Effect study of Mao-coatings heat treatment on their structure, phase composition, physical and mechanical properties

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Abstract. The structure, phase composition and physical and mechanical properties of MAO-coatings on deformable aluminum alloys after heating with subsequent holding were studied. It is revealed that in the temperature range from 50 to 600 °C in MAO-coatings there are changes of three types, manifested in increasing the porosity of MAO-coatings and increasing the content of substances with higher physical and mechanical properties. It is shown that the surface hardness, wear resistance and electrical resistance of MAO-coatings increase, but the breakdown voltage decreases. It is established that the simultaneous happens of changes of different types leads to an increase in number of cracks and ruptures in the structure of MAO-coatings and a decrease in their physical and mechanical properties. To maximize the surface hardness, wear resistance and electrical resistance of MAO-coatings, it is proposed to conduct their heating with sequential stepped holding, ensuring a consistent implementation of changes of all three types.

1. Introduction

Anode-cathode micro-arc oxidation (MAO) implemented in electrolyte solutions and also known as plasma electrolytic oxidation (PEO) allows to obtain dense ceramic coatings (MAO-coatings) with high physical and mechanical properties on the surfaces of details made of aluminum alloys [1-4]. MAO-coatings mainly formed by the interaction of aluminum located in the surface layers of details and oxygen appearing from the electrolyte solution [5,6], and is primarily composed of crystalline modifications of aluminum oxide, and also contain amorphous aluminum oxide, aluminum hydroxide and substances, consisting of components of the electrolyte solution and the material of details [6-9].

The physical and mechanical properties of MAO-coatings depend on their thickness, structure and phase composition, which, in turn, are determined by the chemical composition of the details material, the duration of MAO-process, the electric current density on the oxidized surfaces of the details, the chemical composition and temperature of the electrolyte solution, and also some other parameters of MAO-process [3,6,7]. At the same time, the structure, phase composition and physical and mechanical properties of MAO-coatings can be changed after the MAO-process by means of additional processing. In particular,
this can be done by heat treatment, which consists in heating the MAO-coatings to specific temperatures and holding at these temperatures for the transition of aluminum hydroxide into its crystalline oxide, which has increased physical and mechanical properties [7]. However, on the one side, heat treatment of MAO-coatings is a simple and well-controlled process that does not demand additional materials, but, on the other side, requires knowledge of the peculiarities of changing the structure and phase composition of MAO-coatings for change their physical and mechanical properties in the right direction. Therefore, in order to develop reasonable recommendations for the thermal treatment of MAO-coatings, research is needed to study its specificity.

2. Research methods
MAO-coatings formed on discs with a diameter of 30 mm and a thickness of 10 mm made of deformable aluminum alloys AMg3 and D16 were used as objects of researches. MAO-process was carried out for 80 minutes in an aqueous solution of caustic potassium KOH (5 g/l) and sodium silicate Na₂SiO₃ (6 g/l) at its average temperature of 20 °C and the average current density on the disk surfaces in the anode half-cycle of 20 A/dm².

Heat treatment of disks with MAO-coatings, including their heating and subsequent holding, was carried out in a fireproof furnace SNOL 3/10 at the heating temperature ranging from 50 to 600 °C and an holding time of 1 to 300 minutes.

The structure of the formed MAO-coatings was studied using MIM-8 metallographic microscope and JSM-7700F and JCXA-733 scanning electron microscopes with digital image processing system providing a measurement error of not more than 0.1 %. The phase composition of MAO-coatings was studied using DRON-3M and DRON-4 diffractometers according to the tested method [10] providing an error in determining the quantitative content of α-Al₂O₃ and γ-Al₂O₃ of not more than 3%. The hardness, breakdown voltage and electrical resistance of MAO-coatings were measured respectively using PMT-3M microhardness meter, UPU-1M breakdown setup, and E6-3 and E6-7 teraohmmeters. The wear resistance of the surface layers of MAO-coatings was determined by the results of friction and wear tests on X4-B modernized setup according to the pin-on-disk configuration. Due to the significant error of the quantitative X-ray phase analysis, the change in phase composition MAO-coatings was estimated not only by the direct sign – the change in the content of phases α-Al₂O₃ and γ-Al₂O₃, but also by indirect signs – the change in porosity and physical and mechanical properties of MAO-coatings.

