Coating effect on thermal-physical and corrosion characteristics of ultralight Mg-based alloy

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Abstract. Due to its unique properties, magnesium alloys at present are widely used in aircraft and defence technologies, despite the significant drawback as low corrosion resistance. The most effective method of alloys protection is micro-arc oxidation (MAO). But firstly, the alloys oxidation has a number of difficulties, and secondly, the ceramic coatings have an effect on thermal-physical characteristics of modified material. The presented report devotes of the developed technological mode of a protective coating forming on the ultralight alloy Mg-8Li-1Al-0.6Ce by the MAO method. The role of cathodic polarization at the treatment was mentioned. An integrated assessment of the ability to thermal conductivity and corrosion resistance of the modified alloy was made. Despite the relatively small thickness and the presence of pores, the resulting coating provides sufficiently high corrosion resistance; the formed coating slightly (not more than 5%) reduces the thermal conductivity of the ultralight Mg alloy.

1. Introduction

Among the metallic materials, magnesium alloys are of keen interest because of their special characteristics [1]:

• low density (1.35–1.85 g/cm³), about a half of aluminum or one fourth of steel.
• high specific strength and stiffness.
• high ability to absorb energy of impact and reduce vibration, damping property is 100 times higher than that of aluminum alloys.
• good electromagnetic shielding, high heat conductivity and heat capacity.
• stability of the sizes at long operation and storage.
• good machinability.

In addition to the listed advantages, magnesium is non-toxic, biologically and mechanically compatible with bone and muscle tissues. Magnesium is the fourth largest cation in the human body and the most bio tolerant metal, involved in many metabolic processes. For this reason, magnesium alloys are actively used for the manufacture of orthopedic, surgical and vascular implants, invasive devices, various tools and medical equipment [2, 20, 21].

However, it is well known that the main negative feature, which limits application of magnesium-based alloys, is their high chemical activity resulting a low resistance to corrosion degradation in various media [2-4, 9, 10, 12-17, 26].
Nevertheless, a steady close interest on the part of aircraft and defense industries in magnesium alloys has been noted since the 1940s [9]. This is due to the fact that magnesium is optimal in terms of SWaP (size, weight, and power). At present Mg alloys are used at the manufacture of engines parts, aircraft fuselages, ships, and cars. The lightweight of magnesium means systems for night vision and target acquisition can be weapons-mounted, improving functionality while maintaining the balance and feel of the weapon itself. Magnesium alloys is also considered as material of casings and elements of structure for modern devices, and even for armour plating [10].

Mg-Li-Al-Ce alloys have a density of 1400-1600 kg/m³ and are well established in the manufacture of parts of instruments and devices operating at room and low temperatures, because they have high plasticity and low tendency to crack formation [5, 8, 19]. Doping with lithium is attractive not only owing to option of the specific weight reduction, but also due to formation of plastic phase (bcc β-phase) at Li content > 5.5 wt% (> 17 at%) [29]. Additive of Al a little bit improves corrosion stability; the rare earth elements can improve the strength and plasticity of the Mg-Li alloys [27, 28]. However, the problem of insufficient corrosion resistance remains unsolved.

The development of effective corrosion protection techniques by surface modifying of magnesium alloys could be an advance in the problem solving. For this purpose, the methods of plasma-electrolyte treatment, in particular, micro-arc oxidation (MAO) is increasingly used. The use of MAO technology enables to synthesize on the surface of magnesium alloy high adhesive nanoceramic layers. The composite thus obtained acquires fundamentally new properties; in particular, its corrosion resistance is several orders of magnitude higher than that of untreated alloys [2-4, 10, 12-17, 26].

At the same time, the formation of non-metallic ceramic-like layers on the metal surface causes significant changes in the thermal-physical characteristics of the part as a whole. This is very important for materials operating under high gradient of temperatures conditions or transmitting big heat flows. In this regard, it seems relevant studying of thermal-physical properties of coated Mg alloy.

