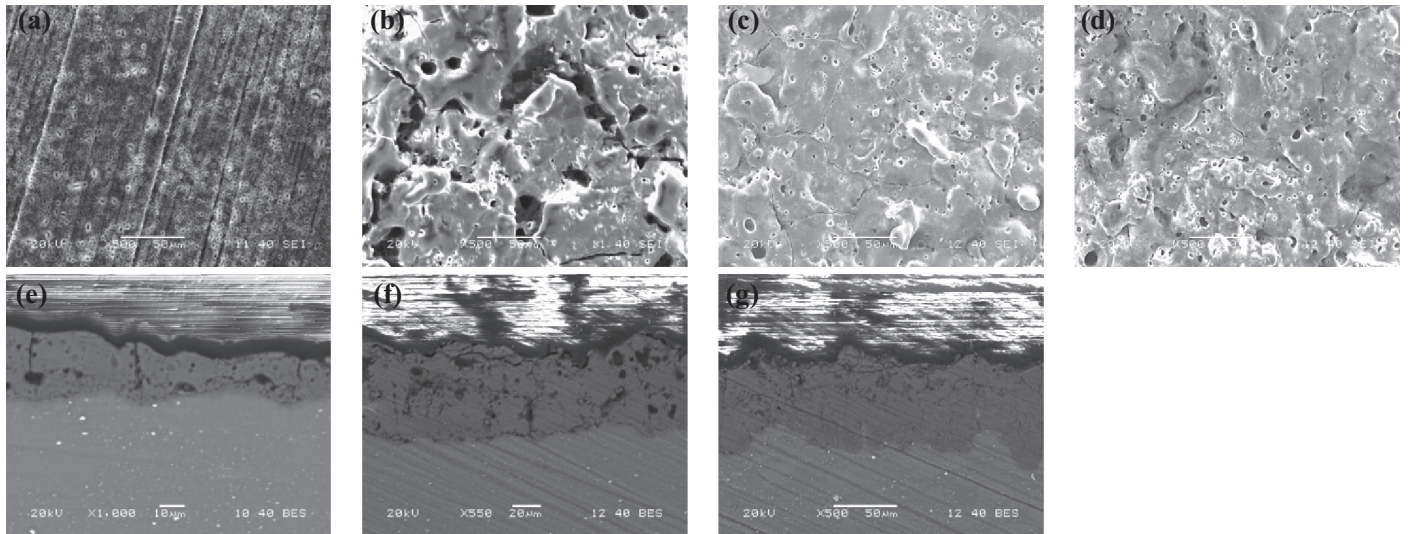


Fig. 3. Surface and cross-section micromorphologies of MAO coating at the current of 1.8 A.

ultrathin layer is formed on the surface which is hard to measure accurately. At the rapid growth of MAO stage from 70 to 200 s, the film thickness of two sides both increased significantly and the growth rate also reach their extreme value of 13.43  $\mu\text{m}/\text{min}$  and 12.87  $\mu\text{m}/\text{min}$ , respectively. Compared with the previous stage, the growth rate reduces to a certain degree after 200 seconds, but the coating thickness all sides, so the two sides of the coating can grow together basically. However, the discharge concentrated on one side and stimulated the continued increase up to the end at a steady rate of 3.30  $\mu\text{m}/\text{min}$ . Finally, the average coating thickness is 66  $\mu\text{m}$ . It can be speculated from the above laws that the available energy budget provided by the high-current is sufficient to meet the discharge requirement in growth of film at the same side by low-current MAO. Consequently, the two sides of coating fabricated by low-energy MAO grew together in the initial of MAO process, but evolved asynchronously in the late process of MAO, and consistently in the end [12].

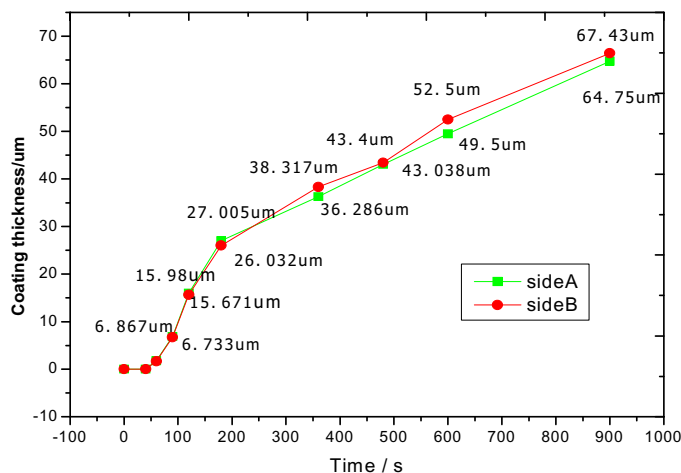


Fig. 4. Growth rate of MAO coating at the current of 1.8 A.

