Preliminary Study on Preparation of Black Ceramic Coating Formed on Magnesium Alloy by Micro-arc Oxidation in Carbon Black Pigment-contained Electrolyte

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Abstract

Based on orthogonal design, black ceramic coating was obtained on AZ91D magnesium alloy with addition of carbon black pigment in electrolyte by micro-arc oxidation (MAO). The blackness, thickness, phase, morphology and composition of the coating were analyzed by visual detection, eddy current thickness meter, XRD, digital cameras and EDS. The reasonable preparation parameters were obtained, and the influences of current density, carbon ink concentration, Na₂WO₄ concentration, Na₂SiO₃ concentration and sodium citrate concentration on the blackness and thickness of the coating were studied. The results showed that adopting constant current mode, the ceramic coating with good color uniformity, blackness of 0.9 and thickness over 30µm could be prepared on AZ91D magnesium alloy surface by MAO under the conditions of current density 3A/dm², carbon ink concentration 25mL/L, Na₂WO₄ concentration 1.5g/L, Na₂SiO₃ concentration 6g/L and sodium citrate concentration 0.3g/L. Carbon ink concentration and current density were the main effect factors of the coating blackness and thickness, respectively. Coating blackness rose significantly with the increasing of carbon ink concentration and coating thickness increased with the increasing of current density at first and then decreased. Coating blackness and thickness all increased with the increasing of Na₂WO₄ concentration. As Na₂SiO₃ concentration increased, coating blackness gradually decreased, and there was little change of coating thickness. Sodium citrate concentration has little influence on coating blackness, while coating thickness decreased as it increased.

Keywords: Magnesium alloy; micro-arc oxidation; black ceramic coating; influence parameters

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1. Introduction

Due to their low density, excellent thermal and mechanical properties, chemical resistance and self-lubricating capability, carbon/carbon (C/C) composites have become today’s top choice of material for aircraft brake disks [1]. However, the high cost of C/C composites, due to the complex manufacturing production processes, has prohibited C/C composites from being considered as candidate materials in domestic vehicles.

Micro-arc oxidation (Micro-plasma oxidation, MAO) is a relatively new surface treatment method used to form in-situ oxide coating on Al, Mg, Ti and their alloys in suitable electrolyte with the combination of corresponding electrical parameters. During the MAO process, a series of thermo-chemical interactions were generated between the substrate and the electrolyte due to the instantaneous high temperature and pressure in the micro-arc zone. The coating prepared by MAO presents high hardness, high wear and corrosion resistance properties, good adhesion to substrate, high temperature shock, electronic insulation, etc [1, 2]. MAO method is simple and easy to implement functional regulation of the coating. In addition, the process is not complicated and environmental friendly. It is a green metal surface treatment method, which has broad application prospects in aerospace, machinery, electronics, decoration and other fields. Usually for the purpose of protection, it is just need to prepare a layer of ceramic coating on the substrate by MAO; but for some metals and alloys used in aircraft engines, parts of optical instruments and certain military installations, the ceramic coating on their surface is also required to be black to reduce reflection rate or increase thermal radiation. Furthermore, metals and alloys with black ceramic on surface have been used widely in the construction, appliance, automotive manufacturing and other fields owing to their excellent decorative performance [3, 4].

Some researchers have obtained fuscous ceramic coatings on aluminium alloy surface using different inorganic colorants by MAO method, but most of the selected inorganic colorants (such as potassium dichromate, etc.) were harmful to the environment [3-5]. In addition, studies have found that it is difficult to acquire black ceramic coatings on magnesium alloy merely using inorganic colorants-contained electrolyte by MAO [6, 7]. So far the color of micro-arc oxidation ceramic coating formed on magnesium alloy surface is still mainly dominated by a single white [8]. Carbon black pigment whose elemental composition mainly composed of carbon is one of the most mature black substances used in industry, so it has very high stability in light, heat and chemicals, etc. Besides, it has some other characteristics, include good weather resistance, non-toxic, high blackness and excellent tinting strength. Carbon black pigment, however, has not been used as colorant for the preparation of black ceramic coating on metal surface by MAO. Therefore, to research of black ceramic coating prepared in carbon black pigment-contained electrolyte by MAO and discuss the main influence parameters have important guiding significance for promoting the green preparation of black ceramic coating on metal surface.

In this paper, carbon ink was used as the source of carbon black pigment. Black ceramic coating was obtained on AZ91D magnesium alloy by micro-arc oxidation and the main influence parameters were emphatically analyzed, then the fundamental of black ceramic coating prepared on magnesium alloy surface by micro-arc oxidation was studied.

