Features of anodic plasma electrolytic treatment of an ultra-light alloy of the Mg-Li system in an aqueous electrolyte

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Abstract. The possibility of plasma electrolytic treatment of an alloy of the Mg-Li system in an aqueous solution of ammonium chloride, ammonium nitrate and boric acid has been studied. The specific features of the process in the voltage range from 10 to 600 V are determined. The current-voltage and voltage-temperature characteristics during alloy processing are shown, as well as the effect of the processing time on the temperature of the samples. Plasma electrolytic boronitriding of the alloy can be carried out to study the efficiency of the technology at a voltage of 240 V, which corresponds to a sample temperature of 300 ± 10 °C.

1. Introduction
Among the metal materials used in various branches of modern industry, in recent years, increased interest is shown in ultra-light magnesium alloys, which is due to their special properties in combination with low density. Materials based on Mg are particularly attractive for biomedical applications, since they are non-toxic, biologically and mechanically compatible with bone and muscle tissues. Magnesium is the fourth most abundant cation in the human body, is involved in many metabolic processes, and is the most biotolerant of metals [1]. For this reason, magnesium alloys are actively used for the manufacture of orthopedic, surgical and vascular implants, invasive devices, various instruments and parts of medical equipment. The use of ultra-light magnesium alloys can open up wide new opportunities for the development of more convenient devices with improved performance. At the same time, the main negative feature that significantly limits the spread of magnesium-based alloys is their high chemical activity and, as a consequence, low resistance to corrosion destruction in various environments. Tribological characteristics also have a very low level, which ultimately reduces the adaptive potential [2].

The solution to these problems can be the modification of the surface of magnesium alloys. For these purposes, plasma electrolytic treatment technologies are increasingly being used [3]. These technologies have found greater application in the processing of steels, cast irons and titanium alloys, contributing to the hardening of the surface layer due to the diffusion of atoms of light elements and hardening. This is further reflected in an increase in corrosion and wear resistance. Depending on the conditions of surface modification, it is possible to carry out a cathodic or anodic version of plasma
electrolytic saturation of metals and alloys, which can be combined with plasma electrolytic polishing, as well as carrying out microarc oxidation.

Microarc oxidation is most often used to modify the surface of magnesium and its alloys. For example, microarc oxidation effectively protects a magnesium substrate from corrosion in an SBF solution, reduces the corrosion current density by more than 2 orders of magnitude, and the corrosion potential shifts in a positive direction [4].

However, the possibilities of plasma electrolytic saturation of Mg alloys have not been studied at all. At the same time, it is known that magnesium nitride is an effective catalyst for the structurization of solid refractory compounds [5], and the alloy of boron, magnesium and aluminum is known for its low coefficient of sliding friction and high hardness. By analogy with the role of the nitride phases for other valve metals [6], the positive effect of the magnesium alloy nitriding on its properties is not excluded.

In this sense, it is of interest to study the possibility of carrying out and features plasma electrolytic saturation of the Mg-8Li-1Al-0.6Ce-0.3Y alloy in an electrolyte containing boron and nitrogen.

2. Materials and methods
Plates of alloy Mg-Li (Mg-8Li-1Al-0.6Ce-0.3Y) 18 mm long, 5 mm wide and 2.5 mm high were treated in an electrolyte containing 10 % ammonium chloride, 5 % ammonium nitrate and 3 % boric acid using a cylindrical electrolyzer under conditions of longitudinal flow of the sample by the electrolyte. In the upper part of the chamber the electrolyte was being overflowed over the edge into the pallet, from where it was then pumped through the heat exchanger at flow rate of 2.5 L/min. The temperature of electrolyte cooled with tap water was maintained equal to (20±2) °C at the inlet to the electrolyser. During processing, the sample was connected to the positive pole of the DC power supply, and the working chamber to the negative one. After applying voltage to the sample, it was slowly lowered into the electrolyzer at a speed of 1 mm / s to a depth of 14 mm. To study the current-voltage and voltage-temperature characteristics, a voltage from 10 to 600 V was applied to the sample. The current intensity was measured using a DP6 10-2000A ammeter, and the process voltage was controlled using a DC DP6 2/20/200/600V DC voltmeter.

