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INVESTIGATION OF THE INFLUENCE OF TECHNOLOGICAL CONDITIONS OF MICROARC OXIDATION OF MAGNESIUM ALLOYS ON THEIR STRUCTURAL STATE AND MECHANICAL PROPERTIES

V. Belozerov
PhD, Professor*
A. Mahatilova
PhD, Senior Researcher*
O. Sobol'
Doctor of Physics and Mathematics Sciences, Professor*
E-mail: sool@kpi.kharkov.ua
V. Subbotina
PhD, Associate Professor*
A. Subbotin
Researcher*
*Department of Materials Science
National Technical University
«Kharkiv Polytechnic Institute»
Kyrpychova str., 2, Kharkiv, Ukraine, 61002

Наведені дослідження структури і властивостей покриттів, отриманих при мікродуговій обробці на магнієвому сплаві. Обробка проводилася при анодно-катодному режимі в лужному електроліті з різними домішками. Показана можливість формування кристалічних оксидних покриттів різного фазового складу (MgO, $MgAl_2O_4$, Mg_2Si_4, $Mg_3(PO_4)_2$) товщиною до 300 мкм, що мають високу адгезію з основою, гарні захисні властивості і високу твердість, яка досягає 6,6 ГПа

Ключові слова: структурна інженерія, мікродугове оксидування, магнієві сплави, фазовий склад, адгезійна міцність, твердість

Приведены исследования структуры и свойств покрытий, полученных при микродуговой обработке на магниевом сплаве. Обработка проводилась в анодно-катодном режиме в щелочном электролите с разными примесями. Показана возможность формирования кристаллических оксидных покрытий разного фазового состава (MgO, $MgAl_2O_4$, Mg_2Si_4, $Mg_3(PO_4)_2$), толщиной до 300 мкм, которые имеют высокую адгезию с основой, хорошие защитные свойства и высокую твердость, достигающую 6,6 ГПа

Ключевые слова: структурная инженерия, микродуговое оксидирование, магниевые сплавы, фазовый состав, адгезионная прочность, твердость

1. Introduction

The solution of the problem of improving special working properties, reliability and durability of functional elements, devices and machines can be achieved by targeted modifying the shape, structure and surface properties (or, more precisely, near-subsurface layer). This is the basis for the development of priority scientific practical direction in modern materials science – surface engineering [1]. Surface engineering combines methods of directed change in the physical and chemical properties of the surface layers of materials by deformation [2], modification [3], deposition of single-layered [4], multi-period [5], multi-element [6] coatings and protective layers by different combined methods [7]. Innovative character of the surface engineering development is determined by the fact that the main quality indicators of machines are reliability and performance efficiency. These parameters are mainly determined by the properties of the surface layers of parts and joints (endurance limit, corrosion resistance, wear resistance, coefficient of friction, contact stiffness, fit strength, tightness of joints, etc.) [8]. This can be achieve d by modifying the surface with high-performance methods. Surface modification is especially relevant for the lightweight materials (mainly based on aluminium, magnesium and titanium). The effectiveness of their use at present is very high not only in the traditional aerospace and automotive engineering and instrument making, but also for biomedical industry, which critically needs the creation of lightweight alloys with controlled (required) corrosion rate. Thus, surface condition of these alloys defines a set of functional characteristics, which adds prominence to the development of new efficient technologies for the surface modification of structure and properties of lightweight materials.

2. Literature review and problem statement

Each stop of a machine due to the damage of separate parts or reduction in technical characteristics below the permissible level typically entails great economic loss, and in some cases (particularly, in the case of biomedical application) leads to disastrous consequences. This makes it relevant (and in some cases critically required) to improve the operational properties of surface layers based on the method of structural engineering. The structural surface engineering is especially in demand for the material of parts that operate under conditions of friction, for which the decisive factor that determines durability is high wear resistance, which largely depends on the hardness of the surface [9]. In this case, the core of such parts in order to ensure high structural strength requires much lower hardness but higher indicators of plasticity and viscosity. Thus, in the parts that work under conditions of friction, different properties of the surface and the core should be provided, which can be achieved by different types of treatment [10] or by applying composite coatings [11].

In recent years, new methods of the formation of coatings [12] and the strengthening of surface by using highly concentrated energy sources have been developed intensively [13]. One of the most promising modern methods of highly concentrated treatment is the method of microarc oxidation (MAO), which allows obtaining high-density functional coatings on the valve metals [14], in particular protective [15].

Microarc oxidation is a complex process of obtaining the coatings on the surface of material, that is, a working electrode placed in the electrolyte, under the mode of microarc discharges that move at its surface [16].