The rule of dynamic process in the growth of MAO coating shows that the coating thickness is controllable by adjusting the process parameters to meet the different needs in engineering.

### 3.4. Analysis of inward growth and outward growth of the coating

The growth schematic diagram of MAO coating on Mg alloy is presented in Fig. 5. The dashed lines show the original surface of magnesium alloy,  $h$  means the coating's total thickness,  $a$  means the thickness of outward growth part and  $b$  means the thickness of inward growth part [15].  $H1$  means the sample total thickness after MAO.  $H0$  means the blank sample thickness.  $H1$  and  $H0$  were both measured by the micrometer. According to Eq. (1) and Eq. (2),  $a$  and  $b$  can be:

$$a = (H1 - H0)/2 \tag{1}$$

$$b = h - a \tag{2}$$

At present, different opinions about the growth mechanism theory still exist [8–10,13]. In this paper, the inward and outward growth problem at the high current mode is investigated appropriately. Fig. 6 shows that the thickness values of inward and outward growth are both low in the first and second stages, and only a very thin film is formed in the substrate surface. At the rapid growth stage of MAO (70–200 s), the

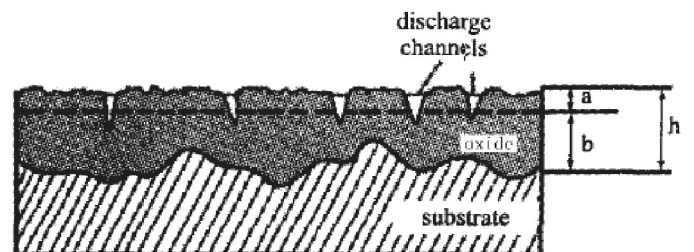


Fig. 5. Schematic diagram of micro-arc oxidation coating on Mg alloy.



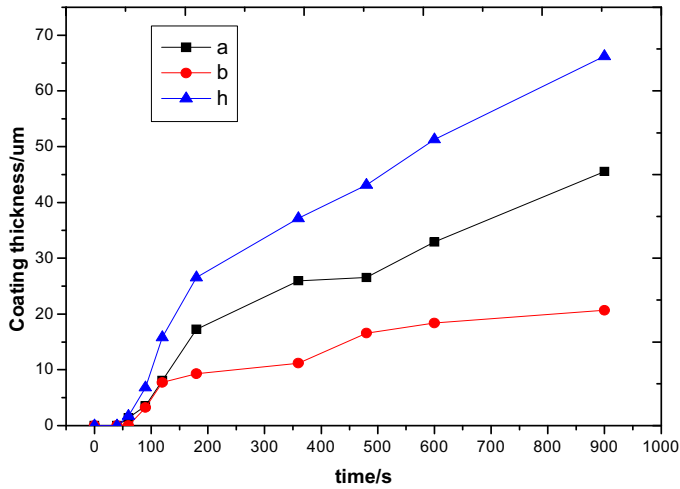


Fig. 6. The growth characteristic of inward and outward micro-arc oxidation coating.

thickness of both the inward and outward growth change significantly. And the inward and outward growth rate both get maximum values that are 7.76 µm/min and 4.66 µm/min respectively. It can be speculated that the ions of Mg alloy substrate and electrolyte reacted rapidly in the discharge channel due to the enormous energy releasing from the spark discharge of micro-arc oxidation under high current and temperature, then the film formed. The inward and outward growth rates both decrease after 200 s when the MAO process enters into the self-repairing stage. The two sides of the coating mainly grow outward later, and the inward growth rate reduces to 0.94 µm/min. This is because only small amount of electrolyte can go through the micro discharge channels and react with the inward substrate; more electrolyte is involved in the outward reaction. Finally, the thickness of the outward growth part takes a larger part of the total thickness.