2. Experimental

Rectangular specimens (30mm×30mm×5mm) of AZ91D magnesium alloy were used as the substrate. The chemical composition (mass fraction) of AZ91D magnesium alloy is Al 9.7%, Zn 0.8%, Mn 0.3%, Si 0.1%, Cu 0.03% and Mg balance. Before MAO treatment, the surface of specimens were ground and polished with 1000 grit SiC abrasive paper, degreased in acetone, rinsed in deionized water and then thoroughly dried.
A 30kW pulsed and DC power was used for the experiments. The treatment was conducted by adopting constant current mode, and the fixed electrical parameters were frequency 600Hz, duty circle 0.2, cathode-anode current density ratio 1.0 and treatment time 20min. The electrolyte was prepared using the solution of silicate-based salt and “Ostrich” brand carbon ink, KOH (2g/L) and NaF (2g/L) served as the auxiliary coating-forming additives; all the electrolyte were prepared by using analytical grade reagents and deionized water. Using L$_{16}(4^5)$ standard orthogonal form, factors and levels design are shown in Table 1.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Level</th>
<th>Current density (A/dm$^2$)</th>
<th>Carbon ink concn. (mL/L)</th>
<th>Na$_2$WO$_4$ concn. (g/L)</th>
<th>Na$_2$SiO$_3$ concn. (g/L)</th>
<th>Sodium citrate concn. (g/L)</th>
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MAO coating consists of dense layer (close to the substrate) and loose layer (close to the surface), and blackness of loose layer was taken as the evaluation object in this paper. A model of illustrative plates of black saturation was established by introducing non-color hierarchy, as shown in Fig. 1 [9]. The blackness of the ceramic coating was characterized by the visual detection method specified in the national standard GB/T 14952.3-1994. The thickness of the ceramic coating was measured by TT230 eddy current thickness meter. The phases of the ceramic coating were examined by X-ray diffraction. Digital camera was used to observe the macromorphology of the ceramic coating. The chemical composition of the ceramic coating was analyzed by energy dispersion X-ray spectrometry carried by scanning electron microscopy.

Fig. 1. A collection of illustrative plates of black saturation.

3. Results and Discussion

3.1. Results of orthogonal experiments and range analysis

Taking blackness and thickness of the ceramic coating prepared on AZ91D magnesium alloy through orthogonal experiments as evaluation index, the results of orthogonal experiments and range analysis are shown in Table 2.

From the analysis of Table 2, the blackness of the ceramic coating prepared on AZ91D magnesium alloy is affected by factors B>C>D>A>E in turn, the optimal level is B$_4$-C$_3$-D$_1$-A$_4$-E$_2$. That is carbon ink concentration affects the coating blackness most, followed by Na$_2$WO$_4$ concentration and Na$_2$SiO$_3$ concentration, current density and sodium citrate concentration have little influence on it. The thickness of the ceramic coating prepared on AZ91D magnesium alloy is affected by factors A>B>C>E>D in turn, the optimal level is A$_3$-B$_2$-C$_4$-E$_1$-D$_1$. That is current density affects the coating thickness most, followed
by carbon ink concentration and Na$_2$WO$_4$ concentration, sodium citrate concentration and Na$_2$SiO$_3$ concentration have little influence on it.

Table 2. The results of orthogonal experiments and range analysis.

<table>
<thead>
<tr>
<th>Expt.</th>
<th>Current density (A/dm$^2$)</th>
<th>Carbon ink concn. (mL/L)</th>
<th>Na$_2$WO$_4$ concn. (g/L)</th>
<th>Na$_2$SiO$_3$ concn. (g/L)</th>
<th>Sodium citrate concn. (g/L)</th>
<th>Black. (a)</th>
<th>Thick. (µm) (b)</th>
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3.2. Influence of current density on blackness and thickness

According to the results of range analysis, the regulations of the ceramic coating blackness and thickness changed with current density were obtained, as shown in Fig. 2.

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Fig. 2. Influence of current density on blackness and thickness.

As can be seen from the figure, the average blackness value of the coating prepared under different current density is all about 0.6. With the increase of the current density, the blackness value shows a slight increase trend. When the current density is 1A/dm$^2$, the blackness is 0.62, and when the current density rise to 4A/dm$^2$, the blackness only go up to 0.71, changes slightly. It indicates that within the
The average coating thickness increases gradually along with the increase of current density first, it is minimum (23.73µm) when the current density is 1A/dm², and reaches a maximum (32.95µm) when the current density rise to 3 A/dm². But then the coating thickness begins to decrease, it is 29.83µm when the current density is 4A/dm². Figure 2 also shows that when the current density is 3A/dm², the coating is the thickest, while the coating blackness is the lowest (0.59).

