Modifying of magnesium alloys for creation of effective electrochemical power sources

A V Apelfeld¹, B L Krit¹, V B Ludin², N V Morozova³ and M M Serov¹

¹ Moscow Aviation Institute (National Research University), Moscow, Russia
² Russian State Agrarian Correspondence University, 143907, Balashiha, Russia
³ Russian Medical Continuous Professional Education Academy, 123995, Moscow, Russia

E-mail: bkrit@mail.ru

Abstract. The results of researches of the modifying effect on magnesium alloy of the Microarc Discharge Oxidation (MDO) and the Pendant Drop Melt Extraction (PDME) methods are presented. The possibility of changing in electrochemical activity and in specific surface value for the electrodes materials that apply to creation of electrochemical power sources is shown.

1. Introduction
Magnesium and its alloys gain the increasing prevalence in various industries, among other things, as perspective material for production of anodes at creation of electrochemical power sources and supercapacitors [1–6]. Power characteristics and resource of these devices rises with the decreasing of true current density and increasing of dimensional current density [7]. The value of true current density depends on chemical activity of electrode material, the overall dimensional current density is function of the surface area of electrode (anode) participating in electrochemical reaction.

Modifying of magnesium alloys by formation of superficial porous oxide layers may influence on their electrochemical activity and could use both for regulation of the true current density and for increasing in longevity of anode material. Increasing in a specific surface of anodes for increase in dimensional density of current can be reached by production of magnesium anodes with using of the modified fibrous materials.

2. Materials and methods
As material for carrying out researches the magnesium alloy ML10 of the increased corrosion resistance has been chosen (its foreign analog – EA55RS Magnesium Electron Ltd, GB).

For formation of superficial oxide layers, the Microarc Discharge Oxidation (MDO) method that essence and hardware in detail described in the monograph [8] was used. Treatment of samples of the alloy in a condition of delivery (rod) was carried out in silicate-alkaline electrolyte with variation of water glass sodium concentration in ranging from 2 to 8 ml/l and potassium hydroxide – from 3 to 6 g/l. Anodic-cathodic (50 Hz) mode at equal currents relation and total density 11 A/sq.dm was applied. Duration of treatment was changed from 15 to 70 min.

Obtaining of fibers from magnesium alloy ML10 was carried out by Pendant Drop Melt Extraction (PDME) method [9]. One of advantages of the PDME is application of pot-free electron beam melting in a vacuum that does possible producing the fibers even from refractory and chemically active metals.
Extraction of the fiber from melt by PDME method occurs at cooling rate up to $10^6$ K/s. The method allows to form both lengthy fibers, and discrete particles and also porous nonwoven canvases.

The thickness of the oxide layer was measured with an eddy current thickness gauge (BT-201) intended for nondestructive control of coatings, and by metallography on cross sections of fibers. Assessment of porosity was made by the electrochemical technique that is in detail described in the monograph [8]; the value of a specific surface was determined by the BET gas adsorption method with use of the analytical TriStar II 3020 system of Micromeritics. As an indicator of electrochemical activity, the corrosion current density at potentiodynamic polarization tests has been chosen. Receiving of polarizing curves was carried out by potentiostat EP-20A according to the three-electrode scheme in 3% NaCl solution with rate of polarization 1 mV/s. Electron microscopy and EDS researches carried out on the Quanta SEM analysis system with application of the Genesis Software program.

3. Results and discussion

In figure 1 the received dependences of changes of through porosity of coatings and of corrosion current density of the modified ML10 magnesium alloy in the studied concentration intervals of electrolyte components at the above-mentioned mode of treatment are shown. The lowest values of coatings porosity and of electrochemical activity of the modified alloy are recorded when treated in the electrolyte containing 3.5 g/l of potassium hydroxide KOH and 4 ml/l of water glass Na$_2$O(SiO$_2$)$_n$.

![Figure 1](image1.jpg)

**Figure 1.** Influence of electrolyte composition on through porosity of MDO-coatings (a) and on electrochemical activity of the modified ML10 magnesium alloy (b).

Researches of dependences of changes of thickness and through porosity of coatings and also of corrosion current density of the modified alloy samples from treatment duration in electrolyte of above-mentioned composition have shown existence of extremes in the range of modifying duration of 40-50 min (figure 2).

At the second stage of process (coming after 50 minutes of MDO-treatment) the rate of coating formation considerably decreases, it’s through porosity grows and the corrosion resistance of the modified samples reduces. The probable cause of this is hydration and etching of the formed MDO-coating as the result of electrochemical interaction with electrolyte at the long duration of process. Researches have also shown that the alloy treated within 50 min has undergone the minimum degradation (corrosion current density is $2\cdot10^{-3}$ A/sq.m).

By the PDME method the fibers from ML10 magnesium alloy were obtained. Average thickness of fiber was 80 microns, length of fibers was in range of 30–120 mm.

