Development of Innovative Combination Dielectric Coatings

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***Abstract* – In Latvia and abroad the most perspective method for the application of protective coatings onto lightweight structural alloy products is micro-arc oxidation (MAO). Over the last decade there has been a surge in the number of publications on the mechanism and growth kinetics of coatings applied onto surfaces of the valve alloys under various technological operations of MAO process, as well as their properties and structure. MAO is a comparatively new way of surface modification and strengthening of metal materials. The beginning of this method can be seen in traditional anodizing and this is an electrochemical process. Using MAO allows obtaining combined multifunctional ceramic materials with unique qualities: wear resistance, corrosion strengths, electric insulation and decorative overlays.**

***Keywords* – oxidation of micro arc, anodic oxidation, coatings, vacuum technologies.**

I. INTRODUCTION

The development of new environmentally friendly technologies and application of highly reliable coatings for the protection and strengthening of metal parts, undoubtedly, is one of the central problems for science and technology due to the increasing aggressiveness of service conditions, process environment used and, accordingly, more stringent requirements set for construction materials.

Micro-arc oxidation (MAO) is a relatively new type of surface treatment and hardening of mostly metallic parts originating from the traditional anodizing, and thus related to electrochemical processes.

The main technological difference between micro-arc oxidation and other electrochemical processes used in the industry is that the implementation of this technology requires sufficiently high voltage to be ensured in an electrolytic bath (the minimum voltage at which the micro electric spark discharge occurs is about 170 volts). This is due to the fact that the formation of the coating occurs from plasma discharge, which changes its form (smouldering, micro electric spark, micro-arc and arc) Fig.1, 4, depending on the volt-ampere characteristics and the thickness of the coating already formed. The voltage across the electrodes during the processing is constantly growing and the volt-ampere characteristics acquire specific characteristics of MAO (see Fig.1).

With micro-arc oxidation the ceramic-like multifunctional coating with a unique combination of properties, including wear-resistance, corrosion-resistance, heat-resistance, insulating and decorative coatings can be obtained.

Micro-arc oxidation feature is in the being a part of the coating surface micro discharges formation with a very specific effects As a result the composition and structure of the obtained oxide layers differ substantially and the properties compared to conventional anodic films significantly improve.

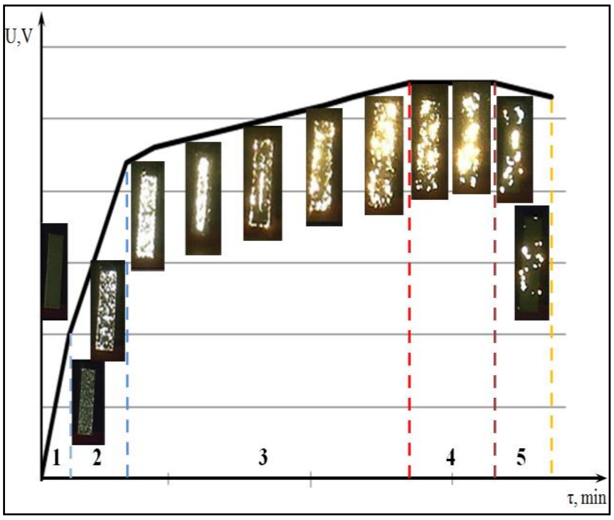

Fig.1 The dependence of the voltage on the electrodes MAO bath on the stage of the process

During the formation of the oxide layer several physical processes occur at the same time: passivation, etching, deposition, electric breakdown. The result of the combined effect of these processes is the formation of coating with a specific structure on the basis of the so-called Keller cell (Fig. 2). Due to its directional porosity, this structure allows the passage of current through the dielectric material and forming a thick oxide coating.

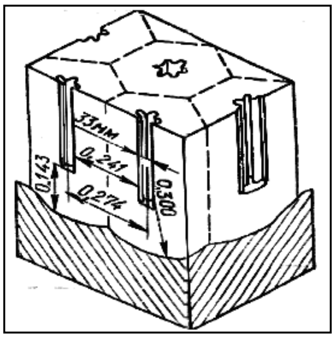

Fig.2. „Perfect" porosity structure of Keller cell anodizing film (dimensions are in μm)

This allows applying MAO treatment not only to pure metals and alloys, but also to those coated in vacuum such as conglomerate, intermetallic, nitride, etc. on the basis of various materials (Mg, Ti, Ta, Nb, Zr, Be etc). At RTU FTME AERTI laboratory, research was conducted on the combined application of ion-plasma deposition and MAO, as an additional treatment of sprayed coatings. Coating based on aluminium and titanium of various structures and chemical composition were studied. It is possible to obtain the oxide coating on the basis of predetermined metal (Mg, Ti, Ta, Nb, Zr, Be etc.) with certain properties and thickness.