The reason is that during the MAO process, the micro-arc discharge energy and the plasma discharge intensity increased with the increasing of current density, which leading to a more drastic oxidation reaction, thus the speed of the coating internal oxidation accelerated. Meanwhile, the diameter of the discharge micropore increased and more molten materials ejected from the micropore, then the stack thickness of the molten materials around the micropore increased by the quenching effect of the electrolyte. When the loose layer (about half of the coating) was polished away, it was found that the blackness of the dense layer was higher than the loose layer. Carbon black pigment would be involved in the whole formation process of the coating. Early in the reaction, the discharge sparks density was high and the discharge channels were tiny, carbon black particles continuously deposited in the dense layer though the channels. In the later stage reaction, the sparks became sparse and their energy was weaken, the discharge channels diameter increased and the growth rate of the coating became slow, thus the deposition rate of carbon black particles decreased. The coating thickness increased in the later stage was mainly due to the growth of loose layer, so when the current density of 3A/dm², the surface loose layer was thicker while the coating blackness was relatively lower.

When the current density was too high, micro-arc oxidation reaction process would become too intense, there was not enough time to cool the molten things and the electrolyte prone to “violent boiling”, the prepared coating surface is rough and there was even ablation and some other defects. Therefore, there was a critical current density, the coating surface quality degraded and the coating thickness decreased when this critical value was exceeded. Under the electrolyte system used in this study, when the current density exceeded 3A/dm², the thickness of the ceramic coating formed on AZ91D magnesium alloy decreased and the coating blackness increased slightly, so the reasonable value of the current density was 3A/dm² in this study.

### 3.3. Influence of carbon ink concentration on blackness and thickness

From the results of range analysis, it could be seen that carbon ink concentration was the main effect parameter of the coating blackness. Figure 3 shows the regulations of the ceramic coating blackness and thickness changed with carbon ink concentration.

![Fig. 3. Influence of carbon ink concentration on blackness and thickness.](image-url)
The figure shows that the blackness of the coating prepared on AZ91D magnesium alloy enhances significantly with the increase of carbon ink concentration. When the carbon ink concentration is 10mL/L, the average value of the coating blackness is only 0.41, and when the concentration rises to 25mL/L, the average value increases to 0.76, the increased value is 0.35. With the increasing of carbon ink concentration, the ceramic coating thickness increases at first and then decreases. When the carbon ink concentration is 10mL/L, the average value of the coating thickness is 26.20µm; and when the concentration is 15mL/L, the value reaches a maximum of 32.03µm. Then continue to increase the carbon ink concentration, the coating thickness decreases instead. Study also found that under this experimental system, the reaction would become extraordinary violent and the electrolyte temperature rise rapidly when the carbon ink concentration exceeded 30mL/L, the surface quality of the coating was very poor and the color distribution was extremely uneven.

This was because the higher carbon ink concentration, the more carbon black particles in the electrolyte, then the number of the particles participated in the MAO process increased, thus macro-morphology of the coating showed that the blackness increased. The analysis results of coating indicate that C element is a main influence factor of the coating blackness. With the increasing of carbon ink concentration, the number of carbon black particles increased, thus the coating blackness also increased gradually.

When the carbon ink concentration was within 15mL/L, as the concentration increased, many carbon black particles were adsorbed in the micro-arc zone to form the foreign impurities discharge center, which lead to more electric breakdown, so the growth rate of the coating increased and then the coating thickness increased in the same reaction time. But when the concentration exceeded 15mL/L, too many carbon black particles deposited in the discharge channel and other active zone in the coating, the adsorption process of other anions to the anodic sample and the ejection process of molten materials were suppressed. Thus the growth of coating was hampered and the coating thickness decreased.

3.4. Influence of Na$_2$WO$_4$ concentration on blackness and thickness

According to the results of range analysis, the regulations of the ceramic coating blackness and thickness changed with Na$_2$WO$_4$ concentration were obtained, as shown in Fig. 4. The figure shows that when the Na$_2$WO$_4$ concentration increases, the coating blackness and thickness have a trend of increase, especially the coating thickness presents almost a linear upward trend. When the Na$_2$WO$_4$ concentration is 0.5g/L, the average value of the coating blackness and thickness is 0.43 and 26.30µm respectively, and when it rises to 1.5g/L, the average value of the coating blackness is 0.65. The coating thickness increases with the increasing Na$_2$WO$_4$ concentration, the average value of the coating thickness reaches 31.73µm as the Na$_2$WO$_4$ concentration of 2.0g/L.

