Conference Article

The Effect of Microarc Oxidation (MAO) Modes on Corrosion Behavior of High-Silicon Aluminum Alloy


Ufa State Aviation Technical University, Ufa, Russian Federation

Received 15 September 2014; Accepted 29 September 2014

Abstract

The investigation studies the properties of hardened surface layers, developed with the microarc oxidation method (MAO) on ingots of a Al-Si alloy. It has been proved that properties of the developed surfaces (microhardness, thickness, porosity and corrosion properties) depend on the concentration of electrolyte components.

Keywords: microarc oxidation, aluminum alloys, micohardness, corrosive behavior

1. Introduction

Al and its alloys gain the lead in industrial scale and application due to their low cost, high specific strength and stiffness. However, their corrosive resistance depend both on the number of impurities or the additives intentionally introduced into the alloy, and on the quality of the surface protective film. The natural oxide film for aluminum is not considered as protective for the base metal (alloy) from corrosion, but this film can be artificially thickened and become more dense.

One of the most advanced techniques of applying the protective coating on the products and constructions of aluminum alloys is the microarc oxidation (MAO) method.

The microarc oxidation is the process of obtaining the hardened layers on the surface of electro-conductive valve materials, when placed in an electrolytic bath under high-voltage, using local micro-charges from the surface during its anode polarization.

The main advantages of MAO are as follows: the possibility to produce corrosive-resistant coatings with improved mechanical properties (hardness, wear resistance, adhesion to the metal matrix, fatigue resistance), has a small area footprint in the plant while being a quick process, because there is no need for detailed preparation of the surfaces.

It is known that the quality of the developed surface layers is determined by the modes of the MAO-process [1-5]. Nowadays the MAO technique is widely used for hardening surfaces of aluminum alloy parts. The possibility to obtain a quality coating has been demonstrated with the alloys of the Al-Cu-Mg, Al-Zn-Mg, Al-Mg-Si systems and etc. [6]. For these materials the influence of various modes on the properties of the MAO-layer, including corrosion resistance, has been studied thoroughly. As for the possibility of obtaining a quality coating on high-silicon aluminum alloys, there is a scarcity of published works on this subject in scientific literature [7], and the conclusions in them are quite contradictory. Besides, there is no any information about corrosive resistance of MAO layers on high-silicon Al alloys.

Thus, the aim of this work is to investigate the effect of the MAO process modes on microhardness and corrosive properties of the coating of high-silicon aluminum alloys.

2. Experiments

The Russian high-silicon aluminum alloy AK12D (Al-Si-Fe) has been chosen for study. The samples were in the shape of a disk, cut out of a rod, and have been treated by the MAO method.

It is known that the quality of the coating depends on a few factors of the MAO process: the electrolyte composition, electric modes and duration of treatment. The output parameters are usually: thickness, microhardness, structure of the MAO-layer and its corrosive characteristics [8-10]. However, the electrolyte has the biggest influence on the MAO-layers. The MAO modes presented in table 1 have been selected for our investigations. These modes differ by the concentration of electrolyte components – soluble water glass Na₂SiO₃ and potassium hydroxide (KOH). Usually [11] during the analysis of the effect of the electrolyte on the behavior of MAO-layer the concentration of one of the electrolyte components remains the same, while the concentration of the second component changes. In our case the content of the two components changes at once, both the soluble water glass and potassium hydroxide while their concentration ratio remaining constant.
During treatment the ratio of the cathode and anode currents remains constant \( I_\text{c}/I_\text{k} = 1 \). The electrolyte temperature did not exceed 45°C.

### Table 1. MAO Modes

<table>
<thead>
<tr>
<th>№ mode/sample</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>concentration KOH ( C_{\text{KOH}} ), g/l</td>
<td>1.5</td>
<td>3.5</td>
</tr>
<tr>
<td>concentration of the soluble water glass ( C_{\text{WG}} ), g/l</td>
<td>1.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>

To estimate the thickness of the coatings the scanning electron microscope (SEM) «JEOL JSM 6390» with a magnification of 500 was used in the mode of the back scattered electrons.

The pores in the MAO layers were also studied with the point contact method by imposing the square grid on the photo.

The hardness of the MAO-layers after Vickers has been determined with a microhardness device «Struers Duramin», for a load of 100 g for 10 seconds.