Herewith it is essential to make such a dielectric coating for aluminium with a disruption voltage of 1000 V and microhardness up to 2 500 kg/mm^2. Some of the promising metalworking methods to gain such results are: micro arc oxidation, anode oxidation of various type, anode oxidation of saline, anode oxidation in the gas plasma and plasma electrolytic anode oxidation

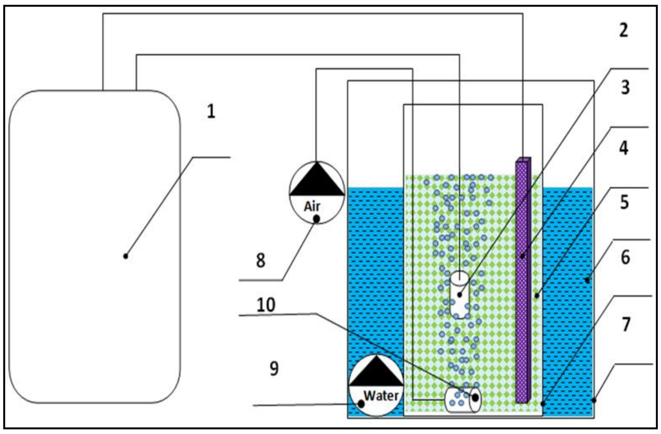

Fig. 3. Scheme of micro-arc oxidation of the experimental setup: 1 – universal power supply; 2 – part; 3 – stainless steel electrode; 4 – electrolyte; 5 – coolant; 6 – internal tank; 7 – external tank; 8 – compressor; 9 – cooling water pump; 10 – sparger aerator.

II. MAO Experimental Unit

The experiments were performed on a specially created unit (Fig. 3), designed to perform MAO on samples with different coatings on the basis of valve materials (Al, Mg, Ti, Ta, Nb, Zr, Be, etc.). This allows saving costly alloys and decreases the weight of the structure and controls the performance of the product. The experimental unit is designed to perform MAO on the parts with thin coatings.

To achieve the goal of the study reversible universal power supply was installed with a constant, pulse and alternating currents up to 1,000 V (Fig. 3, 3), which allows testing in different modes to achieve certain properties of the coatings.

The experimental unit components are: external tank (Fig. 3, 7) – coolant (Fig. 3, 5) for cooling the internal tank (Fig. 3, 6). The tank is also equipped with pump (Fig. 3, 9) for intensive heat removal from the inner tank (Fig. 3, 6) during the MAO, which improves cooling of the electrolyte (Fig. 3, 4). Inner tank is equipped with sparger aerator (Fig. 3, 10) for oxygen saturation of the electrolyte within the area of the micro-arcs formation on the part (Fig. 3, 2) and for mixing and cooling of the electrolyte (Fig.3, 8).

III. Basic Phases of the MAO

The basic phases of the process of MAO are (Fig. 4):

1. Passivation;
2. Glow discharge (glow);
3. Sparking;
4. Intensive micro-arc sparking;
5. The arc discharge.

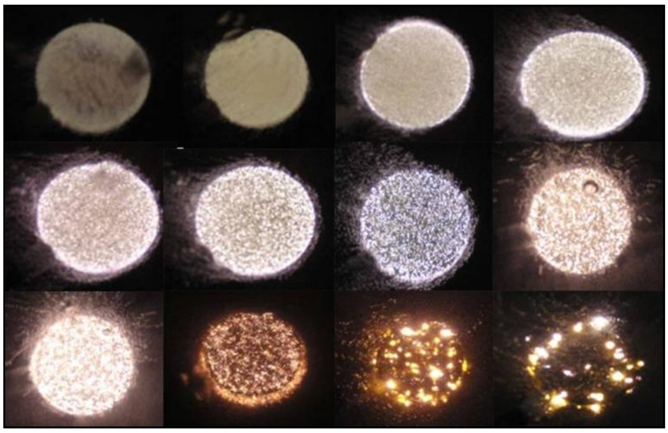

Fig.4. From left to right and top to bottom: passivation; glow discharge; sparking; intensive micro-arc sparking; the arc discharge.