The method of microarc oxidation has significant advantages over the method, which is widely used in industry, alloy anodizing treatment:

1) it does not require, as a rule, thorough preliminary preparation of metal surface of articles or structures;

2) it allows obtaining the coatings characterized by high hardness, wear resistance, corrosion protective properties, adhesion to metal base;

3) it provides the possibility to achieve the condition, optimal for friction, with improved surface hardness and plastic core [17].

The largest effect when using the MAO method had been up to now achieved in the treatment of titanium [18] and aluminum [19] as the metals of valve group (they possess a unipolar conductivity in the system metal – oxide – electrolyte).

Among the metallic materials employed in various sectors of modern industry, magnesium alloys are of special interest. It is due to their special properties. First, it is a relatively low density (1.35–1.85 g/cm^3, which is 1.5–2 times less than that of aluminum alloys and 4–5 times less than that of steel), good mechanical, structural and operational properties in the temperature range from –273 to +350 °C, good machinability and high ability to absorb the energy of impact and reduce vibration.

These properties form the basis for a widespread use of magnesium alloys both in mechanical engineering and instrument making and especially in the biomedical industry, since, in addition to the above advantages, magnesium is nontoxic, biologically and mechanically compatible with the bone and muscle tissues [20].

The main reason that limits the scope of application of alloys based on magnesium is their low wear resistance, primarily due to the high chemical reactivity of magnesium and, as a consequence, low resistance to corrosion destruction. Since the corrosion and wear are surface phenomena, then the methods of surface engineering are used to improve the properties. The most common method of surface engineering for the protection from corrosion of magnesium alloys is the application of inorganic coatings in combination with paints, organic and metallic coatings. At present, however, the problem of improving corrosion resistance can be solved by more productive and efficient methods.

For these purposes, it is promising to apply the method of microarc oxidation, due to which it is possible to conduct at the surface of products made of magnesium alloys the synthesis of nanoceramic layers that demonstrate high strength of adhesion with the base and controlled corrosion-protective capacity [21].

However, the MAO method for magnesium alloys has a significant drawback: the need for a long-term empirical search for the optimal composition of electrolyte for each magnesium alloy [22]. This shortcoming is related to the lack of targeted comparative studies on the kinetics of growth of coatings and the composition, generated in them, at the surface of magnesium alloys different by their composition [23]. It is obvious that the solution to this problem may be found in the systematic research into the optimization of selecting the electrolyte and the modes of magnesium alloys treatment that provide high adhesion strength and surface hardness.

3. The aim and tasks of the study

The aim of present study is to examine regularities in the formation of MAO-coatings, to search for effective formulations of electrolytes and electrolysis modes to form the coatings with high protective properties based on Mg-alloys.

To achieve this goal, the following tasks had to be solved:

– to compare the effect of alkaline electrolytes, electrolytes based on the solutions of silicates and multicomponent composite electrolytes on the stability of the processes for determining the conditions for a stable progress of the MAO process on magnesium alloys;

– to establish the impact of treatment on the created phase composition and surface hardness;

– to determine adhesion resistance of the created coating to the material of the base;

– to explain the effect of phase composition on the protective properties of coatings.

4. Materials and methods for obtaining and examining the coatings fabricated by the MAO treatment

Casting magnesium alloy (Mg – 9 % Al – 0.7 % Zn – 0.3 % Mn) was exposed to the microarc treatment. The treatment was carried out under the anode-cathode mode in the installation with power supply of the capacitor type in the alkaline electrolyte, with the addition of inorganic compounds. Duration of treatment varied from 5 to 120 minutes at current density 20–40 A/dm^2.

The phase composition of coating was estimated by the diffractograms obtained on the diffractometer DRON-3 (Burevestnik, Russia) at radiation K_α–Cu. Images were taken under a point to point mode at step 2θ=0.1°. The quantitative content of the phases was determined by the technique of quantitative x-ray analysis using a pre- built calibration curve according to data from the reference mixtures [24].

Microhardness was determined on the device PMT-3 (Russia) whose operating principle is based on indenting the diamond tip (pyramid) into the examined material under a specified load (0.49–0.98 N).

Corrosion testing of MAO-coatings was conducted by the method of drop [25] and in the chamber of salt spray. In the drop method, the solution of sodium chloride containing phenolphthalein served as the reagent. The time from the moment of applying the drop until the occurrence of pink coloring characterizes protective properties of a coating; for the casting magnesium alloys, the norm is 1 minute.