The corrosive-aggressive solution based on distilled water with sodium chloride (NaCl), potassium nitride (KNO₃) and hydrogen nitrate (HNO₃) has been used for the corrosive tests. The samples have been put into the solution for 6 days (144 hours).

### 3. Results

From the experimental set two samples with MAO-layer were obtained (Fig. 1). It can be seen that following MAO the surface of the samples oxidizes. The samples were treated with various modes to reach a different color (Fig. 1).

![Fig. 1. Samples of the AK12D alloy after MAO: a) sample №1, b) sample №2](image)

The thickness of the coating formed with MAO is non-homogeneous all over the surface of the samples (Fig. 2). Inhomogeneity of the MAO layer was most pronounced for the sample treated in mode 1 (Fig. 2a). The minimal thickness of the coating for sample №1 was 35 \( \mu \text{m} \), the maximum 90 \( \mu \text{m} \). The minimum coating thickness for sample №2 was 90 \( \mu \text{m} \), the maximum was 130 \( \mu \text{m} \). The average thickness of the MAO-coating for sample №1 was \( t_{\text{mean}} = 50 \mu \text{m} \), for sample №2 – \( t_{\text{mean}} = 114 \mu \text{m} \).

From the corrosive tests the rate of corrosion was been calculated. Sample №2 had the highest one at \( 2.3 \cdot 10^{-5} \text{ g/m}^2 \cdot \text{h} \). The rate of corrosion of sample №1 was \( 9.3 \cdot 10^{-5} \text{ g/m}^2 \cdot \text{h} \). The samples after the corrosive tests had preserved the color obtained in MAO (Fig. 3).

![Fig. 2. Interface of AK12D alloy and MAO-layer: a) sample №1, b) sample №2; 1 – metal; 2 – transition layer; 3 – base layer; 4 – epoxide resin](image)

The average value of the porosity all over the thickness of the MAO-layer for sample №1 has come to 6.3%, for sample №2 – 4.5%. However, while calculating the material volume of the pores then for sample №1 it is equal to 23.3 mm³, and for sample №2 to 37.9 mm³. This is the reason why sample №2 has the biggest volume, when taking into account the pores, and therefore most of them are open to corrosion effects.

The aluminum oxide \( \text{Al}_2\text{O}_3 \) which is the base of the working layer, as it is known, is characterized by high microhardness and resistance to corrosion. Microhardness results show the development of the aluminum oxide during the MAO-treatment of the samples under investigation (Fig. 4).
porosity should have increased due to the development of a microha-

value of microhardness. At a greater distance away from the surface:  

Fig. 4. Porosity and microhardness of the coatings along the sample surface: a) sample № 1, b) sample № 2

layer of mullite, which is characterized by low values of microhardness. However, in our case the increase of porosity with the simultaneous microhardness decrease didn’t develop, as most of the mullite had been removed during the preparation of the samples.

4. Discussion

It is well known that there are many difficulties to obtaining a quality MAO coating while MAO treating high-silicon aluminum alloys. This is usually related to the presence of silicon in the composition of cast alloys. This develops areas of pitting, impeding the interaction between aluminum and oxygen, blocking up the development of an oxide layer and escaping from the working surface during treatment. Where this happens either the surface does not develop or its quality is not satisfactory [7]. A few other factors influence the quality of the MAO coating the most important of which are the composition and the concentration of electrolyte. In our experiments the MAO modes differed in concentration of the water glass and potassium hydroxide. The quantity of the two components was changed once while their relative proportion stayed constant.

The analysis of the results has shown that the MAO method produces quality coatings on the high-silicon aluminum alloy AK12D containing up to 13% of silicon.

The increase of the concentration of the water glass and potassium hydroxide in the electrolyte has produced thicker coatings (114 µm) and higher microhardness (1150 HV) (Fig. 4). The maximum microhardness shows in the working layer. The microhardness increase in the thicker sample is obviously related to the fact that MAO-layers have low heat conductivity [13]. This property allows the development of high-temperatures and hard phases of aluminum oxide $\alpha - \text{Al}_2\text{O}_3$ [6] throughout the hardened layer.