![Fig. 4. Influence of Na$_2$WO$_4$ concentration on blackness and thickness](image-url)
This was because, during the MAO process, \( \text{WO}_4^{2-} \) was absorbed in the discharge channel and other active zone, a series of electrochemical and thermo-chemical reaction would occurred due to the instantaneous high temperature and pressure produced by micro-arc discharge, then different oxides of tungsten were generated. At the same time, some W would be generated from the oxides, and it could react with C of carbon black to form tungsten carbide. Therefore, the MAO coating formed on AZ91D magnesium alloy in the base electrolyte consisted mainly of MgO and Mg_2SiO_4, while the coating formed in electrolytes with addition of carbon ink and Na_2WO_4 also contained WO_{2-3} and W_{1-2}C. The MAO coating became darker as WO_3 was yellow and WO_2 was brown [10]. WC and W_{2}C were black, which would further increase the coating blackness. The electrolyte conductivity increased with the increasing Na_2WO_4 concentration, then the growth rate of the coating accelerated, so the coating thickness increased.

3.5. Influence of Na_2SiO_3 concentration on blackness and thickness

The regulations of the ceramic coating blackness and thickness changed with Na_2SiO_3 concentration were shown in Fig. 5. The figure shows that when the Na_2SiO_3 concentration is 6g/L, the average value of the coating blackness and thickness is 0.77 and 30.08µm respectively. The coating blackness and thickness tends to decrease when the Na_2SiO_3 concentration increase. When the Na_2SiO_3 concentration is 10g/L, the average value of the coating blackness and thickness is 0.55 and 28.60µm respectively. This was because the adsorption of ion in the electrolyte to the ceramic coating was selective during the MAO process and the adsorption capacity of SiO_2\(^{2-}\) was the strongest [11]. There were more SiO_2\(^{2-}\) in the electrolyte when the Na_2SiO_3 concentration increased, the absorbance of SiO_2\(^{2-}\) increased. Then the adsorption of carbon black particles and WO_4\(^{2-}\) was affected, so the coating blackness and thickness decreased to some extent. And as more SiO_2\(^{2-}\) was adsorbed on the coating, the discharge channels were “blocked” relatively. So when the Na_2SiO_3 concentration exceeded 8g/L, the average value of the coating thickness was almost constant. Therefore, the Na_2SiO_3 concentration should not be too high in the electrolyte to prepare black ceramic coating on AZ91D magnesium alloy in this study.

![Fig. 5. Influence of Na_2SiO_3 concentration on blackness and thickness.](image)

3.6. Influence of sodium citrate concentration on blackness and thickness

The regulations of the ceramic coating blackness and thickness changed with sodium citrate concentration were shown in Fig. 6. It can be seen from the figure that the average blackness value of the coating prepared under different sodium citrate concentration is all about 0.6. The impact of sodium citrate concentration on the coating blackness is not significant. But the coating thickness decreases gradually as the increasing of the sodium citrate concentration. When the sodium citrate concentration is 0.3g/L, the average value of the coating thickness is 31.10µm, and when the concentration rises to 0.7g/L,
the average value is 26.45µm. Sodium citrate could reduce the arc voltage on both ends of the sample, which could avoid the generation of ablation and other detects on the coating surface. Also, the micro-arc oxidation became weaker owing to the drop of the voltage; thereby the oxide coating formation rate was slow down. As a result, the coating thickness tended to decrease when the sodium citrate concentration increased [6]. It was also for this role of sodium citrate, its impact on the blackness of the MAO coating formed on AZ91D magnesium alloy showed a similar pattern as the current density.

Fig. 6. Influence of sodium citrate concentration on blackness and thickness.

4. Conclusions

(1) Adopting constant current mode, under the conditions of current density 3A/dm², carbon ink concentration 25mL/L, Na₂WO₄ concentration 1.5g/L, Na₂SiO₃ concentration 6g/L and sodium citrate concentration 0.3g/L, the ceramic coating with good color uniformity, blackness of 0.9 and thickness over 30µm could be prepared on AZ91D magnesium alloy surface by MAO.

(2) Carbon ink concentration and current density were the main effect factors of the coating blackness and thickness, respectively. Coating blackness rise significantly with the increasing of carbon ink concentration, and coating thickness increased with the increasing of current density at first and then decreased. In this study system, when the carbon ink concentration was 25mL/L and the current density was 3A/dm², a high quality ceramic coating could be obtained.

(3) Coating blackness and thickness all increased with the increasing of Na₂WO₄ concentration. As Na₂SiO₃ concentration increased, coating blackness gradually decreased, and coating thickness did not changed much. Sodium citrate concentration had little influence on coating blackness, while coating thickness decreased as it increased.

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References