IV. Structure and Properties of the MAO Coatings

Dependence is determined by the nature of the material and technological parameters of the process:

- The electrolyte;
- Mode;
- Duration of treatment.
- Electrolyte

Electrolyte composition mode and time of treatment, along with the base material, is the determining factor in the process of MAO, significantly affecting the composition, structure and properties of the coatings. Conditionally electrolytes for MAO can be divided into two groups. The first group includes electrolytes not containing elements forming insoluble oxides, such as solutions of sulphuric acid or alkali. Coatings formed in such electrolytes can penetrate deeper into the metal due to its oxidation, for example, by the reactions:

2Al + 6OH-aq - 6e ® 2Al (OH) 3 ® Al_2O_3 + $3H_2O$; Al - 3e + + K + aq + 4OH-aq ® $2H_2O$ + $KAlO_2$,

Where in $KAlO_2$ is a part of coating composition on base of b-Al_2O_3 (1).

If the quality of distilled water is not good, the MAO mode does not work. Instead of coating the intense destruction of the detail takes place. Loose formation on the surface can be observed – a consequence of localized corrosion. Checking the quality of the water used must necessarily be carried out by the measurement of pH and specific conductivity.

TABLE 1

THE CHEMICAL COMPOSITION OF THE ALUMINIUM ALLOY SAMPLE 14

Spectrum: MDO+14					
El	AN	Series	unn. [wt.-%]	C norm. [wt.-%]	C Atom. [at.-%]
Na	11	K-series	3.86	3.25	2.80
Al	13	K-series	38.37	32.34	23.71
Si	14	K-series	8.37	7.06	4.97
K	19	K-series	3.85	3.24	1.64
O	8	K-series	64.2	54.11	66.89
		Total	118.65	100.00	100.00

<u>Modes of MAO</u>

Technology of MAO process is applied to the valve metals and their alloys and coatings (Al, Mg, Ti, Ta, Nb, Zr, Be, etc.), i.e. metals on which oxide films formed by electrochemical reactions have unipolar conductivity in metal-oxide-electrolyte.

Modes of MAO and power supplies –sources of technological current are much more varied and complex than in the anodising process. Applicable modes can be classified as follows: by the nature of the current (DC – direct current, AC – alternative current, or their superposition), by polarity of the applied voltage (anode, cathode, anode-cathode, alternately regimes of different polarity with dead time) (3, 4, 1); by change of the electrical parameters (galvanostatic, galvanodynamic, potentiostatic, potentiodynamic, constant power mode, incident power mode, etc.); by the nature of the discharge (spark, micro-arc, arc, arc electrophoresis); by the degree of control (manual, semi-automatic, automatic); by the method of discharge formation (soft, soft-hard, hard-soft, hard). (4, 6) The latter should be considered separately, since the stiffness of the discharge (through time of the pure electrochemical and micro-arc exposure to the material, as well as through the effective values of currents that determine the temperature of the discharge) affects the final characteristics of MAO coatings, such as hardness, porosity, breakdown voltage, etc. These modes are determined by the output parameters of power supplies for MAO influencing the beginning and termination of micro-arc discharge in each half-cycle. Soft mode means natural breakdown of the formed top coating when the electric field strength at the border of the MOE smoothly in accordance with the shape of the input voltage reaches a critical value at which the breakdown starts. Hard mode is when the initial potential difference is known more critical that results a forced breakdown. Terminating discharge for the soft mode is determined by the capacity of the power source and is classified as natural, but for the hard – as a form of voltage and is classified as forced. Thus, the soft mode is a natural beginning and natural end of the discharge, soft-hard – natural beginning and forced ending, hard-soft – forced start and natural end, hard mode – forced beginning and forced end of the discharge.

Sources of the MAO technological current, regardless of polarity mode, are divided into the transformer type using step-up transformers and capacitor type providing the supply voltage doubling due to the valve nature of the load (MOE). Moreover, it is possible to use the thyristor converters and for the processing in the anode mode – standard stabilized DC power sources or their sets giving 600-1,000 V output. Power of any power source is selected in accordance with the requirements of the coated surface area [7].

V. COMPOSITION OF DIELECTRIC COATINGS

The results of studying and scanning of the samples with electron microscope SEM Hitachi S3000N and X-ray dispersion microanalysis system BRUKER AXS are presented in Table 1 and 2 and Fig. 5 and 6. The aluminium alloy sample was fully covered after 14 procedures (Fig. 5). The resultant microhardness was 881.524 kg/mm^2 and the dielectric indicator 40 MOm at 1,000 V.

