Plasma-electrolytic treatment of magnesium alloy fibers

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Abstract. The results of researches of the modifying effect of the Pendant Drop Melt Extraction (PDME) and the Plasma-Electrolytic Treatment (PET) methods for ML10 magnesium alloy are presented. Particularities of PET for fibrous magnesium alloy are studied. Metallography, morphology analysis and corrosion tests are executed. The conclusion that application of the PET and PDME methods for purposeful modifying is capable to significantly expand possibilities of magnesium alloys using was made.

1. Introduction
Many industries apply magnesium and its alloys for various purposes [1–4]. The keen interest to these materials and its increasing prevalence is caused by their special characteristics:
• low density (1.35–1.85 g/cm\textsuperscript{3}), about two-thirds of aluminum alloys or one-fourth of steels.
• high specific strength and stiffness, good performance characteristics.
• high ability to absorb of impact and vibration energy (damping property is 100 times more than that of Al alloys).
• good electromagnetic and antinoise shielding, high heat conductivity and heat capacity.
• stability of the sizes at long operation and storage.
• good machinability.
• absence of ageing effect which always exists in constructional alloys and plastics.
• not deficiency: Mg Clark concedes only Al, Fe, Ca, and Na, exceeding this indicator for carbon.

At the same time, the main negative feature of a magnesium is very high chemical reactivity and, as a result, low resistance to corrosion destruction. This factor significantly limits implementation of magnesium-based alloys. The problem in particular is relevant for the dispersed materials (for instance, in fiber condition) as a result of its surface increasing. Various fibrous substances recently acquire the increasing popularity both for immediate use, and as a feed stock for creation of composites and for production of compact materials. The products made of fibrous materials show higher characteristics in comparison with produced ones by casting or deformation technologies. Practically any alloys (including Mg alloys) can be turned to fiber state by Pendant Drop Melt Extraction (PDME) method [5–9].

To avoid the above-mentioned demerit of magnesium alloys, many technologies can be used. Most effective solution is development of new technologies of surface engineering. For protection against
external influences and also collimating of additional functional properties, formation of the modifying layers and coatings on a surface is possible. The promising technological process for modifying of metals and alloys surface is the method of Plasma-Electrolytic Treatment (PET). Due to PET it is possible to carry out synthesis on a surface of products made from so-called valve materials (to which belong alloys magnesium and its alloys) a nanoceramic layers and coatings having high anchoring strength (adhesion) with a basis and a controlled corrosion protective ability [10]. However, there is no information about modifying of fibrous alloys, including magnesium, therefore in this research we try attempt to find out a specifics of PET process for fibers and to estimate the achieved results.

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

Obtaining of fibers from magnesium alloy ML10 was carried out by 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 10⁶ K/s. The method allows to form both lengthy fibers, and discrete particles and also porous nonwoven canvases.

For formation of superficial oxide layers, the Micro Arc Oxidation (MAO) method as a kind of PET was applied. The essence and hardware of MAO in detail were described in the monographs [10, 11]. Treatment of the alloy samples was carried out in silicate-alkaline electrolyte with variation of water glass sodium Na₂O(SiO₂)n concentration ranging from 2 to 8 ml/l and potassium hydroxide KOH from 3 to 6 g/l. For stabilization of MAO process in relation to magnesium alloy, additives of sodium fluorosilicate Na₂SiF₆ from 0 to 5 g/l into basic electrolyte was entered. Anodic-cathodic (50 Hz) mode at equal currents relation and total density from 5 to 10 A/sq.dm was applied. Duration of treatment was changed from 3 to 60 minutes.

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 [11]; 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
The extraction of fibers of ML10 magnesium alloy from a melt was carried out by the PDME method in the atmosphere of helium with a pressure of 1⋅10⁴ Pa. Average thickness of fiber was 60 - 80 micrometers, length of fibers was in range of 30-120 mm.

In figure 1 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.
It is known that magnesium alloys belong to the category of difficult treating by PET. To initiation and maintaining of micro electric discharges usually apply rather complex electrolytes and high voltages [2, 12]. It leads to undesirable consequences as impossibility of obtaining coatings with the required thickness and to the increased marriage percent owing to an electrochemical etching, or even failure of processing (fading of the discharges). During researches of oxidation process at compact (not fibrous) ML10 and AZ41 alloys, we confirmed existence of a sharp slowdown of anode voltage. The most typical forming curve of the process is shown on fig. 2.

This feature is shown in a bigger degree when object of treatment is the alloy transformed to a fibrous state. Attempts to modify fibers with application of the modes find for compact alloys didn't result in success. The dispersed ML10 alloy extremely difficult is subject to PET because of both the chemical nature of its ingredients, and the considerable energy concentrated on it at plasma-electrolytic impact. The rate of the coating forming decreased in comparison with alloy in a compact state, ignition of fibers at large current densities is noted.

Decrease of a current density to 5 And/sq.dm allowed to provide the acceptable mode for forming of rather thin, but uniform MAO-coatings. This process was carried out in silicate and alkaline electrolyte
of the composition optimized earlier for AZ41 [2] alloy, but with additive of 3 g/l of sodium fluorosilicate. At the same time, the maximum duration of process didn't exceed 10 minutes.

In figures 3 and 4 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 $0.28 \cdot 10^{-2}$ sq.m/g. The same characteristic determined experimentally by the BET method was $(0.79\pm0.003) \cdot 10^{-2}$ sq.m/g for fiber without coating and $(66.85\pm0.003) \cdot 10^{-2}$ 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 1, 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 3](image1.png)

**Figure 3.** External surface view and cross section of the oxidized ML10 alloy fiber.

![Figure 4](image2.png)

**Figure 4.** Energy-dispersive X-ray spectroscopy of the oxidized fiber surface.
Corrosion tests show about 2 time increasing of corrosion resistance despite the small thickness and not continuity of a coating. The averaged value of corrosion current density is 0.398 A/m² against 0.804 A/m² for the untreated ML10 alloy.

4. Conclusions
As a result of executed researches, it has been determined that PET process of the ML10 alloy transformed in fibers by PDME method is 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 the coating formation 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. Formation of MAO-coatings on the surface of magnesium alloy allows increasing corrosion resistance about two times. Application of the PET and PDME methods for purposeful modifying is capable to significantly expand possibilities of magnesium alloys using.

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