3. Results
It is established that MAO-process at the conditions described above allows to obtain high-quality MAO-coatings. Table 1 shows their thickness δ, porosity P, content α-Al2O3 and γ-Al2O3, hardness H, breakdown voltage U, electrical resistance R and linear wear W after the friction and wear test. Moreover, the hardness of MAO-coatings is represented by an intervals of values, since it varies in their thickness, increasing in the direction from the outer surfaces of MAO-coatings to their boundaries with substrates, as shown in figure 1.

| δ, μm | P, % | α-Al₂O₃, % | γ-Al₂O₃, % | H, GPa | U, V | ρ, Ω | W, μm |
|-------|------|------------|------------|--------|------|------|------|
| 171,25 | 5,48 | 42,73 | | | | | |
| 159,67 | 5,97 | 24,95 | | | | | |

Table 1. Characteristics of MAO-coatings not exposed to the heat treatment
Figure 1. Photography of microslice of the sample with MAO-coating after hardness measurement.

It is discovered that heating of disks with MAO-coatings to temperatures not exceeding 180 °C with an holding of up to 300 minutes does not cause any significant changes in the structure, phase composition and physical and mechanical properties of MAO-coatings. However, already heating up to 190 °C with holding of 10 minutes or more leads to a simultaneous increase in the porosity and hardness of the surface layers of MAO-coating thickness of about 40 μm, and also to increase electrical resistance and reduce the breakdown voltage of the MAO-coatings, but without noticeable changes in their granular structure and the content of \( \alpha \)-Al\(_2\)O\(_3\) and \( \gamma \)-Al\(_2\)O\(_3\). Table 2 shows how the characteristics of MAO-coatings change after heating to 190 °C at different holding time \( \tau \).

| \( \tau \), min | P, % | \( \alpha \)-Al\(_2\)O\(_3\), % | \( \gamma \)-Al\(_2\)O\(_3\), % | H, GPa | U, V | \( \rho \), Ω |
|---------------|------|-----------------|-----------------|-------|-----|---------|
| 1             | 5.48 | 15.47...19.83   | 42.73           | 30.46 |     |         |
| 3             | 5.48 | 15.47...19.83   | 42.73           | 30.46 |     |         |
| 10            | 5.49 | 15.49...19.83   | 30.46           |     |     |         |
| 30            | 5.51 | 15.56...19.83   | 2247.54         | 5.76·10\(^{14}\) |     |         |
| 100           | 5.53 | 15.58...19.83   | 2241.15         | 6.55·10\(^{14}\) |     |         |
| 300           | 5.53 | 15.58...19.83   | 2241.15         | 6.55·10\(^{14}\) |     |         |

Table 2. Characteristics of MAO-coatings after holding at temperature of 190 °C.

It is found that the increase in the heating temperature of MAO-coatings from 190 to 270 °C contributes to a faster increase in porosity, hardness, electrical resistance of MAO-coatings and reduce their breakdown voltage. If at a temperature of 190 °C these changes happen in 100 minutes, at a temperature of 270 °C – in less than 30 minutes. With a further increase in the holding time to 300 minutes, no new changes are observed. However, already heating up to 280 °C with holding more than 10 minutes leads to increase in content of \( \gamma \)-Al\(_2\)O\(_3\) in MAO-coatings, complementary increase in the porosity...
and hardness of their surface layers, and also additional increase electrical resistance and reduce the breakdown voltage of MAO-coatings, as shown in table 3.