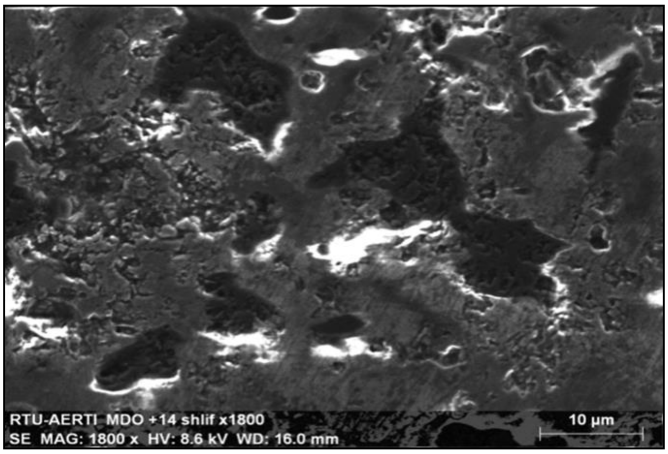

Fig. 5. The structure of the ground surface of the dielectric layer of the sample treated at 14 MAO mode

Depending on the processing and the electrolyte composition oxides $Al2O_3$, $KalO_2$, $NaAlO_2$, $NaSiO_3$, $AlSi_3O_8$, etc. can be present in different ratios in the coating components. An important role is played by the percentage of the elements, which in its turn defines characteristics of dielectric resistance, corrosion resistance, etc.

TABLE 2

THE CHEMICAL COMPOSITION OF THE ALUMINIUM ALLOY SAMPLE 4

Spectrum: MDO+4					
El	AN	Series	unn. [wt.-%]	C norm. [wt.-%]	C Atom. [at.-%]
Na	11	K-series	4.49	4.64	4.84
Al	13	K-series	67.49	69.69	61.95
Si	14	K-series	4.04	4.17	3.65
K	19	K-series	2.83	2.92	1.79
O	8	K-series	17.96	18.57	27.84
		Total	96.72	100.00	100.00

As a result of a series of experiments a preliminary conclusion can be made - that the higher is the density, the higher is the hardness of the coating and its dielectric properties.

It is determined that the coating structure essentially depends on the voltage and frequency of the pulses on the electrodes of MAO bath. Two types of coatings are formed: the first type – single-layer is formed at low voltages and currents. The layer is fully working. But because the thickness of the coating is not big – about 70-80 μm – dielectric capacity and wear resistance are not great; the second type – a two-layer coating at relatively high voltages and currents. This coating has two layers, the first (top) layer technological (Fig 7.a), which is removed after the MAO, and internal working about 70-80 μm (Fig. 7.b, d), which has better performance than the technological regime of the sample 14 of MAO.

The aluminium alloy sample treated after the 4th regimes (Fig. 6) had resultant microhardness – 1,071.2 kg/mm^2 and the dielectric indicator 250 MOm at 1,000 V.

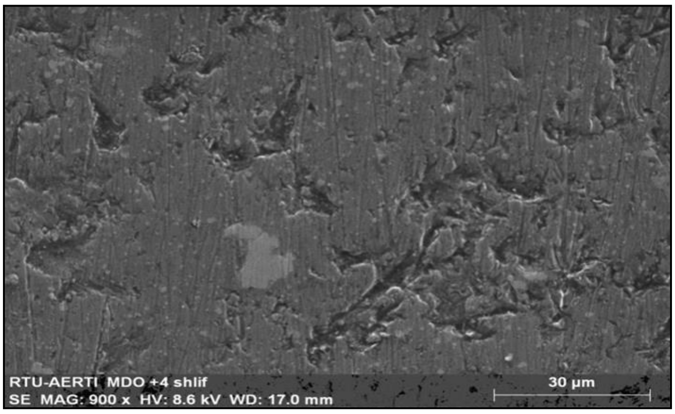

Fig. 6. The structure of the ground surface of the dielectric layer of the sample treated at 4 MAO mode

