Characteristics of MAO coating obtained on ZK60 Mg alloy under two and three steps voltage-increasing modes in dual electrolyte

Jun Yang¹, Ze-Xin Wang¹*, Sheng Lu¹, Wei-gang Lv², Xi-zhi Jiang¹ and Lei Sun¹

¹School of Materials Science and Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China
²Zhenjiang Naisi New materials Co, Ltd. Zhenjiang, 212000, Jiangsu, China

E-mail: 790209828@qq.com

Abstract. The micro-arc oxidation process was conducted on ZK60 Mg alloy under two and three steps voltage-increasing modes by DC pulse electrical source. The effect of each mode on current-time responses during MAO process and the coating characteristic were analysed and discussed systematically. The microstructure, thickness and corrosion resistance of MAO coatings were evaluated by scanning electron microscopy (SEM), energy disperse spectroscopy (EDS), microscope with super-depth of field and electrochemical impedance spectroscopy (EIS). The results indicate that two and three steps voltage-increasing modes can improve weak spark discharges with insufficient breakdown strength in later period during the MAO process. Due to higher value of voltage and voltage increment, the coating with maximum thickness of about 20.20μm formed under two steps voltage-increasing mode shows the best corrosion resistance. In addition, the coating fabricated under three steps voltage-increasing mode shows a smoother coating with better corrosion resistance due to the lower amplitude of voltage-increasing.

Keywords: Magnesium alloy; Micro-arc oxidation; Characteristic; step voltage-increasing

1. Introduction

Mg alloys are the lightest materials among those metals used for structural or mechanical applications [1]. Besides, Mg alloys have many excellent properties such as high specific tensile strength, high dimensional stability, good stiffness and vibration absorption [2, 3]. Thus Mg alloys are widely used in many industries such as aerospace, automobile and communication fields [4]. Though ZK60 is a typical wrought alloy characterized with superior properties [5-7], the poor corrosion resistance, like most Mg alloys, has limited its widespread use [8].

Micro-arc oxidation (MAO), also referred as plasma electrolytic oxidation, is a new electrochemical surface treatment which is considered an attractive method for generating protective ceramic coatings, particularly on light alloys such as Ti, Al and Mg alloys [9-11]. The corrosion and wear resistance can be remarkably improved after the MAO process [12, 13].

Most MAO processes are carried out under constant current mode which is more efficient to obtain superior MAO coatings[14]. However, MAO process under constant voltage mode is hardly used in applications because of its insufficient breakdown ability acting on coating in later period [15]. In order to solve this problem, two steps voltage-increasing mode was developed to improve the coating
quality in previous work [16]. However, the coating characteristics are different under different step
voltage-increasing modes. In the present work, MAO coating was obtained under two and three steps
voltage-increasing modes, the growth characteristic, thickness, growing rate, microstructure and
corrosion resistance were investigated respectively.

2. Experimental
Rectangular coupons (20 mm × 20 mm × 5 mm) of ZK60 magnesium alloy (Zn 4.8-6.2, Zr >0.45
impurities ≦ 0.30, Mg balance) were prepared by means of electric arc CNC wire-cut machine and
polished with alumina waterproof abrasive paper up to 1200 grits. The coupons were then cleaned in
an ultrasonic bath with acetone and ethyl alcohol respectively at room temperature for 10 min before
MAO process.

WHD-20 MAO system with a bipolar pulsed power was employed in MAO experiments. Dual
electrolytes system was prepared from distilled water containing 14 g/L NaAlO₂, 6g/L Na₃PO₄, 4 g/L
NaOH, 3g/L NaB₄O₇, and 4g/L C₆H₅Na₃O₇ [14]. Electric parameters including negative voltage, duty
cycle and frequency kept constant with the value of 20V, 20%, 600 Hz respectively while the positive
voltage was the main parameter to be investigated. All MAO experiments were conducted for 15 min
at electrolyte temperature of less than 35℃ and the current-time curves were recorded automatically
during MAO process. Spark discharge phenomenon were captured by digital camera.

In the experiment, positive voltage could be regulated on line during MAO process to achieve the
increasing of voltage by two or three steps. Under two steps voltage-increasing mode, the first step
was required for 6 min with the initial voltage value of 280V, while the second step was applied with
increase value of 80V for the rest 9 min. When MAO process was carried out under three voltage-
increasing mode, the first step was also required for 6 min with the initial voltage value of 280V, then
the voltage rose to 320V for 360-630s, the voltage was changed to 360V for 630-900s at the third step,
the initial voltage and the final voltage of each mode is identical(280V-360V).