In figure 3 the fractography of the typical extracted fiber is presented, the results of EDS analysis confirmed the compliance of fibers composition with the specified alloy brand.
Attempts to modify fibers by MDO method with application of the mode developed for compact ML10 alloy have shown that at fiber state it is extremely difficult for oxidation because of both the chemical nature of magnesium, and the considerable concentrated energy at plasma-electrolytic treatment. The rate of the MDO-coating formation has decreased in comparison with alloy in a compact state, ignition of some fibers was noted. Reduction of current density to 5 A/sq.dm has allowed to provide the acceptable mode of formation of rather thin, but uniform MDO-coatings. Process of MDO was carried out in silicate-alkaline electrolyte of the optimized early composition with additive of 3 g/l of sodium fluoroaluminate Na₂SiF₆. Duration of the treatment has been limited to fading of the microarc discharges and was about 10 minutes.

In figures 4 and 5 the results of the analysis of the oxidized fiber are presented. It is visible that the average thickness of the received covering is about 2 microns, the layer has uneven thickness that is possibly caused by heterogeneity of a surface of an initial substrate. The energy dispersive analysis of oxide coating of fiber has shown that among basic elements in the formed layer besides Mg and O the Si is present there.

The calculated specific surface for average fiber of the idealized cylindrical form was \(0.28 \times 10^{-2}\) sq.m/g. The same characteristic determined experimentally by the BET method was
(0.79 ± 0.003)·10^{-2} \text{ sq.m/g for fiber without coating and (66.85 ± 0.003)·10^{-2} \text{ sq.m/g for the oxidized fiber. Thus, the measured value of specific surface for real fibers of ML10 alloy almost in three times exceeds the calculated value. It is caused by the fact that a form, size and morphology of the fibers surface (as it is visible on figures 3 and 4) aren't ideal. Oxidation of fibers owing to which a porous ceramic-like layer is forming on the surface of fibers allows to increase their specific surface approximately by two orders of value else.}

Figure 4. External surface view and cross section of the oxidized ML10 alloy fiber.

Figure 5. Energy-dispersive X-ray spectroscopy of the oxidized fiber surface.

4. Conclusions
As a result of the executed researches it has been determined that formation of MDO-coatings on the surface of magnesium alloy promote to significantly increasing of its corrosion resistance. By variation of thickness and of through porosity of oxide layer it is possible to regulate the electrochemical activity and the corrosion degradation of alloy. Treatment by MDO of the ML10 alloy dispersed in fibers by PDME is significantly differs from treatment of this alloy in a compact state, being the operation demanding careful selection of electrolyte composition and parameters of the oxidation mode. Rate of formation of the MDO-coating on fibers rather low, at the same time ignition of some fibers takes place. The measured value of specific surface for magnesium fibers is almost
three times higher than calculated due to their irregular shape and the developed surface morphology. Oxidation of fibers increases their specific surface by two orders of value else. Use of the MDO and PDME methods for purposeful modifying of electrochemical and morphological parameters of the anodes manufactured of magnesium alloys is capable to give a new impetus for increase in their efficiency at creation of modern electrochemical power sources and supercapacitors for energy storage.

Acknowledgment
Works are carried out with financial support of the state represented by the Russian Federation Ministry of Education and Science (the agreement on granting a subsidy No. 14.577.21.0275 from 9/26/2017, the unique identifier of the RFMEFI57717X0275 project). Authors express gratitude to Savushkina S V, the research associate of Federal State Unitary Enterprise Keldysh Research Center for the help at carrying out electron microscopy researches.

References
[1] Kostanyan R K, Karamyan G G, Ivashkin P I, Kalugin M M and Martoyan G A 2017 Prospects of use of magnesium as a renewable source of energy (Moscow: Russian Academy of Sciences) 28 p
[2] Apelfeld A, Krit B, Ludin V, Morozova N, Vladimirov B and Wu R Z 2017 Surface & Coatings Technology 322 127–33
[3] Elkin F M 2007 Technology of light alloys 1 5–18
[4] Onishchenko D V 2007 Issledovano v Rossii URL: http://zhurnal.ape.relarn.ru/articles/2007/130.pdf
[5] Cao D, Wu L, Sun Y, Wang G and Lu Y 2008 Journal of Power Sources 177(2) 624–30
[6] Zhang T, Tao Z and Chen J 2014 Materials Horizons 1 196–206
[7] Varypayev V N, Dasoyan M A and Nikolsky V A 1990 Chemical sources of current (Moscow: Higher school) 240 p
[8] Epelfeld A V, Belkin P N, Borisov A M, Vasin V A, Krit B L, Lyudin V B, Somov O V, Sorokin V A, Suminov I V and Frantskevich V P 2017 Modern technologies of surface modification of a of materials and putting of protective coatings (Moscow-St. Peterburg: Renome) 1 648 p
[9] Antsyferov V and Serov M 2014 Manufacturing of a rapid solidification materials and fibers (LAP LAMBERT Academic Publising) 62 p