However, the concentration increase of the water glass and potassium hydroxide has led to the decrease of corrosive characteristics of the MAO-layer. The thicker coating showed faster corrosion than the thinner one. Such a difference in corrosive resistance of the MAO-layer with thickness is due to porosity. As it is known, the corrosion of a coated part is connected to the penetration of corrosive-aggressive media through the pores. The photo of the interface between the AK12D alloy and the MAO-layer has shown the presence of pores in the MAO-layer for both samples under investigation. Thus, the porous volume has been higher for sample №2. In the MAO-layer of sample №2 there appears a large number of cracks with some of them passing through the whole thickness of it. It is obvious that the larger the thickness of the MAO-layer the higher the possibility of developing defects. A similar association between the thickness of the MAO-layer and the corrosive properties of aluminum 2024 alloy has been noticed before [14].

Therefore the corrosive properties of the samples after the MAO-treatment are mostly determined by porosity than by thickness of the MAO-layer. The development of a thick coating increases the microhardness of the MAO-layer, but at the same time decreases the corrosive properties. This should be taken into account when the modes of the MAO process are selected.

The microhardness distribution is not homogeneous throughout the thickness of the MAO-layer (Fig. 4). During the transition to the parent material, the values of microhardness increase. The maximum value of microhardness appears in sample №2 at 1150 HV at a distance 60 µm away from the surface. With the distance away from the surface increasing, microhardness is decreasing slightly.

The remarks that can be made about the distribution of porosity and microhardness over the thickness of the coating correspond to relationship already described in literature [12]. In this case a great number of pores is observed in the transition layer as well, which is characterized by the low value of microhardness. At a greater distance away from the surface the porosity is decreasing. At the same time the microhardness is increasing due to the development of the working layer, consisting mostly of aluminum oxide $\text{Al}_2\text{O}_3$. With a further increase of the distance away from the surface porosity should have increased due to the development of a

The microhardness distribution is not homogeneous throughout the thickness of the MAO-layer (Fig. 4). During the transition to the parent material, the values of microhardness increase. The maximum value of microhardness appears in sample №2 at 1150 HV at a distance 60 µm away from the surface. With the distance away from the surface increasing, microhardness is decreasing slightly.

The remarks that can be made about the distribution of porosity and microhardness over the thickness of the coating correspond to relationship already described in literature [12]. In this case a great number of pores is observed in the transition layer as well, which is characterized by the low value of microhardness. At a greater distance away from the surface the porosity is decreasing. At the same time the microhardness is increasing due to the development of the working layer, consisting mostly of aluminum oxide $\text{Al}_2\text{O}_3$. With a further increase of the distance away from the surface porosity should have increased due to the development of a

The microhardness distribution is not homogeneous throughout the thickness of the MAO-layer (Fig. 4). During the transition to the parent material, the values of microhardness increase. The maximum value of microhardness appears in sample №2 at 1150 HV at a distance 60 µm away from the surface. With the distance away from the surface increasing, microhardness is decreasing slightly.

The remarks that can be made about the distribution of porosity and microhardness over the thickness of the coating correspond to relationship already described in literature [12]. In this case a great number of pores is observed in the transition layer as well, which is characterized by the low value of microhardness. At a greater distance away from the surface the porosity is decreasing. At the same time the microhardness is increasing due to the development of the working layer, consisting mostly of aluminum oxide $\text{Al}_2\text{O}_3$. With a further increase of the distance away from the surface porosity should have increased due to the development of a
5. Conclusions

1) Using the MAO-process two modes were used to coat the high-silicon aluminum AK12D alloy.

2) The simultaneous increase of the concentration of water glass and potassium hydroxide leads to the development of a MAO-layer with bigger thickness, higher microhardness and lower porosity.

Acknowledgements

The results of this work were produced in the joint project of USATU (Ufa State Aviation Technical University) and UMPO (Ufa Engine Industrial Association) with title “Elaboration and industrial development of high-precision shaping coordinated technologies and superficial hardening of responsible details from Al-alloys with heightened constructional energy efficiency”, implemented under the contract №40/10-30976 sponsored by the Ministry of Education and Science of the Russian Federation (contract №02.G25.31.0010 between UMPO and the Ministry of Education and Science of the Russian Federation) through the Resolution of the Russian Federation Government № 218 from April 9, 2010.

References