The microstructural characteristics of coating and coating thickness phase were investigated by
JSM−6480 SEM. The macro morphology and surface roughness of the coating were investigated by
Digital Camera and Keyence VHX-900 Digital Microscope. Tests of electrochemical impedance
spectroscopy were conducted at a 3.5%NaCl solution to assess the corrosion resistance of the coatings.

3. Results and discussion

3.1. Current-time curves and experimental phenomenon of MAO process
The current-time responses under two and three steps voltage-increasing mode are shown in figure 1.
Under two steps voltage-increasing mode, according to the analysis of current changes during MAO
process, it can be seen that MAO coating experiences the growth of passivation layer, spark discharge
and rapid film-forming before voltage-increasing (0-360s). In this stage, the current rises rapidly at the
beginning and then appears a sharp decline with a peak value 9.0A at 32s. In the previous work, basic
width was put forward, which plays an important role in the growth of MAO coatings, the greater the
width is the stronger the growth momentum will be. The basic width is 250s in this stage and later the
current has a little fluctuation between 0.5A and 0.7A from 250s to 360s. According to the
experimental phenomenon, the discharge sparks are brighter at first and then it becomes finer and
weaker, which lead to a shortage of driving force of breakdown, as shown in figure 2(a). After
increasing the voltage (360s-600s), MAO process comes into second stage in which the coating grows
fast. The current quickly increase linearly and then get down with a lower speed compared with the
first stage. At 367s, it get the peak value 5.2A which is significantly lower than the first stage, for the
former coating has a large insulation resistance [17] which lead to the reduction of current peak when
it is broken down again. In this stage, the baseline peak width is 240s, the growth momentum became
stronger, while the spark quickly became brighter, larger and more intensive which replace the former
weak sparks as shown in figure 2(b).
For three steps voltage-increasing mode, the samples experiences the same process as two steps voltage-increasing mode, however, it can be obviously seen that there is an additional current peak which results from an additional step of voltage-increasing, so the MAO coatings experience twice breakdown and growth with a lower spark discharging due to the reduction of amplitude of voltage-increasing. Before increasing the voltage, the current peak value is 10.3A and the baseline peak width is 250s, the result is roughly consistent with two steps voltage-increasing mode. At the first step of voltage-increasing, voltage increases to 320V, the current peak value is 2.8A and the baseline peak width is 100s which is apparently reduced, about half of what was in the former mode, compared with the two steps voltage-increasing mode. At this stage, the corners of the samples arc first as shown in figure 2(c), which is due to the lower amplitude of only 40V and the voltage now is only 320V, then the driving force of arc will be slightly insufficient.

However, the MAO process always occur first in the weakest point, therefore the corners of the samples which are weaker area are always the first place to be broken down, then the spark discharging in the surface of the samples is gradually homogenized as well as the coating growth. The second step of voltage-increasing which the voltage is adjusted to 360V at 630s. In this period, the current peak value is 2.5 A and the baseline peak width is 100s which is similar with the first period. Due to the first step of voltage-increasing, the coating growth rate is lower of only 0.53 μm/min as shown in Figure 3, the increase of coating thickness is less as well as the increase amplitude of coating insulation resistance, while the second step of voltage-increasing with the voltage of 360V, in the case of little variation of coating thickness, it will provide more adequate driving force of arc compared with the first step, then the coating growth rate reaches 1.10 μm/min, therefore the reaction is rather intense and the surface of the samples resume a new round of breakdown and spark discharging, as show in figure 2(d).

It can be found that, under two steps voltage-increasing mode, the voltage-increasing amplitude is higher (80V) as well as the variation amplitude of the corresponding current, at which the
corresponding reaction is also more intensive; under three step voltage-increasing, the voltage-
increasing amplitude is lower (40 V) in different period, then the MAO process is gentler compared
with the two steps voltage-increasing and the effect of diuretic recovering of MAO coating is better
based on the observation of the coating morphologies.

3.2. The MAO coating growth rate and thickness

Figure 3 shows the MAO coating growth rate of different period under different voltage-increasing
modes. It can be seen that the growth rate of two kinds of mode is 1.38 μm/min. We choose the
average value of 1.38 μm/min under three different situations and the MAO coatings experience a main
growing period. Under two steps voltage-increasing mode (280-360 V), after increasing the voltage
(360-900s), the growth rate of MAO coatings accelerates obviously with the increase of voltage and
the MAO coatings go through a rapid growth period which last for about 4min with a rate of 2.49
μm/min, therefore the electric energy provided by the increase of voltage enhance the growth
momentum of MAO coatings. However, when the current decreases slightly, the MAO process
becomes smooth and steady with a tiny spark discharging and a low growth rate of only 0.37 μm/min.