It is established that the increase in the heating temperature of MAO-coatings from 280 to 470 °C contributes to a faster increase in content of $\gamma$-Al$_2$O$_3$ in MAO-coatings, porosity, hardness, electrical resistance of MAO-coatings and reduce their breakdown voltage without any other significant changes. However, already heating up to 480 °C with holding more than 10 minutes leads to increase in content of $\alpha$-Al$_2$O$_3$ in MAO-coatings, complementary increase in the porosity and hardness of the their surface layers, and also additional increase electrical resistance and reduce the breakdown voltage of MAO-coatings, as shown in table 4.

**Table 3. Characteristics of MAO-coatings after holding at temperature of 280 °C**

| $\tau$, min | P, % | $\alpha$-Al$_2$O$_3$, % | $\gamma$-Al$_2$O$_3$, % | H, GPa | $U$, V | $\rho$, $\Omega$ |
|-------------|------|------------------------|------------------------|--------|-------|----------------|
| MAO-coatings on AMg3 |
| 1 | 5.48 | 42.73 | 30.46 | 15.47…19.83 | 2280.12 | 5.69·10$^{14}$ |
| 3 | 5.49 | 42.73 | 30.48 | 15.49…19.83 | 2277.68 | 5.69·10$^{14}$ |
| 10 | 5.55 | 42.73 | 30.94 | 15.63…19.83 | 2238.47 | 6.67·10$^{14}$ |
| 30 | 5.61 | 42.76 | 33.75 | 15.79…19.83 | 2195.72 | 7.52·10$^{14}$ |
| 100 | 5.64 | 42.80 | 34.25 | 15.92…19.83 | 2172.35 | 8.05·10$^{14}$ |
| 300 | 5.64 | 42.80 | 34.25 | 15.92…19.83 | 2172.35 | 8.05·10$^{14}$ |
| MAO-coatings on D16 |
| 1 | 5.97 | 24.95 | 41.07 | 14.26…18.36 | 2042.65 | 2.92·10$^{14}$ |
| 3 | 5.99 | 24.95 | 41.07 | 14.27…18.36 | 2040.13 | 2.92·10$^{14}$ |
| 10 | 6.06 | 24.95 | 41.64 | 14.38…18.36 | 2005.22 | 3.39·10$^{14}$ |
| 30 | 6.10 | 25.01 | 44.37 | 14.55…18.36 | 1963.39 | 3.84·10$^{14}$ |
| 100 | 6.12 | 25.01 | 45.83 | 14.67…18.36 | 1944.06 | 4.08·10$^{14}$ |
| 300 | 6.12 | 25.01 | 45.83 | 14.67…18.36 | 1944.06 | 4.08·10$^{14}$ |

It is discovered that further increase in the heating temperature up to the values at which the alloys under MAO-coatings begin to melt (~600 °C for AMg3 alloy and ~500 °C for D16 alloy) contributes to a faster increase in content of $\alpha$-Al$_2$O$_3$ in MAO-coatings, porosity, hardness, electrical resistance of MAO-coatings and reduce their breakdown voltage without any other significant changes.

