Vacuum 150 (2018) 155–165

Contents lists available at ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Direct current micro-arc oxidation coatings on Al-Zn-Mg-Mn-Zr extruded alloy with tunable structures and properties templated by discharge stages

Zequan Zhao [a], Qinglin Pan [a, *], Jikang Yan [b], Ji Ye [a], Yaru Liu [a]

[a] School of Materials Science and Engineering, Centre South University, Changsha, 410083, China
[b] School of Materials Science and Engineering, Kunming University of Science and Technology, Kunming, 650504, China

ARTICLE INFO

Article history:
Received 10 December 2017
Received in revised form
20 January 2018
Accepted 22 January 2018

Keywords:
Extruded alloy
Direct current (DC)
Micro-arc oxidation (MAO)
Current density
Micro-arc stage
Mullite

ABSTRACT

In order to improve the surface performance of Al-Zn-Mg-Mn-Zr extruded alloy, alumina coatings were directly prepared on the alloy in silicate electrolytes by direct current micro-arc oxidation technique. The relationship between discharge stages and technology parameters was studied, and then the growth behaviors, structure, composition and properties of coatings were further analyzed. Our work suggests that appropriately prolonging of the oxidation time at a low current density of 2 A/dm^2 can help to extend the action time of the micro-arc stage (Stage III) and to form a thicker layer with fewer inner defects. The compact inner structure promotes the hardness, elastic modulus as well as the corrosion resistance of the coatings. In contrast, the higher the current density, the earlier the discharge enters into the big arc stage (Stage IV), which has an adverse impact on the structure and properties of the coatings. In the Stage IV, the porosity of the coatings increases with the generation of mullite within the coatings comprise of γ-Al_2O_3 and α-Al_2O_3. The growing direction of coatings changes from outward mainly to inward in the late stage of the micro-arc oxidation (MAO) process.

1. Introduction

Al-Zn-Mg-Mn-Zr alloy with moderate strength, good weldability and good extrusion formability is widely used in the high speed train, mobile phone, shipbuilding and automotive industries [1]. However, the alloy surface is usually exposed to the outside environment, thus the damage of the surface corrosion and surface abrasion of the aluminum alloy affects its application ranges and lifespan. The properties of aluminum can be improved by surface modification such as chemistry conversion coating, anodic oxidation, micro-arc oxidation, laser treatment etc. The micro-arc oxidation process (MAO) would form metal-oxide coatings with high hardness and wear resistance on the surface of the alloy [2–5].

The properties and structures of MAO coatings can be influenced greatly by the current density [6–8], the oxidation time [9] and constitution of electrolyte [10,11], the substrate material [12,13] and the type of power supplies [14]. The power supplies of MAO process can be classified into direct current (DC) and unbalanced alternative current (AC). Current studies mainly concentrate on the effects of different technology parameters on characteristics of coatings prepared by AC power supplies, and there has been relatively little research of rules of technology parameters of DCMAO process as well as the optimization of the parameters. ACMAO process is widely used in the fields of transportation and commodity, since the action of the cathodic current of the AC power supply lead to the increase in the compactness, thickness, hardness and other properties of the coatings [14,15]. However, the AC power supply has the shortage such as high cost and inconvenience. There are many fields in which still need porous and thin coatings prepared by DCMAO which is more economical and convenient [16].

The MAO process is characterized by the generation of numerous tiny micro discharge sparks that occurs continuously over the processed surface. Some studies focused on the formation mechanisms of coatings under the presence of discharging behaviors that was marked by discharge sparks [17–19]. Moreover, the sparks can divide the discharge of MAO process into four different stages named anodic oxidation stage (Stage I), spark discharge stage (Stage II), micro-arc discharge stage (Stage III) and big arc discharge stage (Stage IV) [20]. Passive films are formed in the Stage I under a strong electric field [21], then the spark

* Corresponding author.
E-mail address: pql818@163.com (Q. Pan).