Under three steps voltage-increasing mode, it makes the arc energy provided by the voltage-
increasing amplitude of 80 V divided into two parts with 40 V per time, the coating growth rate of
1.10 μm/min in the second time of voltage-increasing increases one time than the first time with the
rate of 0.53 μm/min, the result is corresponding to the discharging phenomenon in MAO process
mentioned above which the reaction in the second time is more intense than the first one as well as the
coating growth rate. The three steps voltage-increasing mode add a voltage-increasing period with
the total voltage-increasing amplitude remain unchanged, it can be known that the coating growth rate
tends to be gentler with a value of only 0.53 μm/min as apparently shown in the first step of voltage-
increasing which is due to the weakening arc driving force, and also it will have an impact on the final
coating thickness under this mode.

![Figure 3. Growing rate of MAO coating between two and three steps voltage-increasing mode.](image)

Comparing the thickness variation under two and three steps voltage-increasing modes, it can be
seen that, the coating thickness of three steps voltage-increasing mode is thinner than that of two steps
voltage-increasing mode in the condition of same final voltage and total amplitude of voltage-
increasing. The coating thickness formed under two steps voltage-increasing mode is 20.20 μm and
the other is 15.76 μm which is obviously thicker than one of 11.22 μm formed under constant voltage
mode.

3.3. The morphologies of MAO coating
The morphologies of MAO coating under two and three steps voltage-increasing mode are shown in figure 4. It can be observed that MAO coating is characterized with a typical porous structure as shown in figure 4(a) and figure (c) [18-21]. Under steps voltage-increasing mode, due to the higher final voltage as well as the electric energy of MAO process, the surfaces of the samples are covered by the melt sprayed from the discharging channels during MAO process which is characterized with a uneven and rough surface with the roughness of 7.5μm and 5.1μm under two and three steps voltage-increasing modes respectively as shown in Figure 5. According to the cross-section morphologies of MAO coating, the coatings formed under the two different modes are relatively uniform and compact as shown in figure 4(b) and (d), the juncture between the coating and the substrate is characterized with a zigzag shape and P. Bala [22] Srinivasan et al. think that way of metallurgical bonding can enhance the bonding force between the coating and the substrate. The distance of two dashed lines is used to indicate the maximum waviness of joint surface of the coating and the substrate which is defined as the bonding degree of the coating and the substrate.

Therefore it can be known that the bonding degrees of two and three steps voltage-increasing mode are 4.53 μm and 6.53 μm respectively. Comparing the surface roughness of outer layer and the bonding degree of internal layer and the substrate, it can be seen that the surface roughness of outer layer is large and the bonding degree of internal layer and the substrate is low under two steps voltage-increasing mode while the result of three steps voltage-increasing is opposite, the results above show that the growth mechanism of MAO coating is different under different voltage-increasing modes. Under the two steps voltage-increasing mode, the melt accumulation on the surface of outer layer is uneven which can lead to a large surface roughness and the outward growth of the coating is more. While under the three steps voltage-increasing mode, the melt accumulation on the surface of outer layer is uniform which contribute to a low surface roughness with a flat surface and the bonding degree of the layer and the substrate is in crescent which can account for the increased inward growth.

According to the comparison of the surface morphologies of the two voltage-increasing modes, It could be found, under two steps voltage-increasing mode, the surface molten coverings of MAO coating connect each other and have a large area and also accumulate obviously with a larger aperture of 5.4 μm. While under three steps voltage-increasing mode, the surface molten coverings of MAO coating are little dispersive and the area is decreased, while the number of micro-pores is increased with the aperture of 3.5 μm, the result analysis of surface morphologies is consistent with that of
roughness. Based on the analysis of the current-time curves of MAO process and the discharging phenomenon of experiment, it can be known that, under three steps voltage-increasing mode, although the total amplitude of voltage-increasing is the same as two steps voltage-increasing mode, due to the additional voltage-increasing step, the voltage-increasing process become more stable, the driving force of once again breakdown and melt-solidification process of MAO coating is decreased, the melts inside the discharging pores of the surface spray little and the accumulation beside the micro-pores is less, therefore the coating formed on the surface is relatively flat.