In order to further testify the conclusion above, there is a way to make half of one sample under MAO; the other half was sealed with resin. The microstructure of inward and outward of micro-arc oxidation coating is presented in Fig. 7. It can be seen

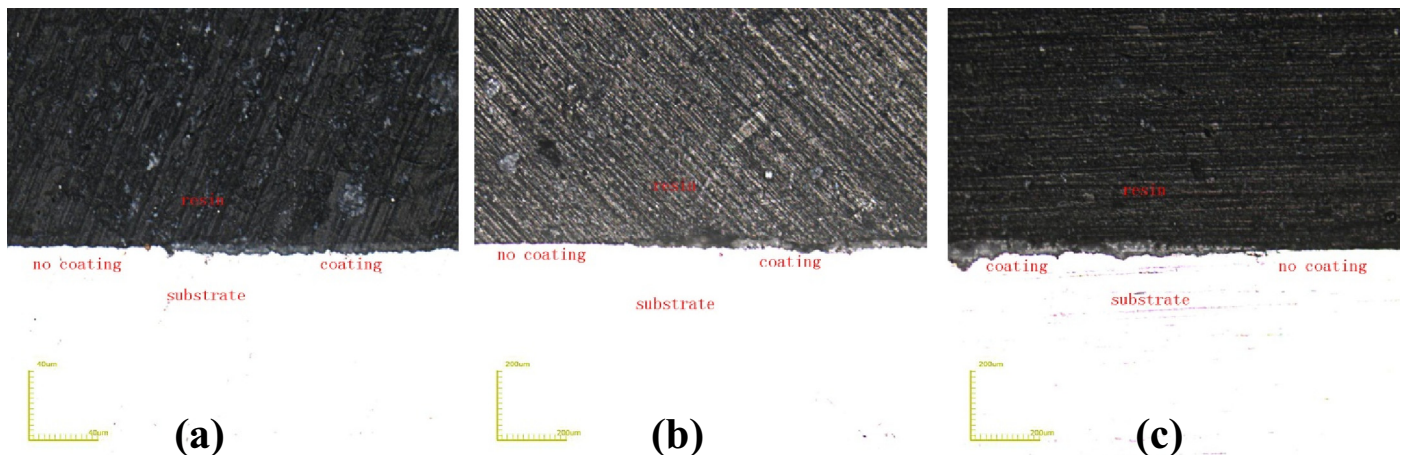


Fig. 7. Microstructure of inward and outward of micro-arc oxidation coating.

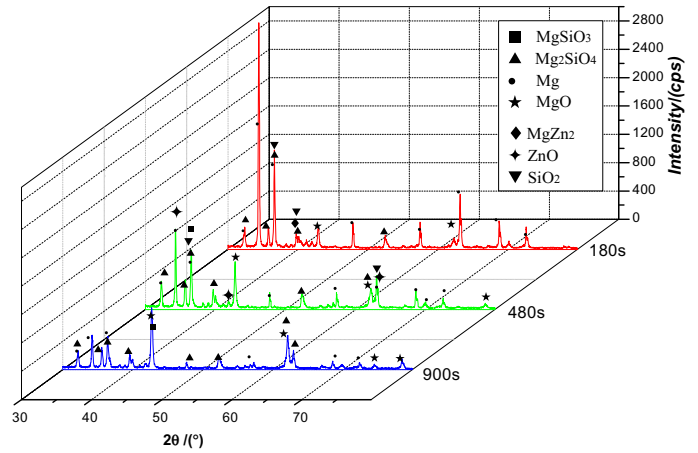


Fig. 8. Phases of MAO coating at the current of 1.8 A.

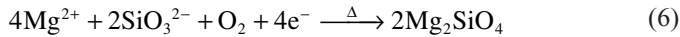
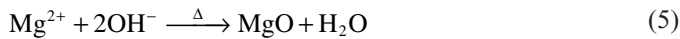
that the thickness appears both on the inward and outward growth at 90 s and 180 s. With the extension of oxidation time, the outward growth part of the thickness gradually takes a larger part of the total thickness at the point of 300 s.

### 3.5. Analysis of the coating phase

Fig. 8 demonstrates the X-ray diffraction results of coatings produced at different stages, respectively.

180 s: When it is at 180 s, the coating in rapid growth stage is mainly composed of Mg, MgO, MgZn<sub>2</sub>, SiO<sub>2</sub> and Mg<sub>2</sub>SiO<sub>4</sub>. Among them, magnesium and MgZn<sub>2</sub> are from substrate. Mg transforms into the Mg<sup>2+</sup> ions at the high voltage and temperature at the first stage of process and this magnesium ions formed during MAO process react with other ions such as OH<sup>-</sup> and SiO<sub>3</sub><sup>2-</sup> in the micro discharge channels. Mg<sub>2</sub>SiO<sub>4</sub> is formed by outward migration of Mg<sup>2+</sup> from substrate metal to discharge channels and inward migration of SiO<sub>3</sub><sup>2-</sup> from electrolyte to discharge channels at high temperature. The main reactions are shown below (Eqs (3–6)):