5. Results of examining the effect of electrolyte compositions and electrolyze modes on the phase composition and properties of MAO coatings

First, in order to optimize the process, we conducted an analysis of effectiveness of different types of electrolytes. It was established that it is not possible to organize the microarc process at the surface of magnesium alloy in the alkaline electrolyte (KOH or NaOH aqueous solution). This is due to the fact that a dielectric barrier layer does not form at the treated surface because of the lack of interaction between magnesium and alkali.

Treatment in an aqueous solution of silicate (Na_2SiO_3 – liquid glass) transfers the process directly into the mode of arc discharges of large capacity sufficient to melt the surface and form large craters.

The MAO process under the mode of microarc discharges is steadily implemented in the multi-component electrolytes that contain solutions of alkali (KOH or NaOH), sodium silicate Na_2SiO_3, sodium aluminate $NaAlO_2$, sodium hexametaphosphate $Na_5P_3O_{10}$.

Table 1 shows compositions of the used electrolytes, in which coatings of thickness up to 300 μm form under the mode of microarc discharges at current density of 20–40 A/dm^2.

Using data on the X-ray diffraction analysis (Fig. 1), it is found that the main phases are MgO, $MgAl_2O_4$, Mg_2SiO_4, $Mg_3(PO_4)_2$, the presence of which in a coating is determined by electrolyte composition and electrolysis parameters (Table 1). In this case, the hardness of coatings is 2000–6600 MPa, which is 3–10 times higher than the hardness of the base (HV=600 MPa). With the increased content of spinel of $MgAl_2O_4$, the hardness increases.

Thus, electrolysis in the resulting electrolytes transforms the surface layer of magnesium alloy into a ceramic coating, consisting of crystalline oxides, spinels and magnesium salts.

Microplasma treatment provides high adhesion between a coating and a base. This is evidenced by the studies adhesion, conducted by tearing the self-adhesive tape off the coating after cross notch (10×10 lines) that cuts it through at step of 1 mm [14]. The results showed that in either case, both in its original state and after immersion in water for 240 hours, no area (1×1 mm) was cleaned.

Table 1

Composition of the used electrolytes, phase composition and hardness of the coatings

No of electrolyte	Composition, g/l					Phase composition	HV, MPa
	KOH	NaOH	Na_2SiO_3	$NaAlO_2$	$Na_5P_3O_{10}$		
1	2	–	12	–	–	MgO+ +Mg_2SiO_4	2000
2	6	–	5	3	–	MgO+ +$MgAl_2O_4$+ +Mg_2SiO_4	4000
3	–	2,5	–	3	–	MgO+ +$MgAl_2O_4$	5500
4	–	2,5	–	3	3	MgO+ +$MgAl_2O_4$+ +$Mg_3(PO_4)_2$	6600

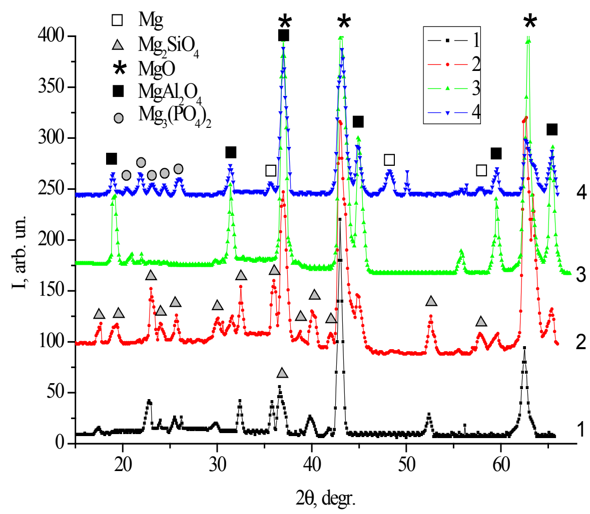

Fig. 1. Fragments of diffractograms (K_α–Cu) of MAO-coatings: 1 – electrolyte No 1, 2 – electrolyte No 2, 3 – electrolyte No 3, 4 – electrolyte No 4

Corrosion tests in salt spray comprised measuring the maximum width of corrosion along the section line on samples with X-shaped slit in the coating. The corrosion cycle included irrigation (1 hour) and drying (1 hour) for two months. The results showed that in the case of alloy (Mg – 9 % Al – 0.7 % Zn – 0.3 % Mn), the signs of corrosion were not detected (width of corrosion ≤ 0.5 mm) in electrolytes No. 3 and No. 4; 1–5 mm in electrolytes No. 1 and No. 2. The drop method yielded similar results – maximum corrosion resistance is demonstrated by coatings in electrolytes No. 3 and No. 4.