https://doi.org/10.1016/j.vacuum.2018.01.040
0042-207X/

discharges, which characterize the Stage II - IV, happen when the passive films are penetrated by the breakdown voltage. In order to deepen the understanding of the formation mechanisms of MAO coatings, many researchers proposed discharge models by simulating the microscopic discharge behaviors of MAO process. Albella et al. [22] established the Electrical Breakdown Model, suggesting that particles from electrolyte went into the inner coatings to form the discharge centers which inducted the plasma discharges with strong thermal effects. As a result, the deposition of the discharging products on the substrate surface led to the growth of coatings. Wang et al. [23] established the discharge models by detecting the change of plasma by emission spectrography, which suggested that the bubble breakdown occurred before the dielectric breakdown on barrier layers. Hussein et al. [19] and Cheng et al. [24] monitored the temperature variation and the constitution of plasma, then combined the coating structures and microanalysis to establish the discharge models which showed four coexistence discharge types during the MAO process. Their studies suggested that the microscopic discharge characteristics had some corresponding relationships with coating structures and inferred the possible discharge types of Stage II – IV, but the researches were underway in order to further understand the detailed discharge mechanisms at different stages. These models generalized the discharge mechanism of MAO process from different aspects. Based on these researches, later studies could combine the analysis of the plasma's characteristics, discharge evolution as well as coating structure changes under a certain experimental system with previous discharge models to discuss the discharge behavior of different discharge stages in detail to build a more complete understanding of growth mechanism of MAO coatings. Yerokhin et al. [25]. suggested that every discharge stage had the specified initial and terminating conditions which were closely connected to electrical parameters. Their follow-up study [26] suggested that electrical parameters could influence the duration of discharge stages by affecting the forms and evolution of sparks, then further affected the characterization of coatings. Hussein et al. [18] also suggested that the plasma discharge behavior was affected by technology parameters (i.e. current density and oxidation time) during the MAO process. However, there is only limited information about controlling the action time of different discharge stages by adjusting time and electrical parameters. In addition, the spatial characteristics of discharges were changing with the coating growth [26], and many studies suggested that structures of coatings were distinct in different MAO discharge stages due to the difference in the intensity of discharges [27–29]. Nevertheless, current studies still lack the understanding of the combined effects of discharges in different stages on the growth behaviors and properties of coatings. Understanding the relationship of technology parameters and discharge stages, and the influence of different stages on the formation of coatings contributes positively to the optimization of MAO technology parameters. Controlling discharge stages may also broaden research ideas and provide a reference for other researchers when they are trying to optimize MAO process under a certain system. This work mainly focuses on the influence of the longest stage among all, i.e. the Stage III as well as the final Stage IV, on discharge phenomenon, composition, structure, and properties of DCMAO coatings such as corrosion resistance, elastic modulus and hardness. Then the discharge models of Stage III and IV are proposed based on the studies of Hussein et al. [19] to build the relationship between coating structures and microscopic discharge characteristics.

2. Material and method

Al-Zn-Mg-Mn-Zr extruded alloy test pieces with size of $10 \times 10 \times 20\ mm^2$ were used as substrates. The actual composition of the alloy is shown in Table 1. The test pieces were treated by solid-solution heat-treated at 470 °C for 1 h and then quenched with water. Subsequently an aging treatment was carried out at 120 °C for 24 h.

DC unit used in this work consisted of an electrolyte bath with stirring and cooling systems with a power supply. Electrolyte consisted of Na_2SiO_3 8 g/L, NaOH 1 g/L, Ethylenediaminetetraacetic acid disodium salt (Na_2EDTA) 2 g/L and Na_2WO_4 1 g/L. The temperature of the electrolyte was controlled at 20 °C - 35 °C. The maximum voltage output of the DC power supply was 600 V. The MAO coatings were obtained under current density of 2 A/dm^2, 4 A/dm^2, 6 A/dm^2, 8 A/dm^2, 10 A/dm^2 respectively for 30 min. Constant current density was maintained by controlling the output voltage during the deposition process. To further investigate the role of the Stage III and IV on the subsequent formation of the MAO coatings, test pieces were deposited under 2 A/dm^2 and 8 A/dm^2 for 45 min, 60 min, 90 min respectively.

The microstructure of coatings was investigated using an FEI QUANTA-200 scanning electron microscope (SEM) equipped with an Energy Dispersive Spectrometer (EDS). Values of thickness were obtained by measuring the section length of coatings under SEM. Ten measurements were carried out evenly on different positions of the coating. Corresponding percentage of open pores (P_o) of coatings were acquired by making use of Image J software to analyze SEM images.

The hardness and elastic modulus of alumina coatings at the direction of cross section was evaluated using a nano-indenter with a max load of 20 mN. The cross section of samples was polished by abrasive paper. Each sample taken from 5 testing points on the inner compact layer.

The corrosion resistance and through porosity (P_t) of the coatings was evaluated by means of potentiodynamic electrochemical tests. 3.5 wt. % NaCl solution was used as corrosive medium. A platinum electrode was used as counter electrode and the saturated KCl aqueous solution was used as reference. The dimension of working electrode had an area of 1 cm^2 in contact with the electrolyte. The potentiodynamic polarization voltage swept from 500 mV below to 500 mV above the open circuit potential with a scan rate of 10 mV/s.

The constitution of coatings was identified using X-ray diffraction (Cu K_a radiation) and Energy Dispersive Spectrometer (EDS). The X-ray generator settings were 40 kV and 250 mA, and the scans were acquired from 20° to 80° (in 2θ), scanning speed was 0.02°s^{-1}.

3. Results and discussion

3.1. The growth behaviors of coatings

According to the appearance of electric sparks under different electrical parameters, four main discharge stages could be observed during the MAO process. The process of anodic oxidation, that gas bubbles appeared on the surface of the test piece with metal solution, was observed in the Stage I. The voltage changed in a linear trend, which mainly maintained for a short time then passive films had been formed on the surface. Then the increased voltage accelerated electrons in discharge channels and electron avalanches happened under the constant collisions of atoms with

Table 1
Chemical composition of the alloy (mass fraction).

Zn	Mg	Mn	Zr	Cu	Cr	Ti	Al
6.1	0.85	0.20	0.25	0.15	0.12	0.1	balance