3.4. The corrosion resistance of MAO coating

The results of electrochemical impedance spectroscopy (EIS) of ZK60 magnesium MAO coatings formed under different voltage-increasing modes are shown in figure 6. As the Nyquist shown in figure 6 (a), all the impedance plots presented in Nquist plots are characterized with a small capacitive loop at high frequency and a large capacitive loop at low frequency. Compared with constant forward voltage mode, the MAO coating formed under steps voltage-increasing mode has a larger radius of capacitive loop which indicate a good corrosion resistance and the MAO coating formed under two steps voltage-increasing mode exhibits the largest radius of capacitive loop. Corrosion resistance assessed by low frequency impedance shown in figure 6 (b) indicates that MAO coating formed under two steps voltage-increasing mode would show best resistance with highest value of low frequency impedance of $1.414 \times 10^5 \text{ohm.cm}^2$, also the coating thickness is thickest and densest which can be seen from the morphologies of MAO coating. The value of low frequency impedance under three steps voltage-increasing mode is $6.143 \times 10^4 \text{ohm.cm}^2$ which decreases by 1 order of magnitude compared to $1.414 \times 10^5 \text{ohm.cm}^2$ under two steps voltage-increasing mode. Although the coating is still denser, the coating thickness is decreased compared to the former which shows a poorer corrosion resistance, however the value of impedance is increased much compared with the constant forward voltage mode.

Based on the general research [23], the coating thickness and compactness is the main factor related to the corrosion resistance of MAO coating which mainly consider the barrier effect of MAO coating against the outside corrosive medium. Also the other consider [24] that the coating corrosion resistance is certainly related to the different ceramic phases. The two steps voltage-increasing modes researched in this article which think the amplitude of voltage-increasing has a great effect on coating thickness, comparing the two and three steps voltage-increasing modes, it can be seen that: under two steps voltage-increasing mode, the amplitude of voltage-increasing is higher, the process of once again breakdown and melt-solidification is more intense and the driving force of coating growth provided is sufficient so that the coating is thicker and denser which also shows an improved corrosion resistance. While under three steps voltage-increasing mode, the amplitude of voltage-increasing is lower, the process of voltage-increasing is stable which contributes to a flat coating, however, the coating thickness is thinner with a poorer corrosion resistance.
Figure 6. Electrochemical impedance spectroscopy of MAO coated ZK60 alloy specimens in 3.5% NaCl solution (a) Nyquist (b)Bode.

4. Conclusions

1) Under two steps voltage-increasing mode, the MAO process experience a new round of breakdown and regrowth period, the higher amplitude of voltage-increasing can provide a larger driving force of coating growth with a growth rate of 2.5μm/min which realize a rapid growth of MAO coating with a rather thick coating, while under three steps voltage-increasing mode, there is an additional regrowth stage in the MAO process, the amplitude of voltage-increasing is reduced to half of the former, the process is relatively stable, the coating is uniform and dense but the thickness is thinner than the former.

2) Due to the lower amplitude of voltage-increasing under three steps voltage-increasing mode, the MAO process is relative stable, the coating formed under this mode is uniform and dense compared with one of two steps voltage-increasing mode, the aperture is smaller of 3.5μm and the coating roughness is lower of 5.1μm.

3) The corrosion resistance of MAO coating can be improved much by steps voltage-increasing mode. Corrosion resistance assessed by low frequency impedance indicates that MAO coating formed under two steps voltage-increasing mode would show best resistance with highest value of low frequency impedance of 1.414×105 ohm.cm² which increases by 1 order of magnitude compared to the single voltage mode.

Acknowledgments

The present work was financially supported by a project funded by the priority academic program development of Jiangsu Higher Education Institutions and the key laboratory of advanced welding technology of Jiangsu Province, China (JSAWT-11).

References

[1] Fan X, Wang Y and Zou B 2014 Preparation and Bond Properties of Thermal Barrier Coatings on Mg Alloy with Sprayed Al or Diffused Mg-Al Intermetallic Interlayer Thermal Spray Technology 23 304
[2] Jiao Miao, Bing Ye and Qudong Wang 2013 Mechanical properties and corrosion resistance of Mg–10Gd–2Y–0.5Zr alloy by hot extrusion solid-state recycling Journal of Alloys and Compounds 561 184–192
[3] Shuyan Wang et al. 2014 Preparation and performance of MAO coatings obtained on AZ91D Mg alloy under unipolar and bipolar modes in a novel dual electrolyte Ceramics International 40(1) 93–99
[4] Shang J et al. 2012 Effect of joining temperature on microstructure and properties of diffusion bonded Mg/Al joints Transactions of Nonferrous Metals Society of China 22(22) 1961–1966
[5] Huang Z H 2013 Microstructures and Mechanical Properties of ZK60-XHo Wrought Magnesium Alloys Materials Science Forum 36(3) 437–445
[6] Yu W et al. 2008 Microstructure and mechanical properties of ZK60–Yb magnesium alloys
[7] Yan-Long M A, Pan F S and Zuo R L 2004 Review on the Research of High-strength Wrought Magnesium Alloy ZK60 *Journal of Chongqing University* **27**(9) 80–85