The temperature of the sample was measured by a thermocouple made of chromel and alumel wire 0.5 mm in diameter, which were insulated, and at the end twisted and welded in graphite powder with borax at a potential of 200 V, set using an alternating current source. The thermocouple was connected to an APPA 103N digital multimeter and inserted into a 1 mm diameter hole in the plate, which was drilled with a drill to a depth of 5 mm. The upper part of the plate with the thermocouple was insulated with a heat-shrinkable tube to eliminate contact with the electrolyte and the purity of the experiment.

3. Results and discussion
Figure 1 show the current-voltage characteristic obtained during the anodic plasma electrolytic treatment (PET) of the alloy. Depending on the voltage applied to the sample, the nature of the process changes. In the voltage range of 10–30 V, an electrolysis regime is observed (\(T_{\text{sample}} = 80–110\) °C (figure 2)), which changes to an interrupt regime when the voltage increases to 40 V and exists up to 90 V inclusively (\(T_{\text{sample}} = 60–95\) °C (figure 2)). In the interrupt regime, the current values vary in the range of 1.5–8.5 A (figure 1). In these conditions, the energy is insufficient for the formation of plasma around the anode, however, a high speed of anodic dissolution of the alloy is observed.

After increasing the voltage to 100 V, an electrolytic plasma is formed and the interrupt regime changes to the heating regime (\(T_{\text{sample}} = 200\) °C (figure 2)). When the voltage increases to 440 V, the plasma resistance rises and the current intensity reduces (figure 1), as also the temperature of the sample increases (figure 2). At the starting voltage \(U_0 = 240–320\) V, reported to the system, and the contact of the sample with the electrolyte, the alloy heats up to extremely high temperatures and reacts chemically with water, which is accompanied by burning and the formation of the corresponding oxides. So the existence of stationary heating is valid at \(U_0 = 120–220\) V, at which a dielectric oxide
layer forms on the surface of the alloy in contact with the electrolyte, preventing heating to a critical temperature and burning in the aqueous medium.

At $U_0 = 350\text{–}400$ V and operating $U = 320\text{–}400$ V, there is a plasma electrolytic polishing regime in which, depending on the voltage, the sample temperature does not exceed $120$ °C (figure 2). In these conditions, the current is minimal and increases with increasing voltage (figure 1). Reducing the working voltage to $U \leq 310$ V leads to a change in the polishing regime to the heating regime and the alloy is heated again to a critical temperature and burns in the aqueous medium.

At higher voltages $U \geq 460$ V, the anodic polishing regime changes to the electrolyte spraying regime, which indicates the maximum plasma resistance and is accompanied by a decrease in the current intensity (figure 1). In these conditions, the sample temperature does not exceed $100$ °C (figure 2).

**Figure 1.** Current-voltage characteristic during plasma electrolytic treatment of Mg-LI alloy in the electrolyte containing NH$_4$Cl, NH$_4$NO$_3$ and H$_3$BO$_3$.

**Figure 2.** Voltage-temperature characteristic during plasma electrolytic treatment of Mg-LI alloy in the electrolyte containing NH$_4$Cl, NH$_4$NO$_3$ and H$_3$BO$_3$. 
Figure 3 shows the dependence of the temperature of samples from the Mg-Li alloy on the time of plasma electrolytic treatment at constant voltage. It was found that the $T_{\text{sample}} = 300 \pm 5$ °C does not change for 5 minutes at a processing voltage of 240 V. That is why PET can be carried out in these conditions, for example, by varying the process time.

![Figure 3](image.png)

**Figure 3.** The dependence of the temperature of samples from the Mg-Li alloy on the time of plasma electrolytic treatment at constant voltage in the electrolyte containing NH$_4$Cl, NH$_4$NO$_3$ and H$_3$BO$_3$.

**4. Conclusions**

The possibility of plasma electrolytic treatment of an alloy of the Mg-Li system in an aqueous solution of ammonium chloride, ammonium nitrate and boric acid has been studied.

It was found that during processing in the voltage range from 10 to 30 V the electrolysis regime is observed, from 40 to 90 V – the interruption regime, from 100 to 440 V – the heating regime, from 460 to 600 V – the electrolyte spraying regime.

At the starting voltage $U_0 = 240$–320 V, reported to the system, and the contact of the sample with the electrolyte, the alloy heats up to extremely high temperatures and reacts chemically with water, which is accompanied by burning and the formation of the corresponding oxides. At $U_0 = 350$–400 V and operating $U = 320$–400 V, there is a plasma electrolytic polishing regime.

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