Magnesium exhibits its specific features at plasma-electrolyte treatment as well. Magnesium alloys, unlike aluminum alloys, are known to be difficult for micro-arc oxidation, because of a sharp drop of anodic voltage during the process [12, 13, 16]. The voltage drop is accompanied by the extinction of the micro-arc discharges and produces many defects caused by etching of the formed oxide layer. The etching of coating makes it entirely inappropriate for obtaining the required protective properties and completely unsuitable for practical application. The onset of the voltage drop depends on the compositions of the treated alloy, the electrolyte, the treatment modes, and the features of the equipment. It usually occurs within 5-60 minutes after the start of the treatment. Thickness of the formed coatings is able to reach 5-60 µm, at the same time protective properties of coatings fall with reduction of their thickness [14, 15, 18].

MAO coating growth is realized mainly at anodic polarization [3, 4, 23]. During the cathodic polarization, the restructuration of electrical double layers (so called Helmholtz and Gouy–Chapman layers) occurs, which leads to reduced ion transport and difficult access of reagents to the treatment zone. The consequence is a local disruption of previously formed anode films and a slowdown in coating growth. Besides, due to cathode component of current, the internal part of formed layer is heated, which contributes to formation of high-temperature phases, causing the increase of density and the reduction of porosity and thickness of coating [3, 4, 22-24].

After the analysis of relevant sources of information, although there are some literatures about the emissivity of MAO [30, 31], there is no publication devoting to the influence of MAO coatings on the thermal-physical characteristics of ultralight magnesium alloys. Therefore, the purpose of this paper is an integrated assessment of corrosion resistance and ability to thermal energy conductivity for a magnesium-based ultralight alloy modified with MAO.

2. Materials and Methods
The alloy Mg-8Li-1Al-0.6Ce was chosen as research object. This alloy has high ductility and it is usually designed to produce relatively low loaded structures operating at room and cryogenic
temperatures and where rigidity and increased resistance to compressive are required [7]. The alloy was prepared by melting the ingots of commercially pure Mg (>99.99 wt.%), Li (>99.9 wt.%), and Mg-20Ce master alloy in a vacuum medium frequency electromagnetic induction furnace under the protection of argon at 993 K for 20 min. The melt was poured into a permanent mold (130mm×110mm×40mm) at 973 K. Then the as-cast alloy was cut into plates with dimensions of 40x40x3 mm.

MAO treatment was carried out in the aluminate electrolyte containing KOH (1.2 g/l) and NaAlO₂ (15 g/l) in the anodic-cathodic mode at a voltage of 375–465 V and with a current density of 10 A/dm² and a currents ratio of Ia/Ic = 0.9. MAO modification procedure and used equipment are more fully described in [12]. The coating roughness immediately after MAO was Ra = 2.5 and Rz = 12.5. Mechanical grinding with grain type 500 abrasive SiC paper-based was carried out for finishing of the samples surface.

For the quick, accurate and nondestructive thickness measurement of non-metallic coatings on a metal non-magnetic base, the BT-201 eddy current gauge was applied. To taking off surface profilograms, TESA Rugasurf 20 was used. The methodology and device for the through porosity measuring was similar to presented in Ref. [12].

The microstructure of coating was studied on high-resolution electron microscopes Philips XL-30 and Quanta SEM FEI, equipped with a Genesis system for X-ray energy dispersion (EDX) analysis.

Thermal-physical studies of the samples were performed using an LFA 467 HyperFlash (NETZSCH) instrument with an increased data read rate to 2 MHz. As a criterion characterizing the level of thermal-physical properties, the coefficient of thermal diffusivity was chosen, the total systematic error of its determination was ± 0.2 mm²/s.

During the measurement of thermal-physical property, the underside of the thin sample located in the holder inside the furnace with maintaining specified temperature is irradiated with a high intensity short pulse by means of a xenon flash, which leads to an even increase in the temperature on the upper side of the sample. A high-speed IR detector fixes this temperature rise, and the thermal diffusivity is calculated from the sample thickness and temperature rise rate. First, the thermal diffusivity of the alloy sample coated on both sides was determined. The measurements were then made after the modified layer had been removed first from one plane and then from the other plane.

The value obtained in the latter case was taken as an index of the thermal diffusivity for the untreated alloy. The average thickness of the double-coated test pieces was 2.99 mm, single-coated was 2.93 mm, and uncoated was 2.86 mm.

Corrosion resistance tests of coated samples were performed in an ASCOTT S450iS/S450iP salt spray chamber at the temperature of 35 ± 2°C, as well as in a climate chamber GDJS-750-CA at the temperature of 35 ± 2°C and the humidity of 95 ± 3%, the duration of the tests was 450 hours in each case [6, 11].