6. Discussion of results of examining the structure and properties of MAO modified surface

An analysis of the obtained results revealed that the protective properties of a coating depend on its phase structure. Thus, the existence in the coating of spinel of $MgAl_2O_4$ along with MgO increases protective properties of the coating (Fig. 2). This result can be explained by the fact that the presence of spinel in the coating increases specific volume of coating relative to the base (ratio of the specific amount of MgO and the volume of $MgAl_2O_4$ spinel to the volume of Mg is 0.79 and 2.83, respectively). An increase in the specific volume of coating in relation to the base predetermines the occurrence of compressive stresses in the coating and consequently contributes to the formation of the more solid oxide films.

In order to increase anti-corrosive properties of MAO-coatings on magnesium alloys, it is necessary to increase the spinel content in a coating, which is achieved by the introduction of inorganic additives that contain aluminum into electrolyte. Thus, the MAO-technology can be successfully employed to improve corrosion resistance and surface hardness of magnesium alloys.

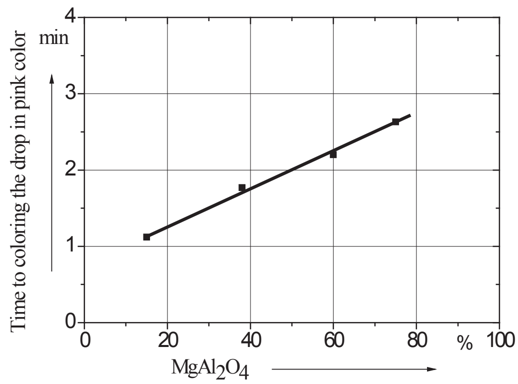

Fig. 2. Effect of magnesium aluminate on the resistance properties of MAO-coating (width of coating h≈50 μm, electrolyte No. 3)

It should also be noted that the morphology of the coating surface (Fig. 3) is characterized by high development (R_z=5–15 at the thickness of coating h≈50 μm).

Such a large development of the surface allows using the MAO-coating as a sub-layer for additional improvement of corrosion resistance by applying other protective coatings (paints, varnishes, polymers, etc.), providing their good adhesion at that.

Thus, the conducted study allowed us to demonstrate the feasibility of employing the MAO-technology to form protective coatings on the casting magnesium alloys. Specific recommendations are given regarding the parameters of electrolysis, which provide enhancement of corrosion resistance in MAO-coatings.

Results of the research might be used for strengthening and improving the protective properties of parts in the motors of brake drums, brackets, housings and other articles made of casting magnesium alloys.

In the future, we plan to conduct similar studies on deformable magnesium alloys of various chemical compositions.

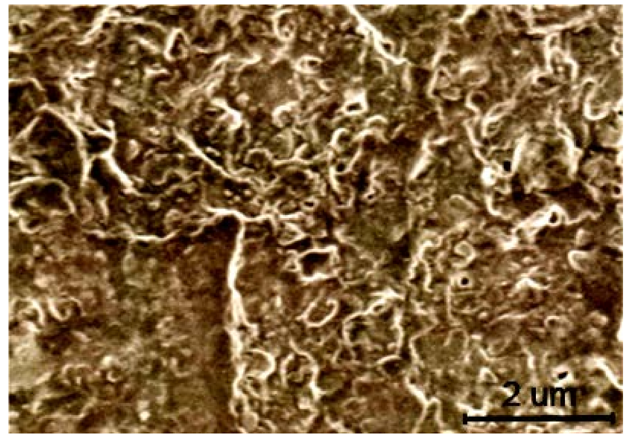

Fig. 3. Morphology of the surface of MAO-coating on magnesium alloy (h≈50 μm)

7. Conclusions

1. It is established that multi-component electrolytes containing solutions of NaOH alkali, sodium aluminate $NaAlO_2$, sodium hexametaphosphate $Na_5P_3O_{10}$ are the most effective ones. The use of these electrolytes makes it possible for the process of microarc oxidation to proceed steadily under the mode of microarc discharges.

2. It is revealed that the main phases are MgO, $MgAl_2O_4$, $Mg_3(PO_4)_2$, the content of which in a coating is defined by the electrolyte composition and the parameters of electrolysis. Hardness of coatings is 2000–6600 MPa, which is 3–10 times higher than the hardness of the base (HV= =600 MPa).

3. It is established that microplasma treatment provides high adhesion between coating and the base, as evidenced by the studies on adhesion, conducted by tearing off the self-adhesive tape.

4. It is shown that the presence of $MgAl_2O_4$ spinel in a coating, along with MgO, increases protective properties of the coating, which is due to the increased specific volume of the coating during formation of the spinel, the occurrence of compressive stresses at that and, consequently, the formation of thicker coatings.

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