**Table 4. Characteristics of MAO-coatings after holding at temperature of 480 °C**

| $\tau$, min | P, % | $\alpha$-Al$_2$O$_3$, % | $\gamma$-Al$_2$O$_3$, % | H, GPa | $U$, V | $\rho$, $\Omega$ |
|-------------|------|------------------------|------------------------|--------|-------|----------------|
| MAO-coatings on AMg3 |
| 1 | 5.49 | 42.73 | 30.46 | 15.48…19.83 | 2278.61 | 5.71·10$^{14}$ |
| 3 | 5.56 | 42.79 | 30.78 | 15.52…19.83 | 2237.24 | 6.84·10$^{14}$ |
| 10 | 5.63 | 43.24 | 31.67 | 15.69…19.83 | 2180.35 | 7.76·10$^{14}$ |
| 30 | 5.86 | 45.98 | 34.25 | 15.97…19.84 | 2092.17 | 10.92·10$^{14}$ |
| 100 | 5.89 | 46.43 | 34.25 | 16.17…19.85 | 2077.98 | 13.26·10$^{14}$ |
| 300 | 5.89 | 46.43 | 34.25 | 16.17…19.85 | 2077.98 | 13.26·10$^{14}$ |
| MAO-coatings on D16 |
| 1 | 5.98 | 24.95 | 41.07 | 14.28…18.36 | 2041.75 | 2.94·10$^{14}$ |
| 3 | 6.04 | 24.96 | 41.46 | 14.33…18.36 | 2006.39 | 3.47·10$^{14}$ |
| 10 | 6.08 | 25.18 | 42.71 | 14.46…18.36 | 1958.44 | 3.89·10$^{14}$ |
| 30 | 6.17 | 27.09 | 45.83 | 14.71…18.36 | 1876.63 | 5.58·10$^{14}$ |
| 100 | 6.19 | 27.46 | 45.83 | 14.89…18.37 | 1862.57 | 6.71·10$^{14}$ |
| 300 | 6.19 | 27.46 | 45.83 | 14.89…18.38 | 1862.57 | 6.71·10$^{14}$ |
It is established that the MAO-coatings that have passed the sequential (stepped) holding at a heating in three temperature intervals – 190...270, 280...470 and 480...500 °C, have differences from MAO-coatings that have passed a one-time holding at a heating in the temperature interval 480...500 °C. Figure 2 shows the typical fragments of the cross microfractograms of MAO-coatings, from which it follows that MAO-coatings that have undergone a stepped heating in three temperature intervals (a) and (b), have a less defective structure than MAO-coatings that have undergone a one-time heating in the highest temperature interval (c) and (d).

At the same time, despite the approximately identical porosity and the equal content of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$, MAO-coatings that have undergone stepped heating in three temperature intervals differ in higher average values of hardness, breakdown voltage and electrical resistance.

Figure 2. Typical fragments of the cross microfractograms of MAO-coatings, that have undergone a stepped heating (a), (b) and one-time heating (c), (d).

Friction and wear tests found that a one-time heating of disks with MAO-coatings increases their surface wear resistance in dry abrasive friction by 5...6%, and stepped heating in three temperature intervals – by 8...10 %. At the same time, after friction and wear tests with the removal of the outer layers of MAO-coatings with a thickness of about 50 μm, the total content of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ content in MAO coatings on AMg3 and D16 increases to \%97.8 and \%97.78, respectively.

4. Discussion
The presented results of the studies are in good agreement with each other, as well as with the well-known results of the study of the structure of clay minerals [11] and allow us to assert that when heated from 50 to 600 °C with subsequent holding in MAO-coatings, changes of three types happen. Changes of the first type begin at a temperature of about 190 °C and, judging by the constant content of $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$, are associated with transitions of other phases. Taking into account the simultaneous increase in porosity and hardness near the outer surfaces of MAO-coatings, this can be explained by the transition of aluminum trihydroxide at a loss of moisture to a denser and harder aluminum monohydroxide. Changes of the second type begin at a temperature of about 280 °C and, judging by the increase in the content of $\gamma$-Al$_2$O$_3$, are associated with a partial transition of aluminum monohydroxide at a loss of moisture to denser and harder $\gamma$-Al$_2$O$_3$. Changes of the third type begin at a temperature of about 480 °C and, judging by the increase in the content of $\alpha$-Al$_2$O$_3$, are associated with a partial transition of aluminum monohydroxide with loss of moisture to denser and harder $\alpha$-Al$_2$O$_3$.

The fact that significant changes in porosity and hardness happens only in the outer layers of MAO-coatings, located at a depth of not more than 40…50 μm from their outer surface, can be explained by the
predominant location of aluminum hydroxide in these layers of MAO-coatings, because they are more susceptible to hydration due to the long time action of the electrolyte solution.

The greater number of structural defects and lower physical and mechanical properties of MAO-coatings after one-time holding at the temperatures of 480...500 °C may indicate that at such temperatures, different types of changes occur simultaneously, and this leads to a simultaneous accelerated change in the volume of some structural constituents of MAO-coatings and the formation of a defective structure with cracks and ruptures, and also reduce of physical and mechanical properties of MAO-coatings.