480 s: Compared with the previous stage, new phase appears in the coating in self-repairing stage at 480 s, such as MgSiO<sub>3</sub> and ZnO. Zn in the substrate and oxygen in the electrolyte react into ZnO. MgSiO<sub>3</sub> phase can be formed in two different reactions during MAO process. At the first reaction type, the Mg<sup>2+</sup> ions react with the SiO<sub>3</sub><sup>2-</sup> directly owing to the decreasing amount of O<sub>2</sub>. Later, the reaction between MgO and SiO<sub>2</sub> occurs during process at high temperature and MgSiO<sub>3</sub> is created. The two reactions are shown in (Eq (7,8)):



900 s: It is a whole MAO process at 900 s. Major phases are found to be Mg, MgO periclase, Mg<sub>2</sub>SiO<sub>4</sub> forsterite and MgSiO<sub>3</sub>. Due to the drastic discharge of sparks and severe erosion in the last stage, the MgO magnesia and Mg<sub>2</sub>SiO<sub>4</sub> transform into MgO periclase and Mg<sub>2</sub>SiO<sub>4</sub> forsterite under the effect of high temperature and liquating, which has a significant effect on improving the comprehensive performance of the coating.

#### 4. Conclusion

The MAO process and growth mechanism of micro-arc oxidation coating on magnesium alloy at the single constant current mode are systematically investigated. The main results are shown as follows:

1. According to the voltage-time curve, the MAO process can be divided into five parts, named anodic oxidation stage, passive film puncturing stage, rapid growth of

micro-arc oxidation stage, large arc discharge stage and self-repairing stage. Among them, the third stage plays a key role in the thickness of coating, and the last stage plays a main role in the quality of film.

2. The analysis of the growth characteristic shows that the growth rate of the two sides is basically synchronous, and the coating grows inward and outward at the same time in the early stage, but outward growth of the coating is dominant later.
3. The coating is mainly composed of Mg, MgO periclase, Mg<sub>2</sub>SiO<sub>4</sub> forsterite and MgSiO<sub>3</sub>. The comprehensive performance of coated ZK60 alloy might be enhanced due to the main phases MgO and Mg<sub>2</sub>SiO<sub>4</sub> with high-melting-point, high strength and better wear resistance.

#### References

- [1] R.O. Hussein, D.O. Northwood, WIT Transactions on the Built Environment 137 (2014) 531–544.
- [2] X.D. Chen, Q.Z. Cai, Z.W. Deng, L.S. Yin, Appl. Mech. Mater. 496 (2014) 63–70.
- [3] R. Arrabal, A. Pardo, M.C. Merino, M. Mohedano, P. Casajús, E. Matykina, et al., Corros. Sci. 52 (2010) 3738–3749.
- [4] D. Veys-Renaux, C.-E. Barchiche, E. Rocca, Surf. Coat. Technol. 251 (25) (2014) 232–236.
- [5] E.E. Demirci, E. Arslan, K.V. Ezirmik, Ö. Baran, Y. Totik, İ. Efeoglu, Thin Solid Films 528 (15) (2013) 116–122.
- [6] X.-M. Chen, C.-P. Luo, J.-W. Liu, Mater. Sci. Forum 650 (2010) 228–233.
- [7] X.-M. Chen, C.-P. Luo, J.-W. Liu, J. Funct. Mater. 41 (12) (2010) 2075–2079.
- [8] Y.-F. Ge, B.-L. Jiang, C.-J. Wang, Y. Long, Trans. Mater. Heat Treat. 35 (12) (2014) 190–194.
- [9] Y.-C. Guo, J.-P. Li, J.-S. Li, P. Wang, Adv. Mater. Res. 189 (2011) 891–896.
- [10] P. Wang, J.-P. Li, Y.-C. Guo, Z. Yang, Journal of Rare Earths 28 (5) (2010) 798–802.
- [11] P. Wang, D. Liu, J. Li, Z. Yang, Y. Guo, Rare Metal Mater. Eng. 40 (6) (2011) 995–999.
- [12] X.Z. Jiang, The study of growth mechanism of coating fabricated by micro-arc oxidation on magnesium alloys at constant current mode. Jiansu University of Science and Technology, 32–33, 2014.
- [13] Y.-S. Huang, H.-W. Liu, J. Mater. Eng. Perform. 20 (3) (2011) 463–467.