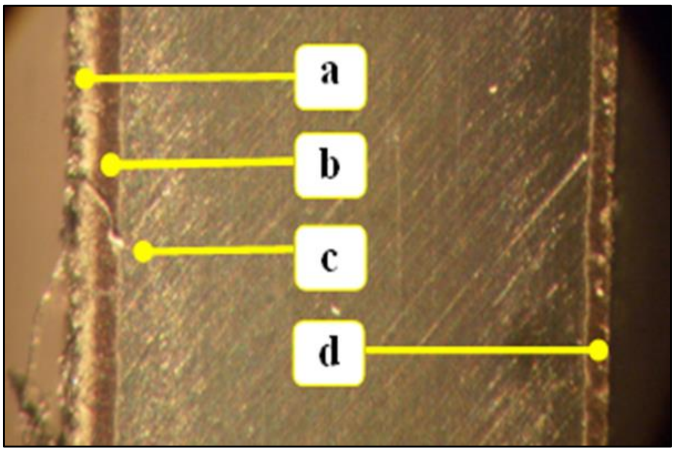

Fig.7. Layers of thin section on the end part after MAO processing. a – technological layer, b, d – the working layer, c – base

VI. CONCLUSIONS

MAO technology is a qualitatively new step towards improving the strengthening treatment, during which the plasma and electrochemical mechanisms of the oxide layer formation are joined. MAO is flexible and environmentally friendly technology for strengthening the surface layer of valve metals and their alloys into the oxide ceramics with a unique complex of properties that allow the product to be used in various branches of industry.

Nanostructured non-metallic coatings have a number of industrially important features: durability, corrosion resistance, heat resistance, low dielectric constant and special reflective and light-absorbing properties.

Defining dependencies between the composition of the treated material, the parameters and conditions of the process will provide improved performance properties of coatings and expand their use. MAO has a wide range of applications, it is only necessary to take into account the fact that this process can be applied to the details of the valve metals, i.e. metals whose oxide films formed in electrochemical way have unipolar (unidirectional) conductivity in the "metal-oxide-electrolyte". These metals primarily include aluminium (Al) and its alloys, and magnesium (Mg), titanium (Ti), tantalum (Ta), niobium (Nb), zirconium (Zr) and beryllium (Be).

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Aleksandrs Urbahs, Vladimirs Zujevs, Konstantins Savkovs, Margarita Urbaha, Darja Andrejeva. Inovatīvu kombinēto dielektrisko pārklājumu izveide
Pētījuma rezultāti balstās uz ilggadējo pieredzi konglomerātu, intermetalīdu un nitrīdu tipa pārklājumu veidošanu ar dilumizturības, augstas temperatūras un pretkorozijas izturības u.c. īpašībām, izmantojot mikroloku oksidēšanas (MLO) tehnoloģijas. Latvijā un ārvalstīs visperspektīvāko metodi, piemērotu aizsargpārklājumu konstruktīviem izstrādājumiem ir mikroloka oksidācijas (MLO), kas liecina straujas publikācijas skaitu pieaugšana pēdējo desmit gadu laikā par mehānismu un izaugsmes kinētiku pārklājumu uz virsmām, ventiļa sakausējumiem pie dažādu tehnoloģiju veidiem, kā MLO procesā, kā arī to īpašībām un struktūrām. MLO ir salīdzinoši jauns veids, kā virsmas modificēšanai un nostiprināšana metāla materiāliem galvenokārt. Sākumā šo metodi var redzēt no tradicionālās oksidēšanas un tas ir elektroķīmiskās process. Izmantojot MLO ļauj iegūt kopā dažādās kombinācijās multifunkcionālās keramiskos materiālos ar unikālām īpašībām: nodilumu, koroziju izturību, dielektriskie un dekoratīvi pārklājumus.

Александр Урбах, Владимир Зуев, Константин Савков, Маргарита Урбаха, Дарья Андреева. Создание инновационных комбинированных диэлектрических покрытий.
Результаты исследования основываются на опыте многолетней работы в области износостойких, термостойких и коррозионно-стойких покрытий с использованием МДО технологий. В Латвии и за рубежом наиболее перспективным методом для нанесения защитных покрытий на легкие конструкционные изделия сплавов микро-дугового оксидирования (МДО), который показывает рост числа публикаций за последнее десятилетие на механизм и кинетика роста покрытий на вентильных сплавах при различных технологических способах при процессе МДО, а также их свойства и структуры. МДО – сравнительно новый способ модификации поверхности и главным образом, укрепления металлических материалов. Начало этого метода начинается с традиционного анодирования и это является электрохимическиим процессом. Использование МДО позволяет получать комбинированные многофункциональные керамические материалы с уникальными свойствами: износостойкость, коррозионная стойкость, диэлектрические и декоративные покрытия.