3. Results and Discussion

It was found that the voltage drop in the MAO process for the studied alloy occurs after 32 minutes. Previous studies showed that the reduction of KOH concentration from 6 to 2 g/l in the electrolyte containing 9 g/l of water glass has a positive effect on the integrated properties of the modified layer [12]. However, a further decreasing (less than 2 g/l) in the KOH content did not allow initiating the ignition of micro-arc discharges in the electrolyte of this type. Taking into account that the presence of sodium aluminate in alkaline electrolyte has beneficial effect on MAO processes due to formation of tetrahydroxoafulminate anions (Al(OH)₄⁻) [22, 25], in this work we used a solution comprising KOH and NaAlO₂. It has made it possible to almost halve of the alkali content, and the electrolyte's operability has been ensured by increasing the concentration of aluminate. The rate of the coating growth compared to the treatment in the silicate-alkali electrolyte was a little bit lower, but this fact could be considered as positive from the point of view of the need to form denser coatings. The selected current ratio Ia/Ic = 0.9 also contributed to reducing the rate of the coating growth due to the increasing role of the cathodic component.
Thus, treatment of the Mg-8Li-1Al-0.6Ce alloy in the electrolyte of KOH (1.2 g/L) and NaAlO$_2$ (15 g/L) for 25 minutes made it possible to form a sufficiently dense and uniform coating with an average thickness of about 65 μm. SEM photographs of the resulting coating are shown in Figure 1.

It can be seen that the coating visually has a pronounced surface porosity (Figure 1A) characteristic for MAO coatings, but the through porosity measurements gives a relatively small value of 2.7 ± 0.2%. The absence of any significant through porosity is confirmed by the SEM image of the sample cross-section (Figure 1B). We assume that the reduction of the through porosity is ensured by the preponderance of the cathodic phase in coating formation pulse according to the mechanism described in the Ref. [24]. However, this hypothesis requires more closely experimental studies for plasma-electrolyte treatment of the ultralight magnesium alloy.

Figure 1. SEM image of formed coating: surface (A) and cross-section (B).

Figure 2 depicts the results of energy-dispersive X-ray spectroscopy elemental analysis of the coating. The main components of modified layer are magnesium and oxygen, the very significant presence of aluminum can be explained by the use of aluminate as a component of the electrolyte.

Figure 2. EDX analysis of coating.
The data of measuring the thermal diffusivity coefficients for the coated and uncoated samples are shown in Figure 3. Mathematical processing for polynomial approximation of experimental data was carried out by least squares method. The resulting curves shows slight differences (about 5% maximum) in the thermal-physical properties of the coated and uncoated alloy. At the same time, the differences appear less significant in the area of relative low (room) temperatures and as they approach the melting temperature.

![Figure 3. Results of thermal-physical studies.](image)

Tests carried out in chambers of salt spray and of controlled climate did not result in any visible corrosion failure, but a change in color caused by the appearance of white plaque was observed (Figure 4).

![Figure 4. Typical view of samples before (A) and after (B) corrosion tests.](image)

Comparison of the obtained results with the scale of evaluation of corrosion state of non-metallic inorganic coatings [11] allowed qualifying the formed MAO coating as compliance to first point (quite stable; with slight color change; without signs of pointed, spotty and ulcer corrosion) on a five-point scale. No any coating delamination from the substrate was observed. Therefore, the formed MAO coatings are able to effectively protection the alloy surface against the influence of the even very aggressive environment.
4. Conclusions
1. Application of described mode of Mg-Li alloy treatment by MAO method makes it possible to obtain oxide-metal corrosion resistance composite with good thermal conductivity.
2. The replacement of water glass with sodium aluminate in the MAO electrolyte allows the formation of coatings with relatively small through porosity on the ultralight Mg alloy.
3. The formed coating slightly (up to 5%) reduces the total thermal conductivity of the composite ultralight Mg alloy, while the deterioration of thermal conductivity is leveled with the temperature decreasing.
4. Despite the relatively small thickness and the presence of pores, the resulting coating provides a sufficiently high corrosion resistance.
5. In order to make fuller using of the cathodic component opportunity for the control of Mg alloy MAO coatings characteristics, additional experiments are necessary.

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