[8] Chen X B, Birbilis N and Abbott T B. 2011 Review of Corrosion-Resistant Conversion Coatings for Magnesium and Its Alloys *Surface & Coatings Technology* **67**(3) 35005–35001

[9] Terleeva O P et al. 2010 Effect of microplasma modes and electrolyte composition on micro-arc oxidation coatings on titanium for medical applications *Surface & Coatings Technology* **205**(6) 1723–1729

[10] S Xin, L Song, R Zhao and X Hu 2006 Influence of cathodic current on composition, structure and properties of Al2O3 coatings on aluminium alloy prepared by micro-arc oxidation process *Thin Solid Films* **515** 326–332

[11] Z Song, Z Xie and G Yu 2015 A novel palladium-free surface activation process for electroless nickel deposition on micro-arc oxidation film of AZ91D Mg alloy *Journal of Alloys and Compounds* **623** 274–281

[12] Li C et al. 2014 Effect of the Micro-arc Oxidation and Cerium Salt Sealing on the Corrosion and Wear Resistance of New 7A85 *Mechanical Science & Technology for Aerospace Engineering* **33**(1) 127–132

[13] Wei-wei Chen, Ze-xin Wang, Lei Sun and Sheng Lu 2015 Research of growth mechanism of ceramic coatings fabricated by micro-arc oxidation on magnesium alloys at high current mode *Journal of Magnesium and Alloys* **3** 253–257

[14] S Lu, Z X Wang, J Chen and X S Zhou 2011 *The Transactions of Nonferrous Metals Society of China*. **21** 929–935

[15] Ping Wang, Jianping Li 2010 Growth process and corrosion resistance of ceramic coatings of micro-arc oxidation on Mg-Gd-Y magnesium alloys *Journal of Rare Earths* **28** 798–802

[16] S Lu, L Tang, X Z Jiang, Z X Wang and J Chen 2011 *Advanced Materials Research* **337** 101–105

[17] Jiang Bai-ling and Liu Dongjie 2011 Scientific aspects of restricting development and application of micro-arc oxidation technology *The Chinese Journal of Nonferrous Metals* **21**(10) 2402–2407

[18] Y M Wang, L X Guo, J H Ouyang, Y Zhou and D C Jia 2009 Interface adhesion properties of functional coatings on titanium alloy formed by Micro-arc oxidation method *Applied Surface Science* **255** 6875–6880

[19] Jun Liang, Litian Hu and Jingcheng Hao 2007 Improvement of corrosion properties of Micro-arc Oxidation coating on magnesium alloy by optimizing current density parameters *Applied Surface Science* **253** 6939–6945

[20] Chen Xian-ming, Luo Cheng-ping, Liu Jiang-wen and Li Wen-fang 2006 Structure of ceramic coating produced by micro-arc oxidation on Mg alloy *Journal of Central South University* **37**(6) 1065–1069

[21] Ge Yangfeng, Jiang Bailing, Li Yulei and Yagin Zhiyuan 2011 Microstructure and Corrosion Resistance of Composite Micro-arc Oxidation and SiO2 Coatings on Magnesium Alloy *Chinese Journal of Materials Research* **25**(1) 79–83

[22] P Bala Srinivasan, J Liang, C Blawert, M Störmer and W Dietzel 2009 Effect of current density on the microstructure and corrosion behaviour of plasma electrolytic oxidation treated AM50 magnesium alloy *Applied Surface Science* **255**(7) 4212–4218

[23] Hu Hui-li, Gao Ning-ning, Yu Yuan-chun and Li Ning 2009 Research progress on formation process of micro-arc oxidation ceramic coatings on magnesium alloy *Electroplating & Finishing* **28**(12) 35–42

[24] Qu L et al. 2013 Microstructure and corrosion resistance of ultrasonic micro-arc oxidation biocoatings on magnesium alloy *Journal of Advanced Ceramics* **2**(3) 227–234