5. Conclusion

1. At the heating of MAO-coatings on details made of aluminum alloys in the temperature interval of 50...600 °C with subsequent holding in their outer layers, located at a depth of not more of 40...50 μm from the outer surfaces, there are three types of changes in the structure and phase composition with a simultaneous increase in surface hardness and wear resistance, an increase in the electrical resistance of MAO coatings and a decrease in their breakdown voltage.

2. Changes of the first type, occurring at temperatures from 180 °C and more, consist in dehydration of aluminum trihydroxide with transition to monohydroxide and can cause an increase in the electrical resistance of MAO-coatings by 12...15% without significant changes in their surface hardness and breakdown voltage.

3. Changes of the second type, occurring at temperatures from 280 °C and more consist in partial dehydration of aluminum hydroxide with transition to γ-Al₂O₃ and can cause an increase in the surface hardness and electrical resistance of MAO-coatings by 2.5...3 % and 39...42 %, respectively, and also a decrease in their breakdown voltage by 4.5...5 %.

4. Changes of the third type, occurring at temperatures from 480 °C and more consist in partial dehydration of aluminum hydroxide with transition to α-Al₂O₃ and can cause an increase in the surface hardness and electrical resistance of MAO-coatings by 4...4.5 % and 228...235 %, respectively, and also a decrease in their breakdown voltage by 8...9 %.

5. Sequential stepped holding of MAO-coatings in three temperature intervals – 190...270, 280...470 and 480...500 °C provides consistent flow and completion of the described changes in MAO-coatings, thereby preventing accelerated changes in the volume of individual structural constituents of MAO-coatings and the formation of a defective structure with with cracks and ruptures, providing higher values of physical and mechanical properties.

References

[1] Markov G A, Mironova M K and Potapova O G 1983 Structure of anodic films formed by the microarc oxidation of aluminum J. Inorg. Mat. 19 1000

[2] Malyshev V N, Markov G A, Fedorov V A, Petrosyants A A and Terleeva O P 1984 Features of the structure and properties of coatings applied by the method of microarc oxidation J. Chem. Petrol. Eng. 20 41-3

[3] Malyshev V N 2016 Modification of friction knots work surfaces on the basis of microarc oxidation method Int. J. Sci. Res.Sci, Eng. Tech. 2 464-80

[4] Shi-Gang X, Li-Xin S, Rong-Gen Z and Xing-Fang H 2005 Properties of aluminium oxide coating on aluminium alloy produced by microarc oxidation J. Surf. Coat. Techn. 199 184-8

[5] Sharma M K, Jang Y J, Kim J M, Kim H T and Jung J P 2014 Plasma electrolytic oxidation in surface modification of metals for electronics, J. Weld. Join. 32 27-33

[6] Chufistov O E, Chufistov E A, Artemiev V P 2010 Technology, structure and properties of coatings, formed by anodic oxidation methods on aluminum and its alloys J. Non-Ferr. Met. 2 37-40
[7] Atroshchenko E S, Chufistov O E, Kazantsev I A and Kamyshanski S I 2000 Formation of structure and properties of coatings deposited by microarc oxidizing on parts fabricated from aluminum alloys J. Met. Sci. Heat Treat. 42 411-5
[8] Curran J A and Clyne T W 2005 The thermal conductivity of plasma electrolytic oxide coatings on aluminium and magnesium J. Surf. Coat. Techn. 199 177-83
[9] Gębarowski W and Pietrzyk S 2013 Influence of the cathodic pulse on the formation and morphology of oxide coatings on aluminium produced by plasma electrolytic oxidation J. Arch. Metall. Mat. 58 241-5
[10] Kolerov O K, Skryabin V G, Kalyshenko M F, Logvinov A N and Yushin V D 1985 On X-ray diffractometric study of the fine structure of polycrystals J. Zavod. Lab. 51 46-8
[11] Bailey S W, Brindley G W, Brown G, MacEwan D M C, Wilson M J and Reynolds M C 1980 Crystal structures of clay minerals and their X-ray identification ed G W Brindley and G Brown (London: Mineralogical society) 495 p