Mechanical properties and corrosion resistance of Mg-RE cast alloys and their plasma electrolytic oxidation

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Abstract. The effect of heat treatment on the mechanical properties (hardness, plasticity, yield and tensile strength) and corrosion resistance of several cast magnesium alloys with additions of rare earth metals (Y, Nd and Gd), and their surface modification by plasma electrolytic oxidation (PEO) were investigated. It was found that the heat treatment of the alloys results in formation of Mg12YZn, Mg3Zn3Y2 and Mg24Y5 based LPSO-phases and causes an increase in hardness and tensile strength by 5-7 and 20-25%, respectively, but at the same time, corrosion resistance of the alloys drops by 10-20 times. PEO of the alloys after heat treatment reduced the corrosion currents by 1-3 orders of magnitude without changing the corrosion potential.

1. Introduction
Magnesium alloys are the lightest metal materials that are most in demand for structures requiring weight reduction, mainly in transport systems: aerospace, automotive, high-speed railway equipment. Accordingly, progressively higher requirements are imposed on such alloys every year, both in terms of strength characteristics, and technological and functional properties [1].

There are various ways to improve the properties of magnesium alloys, many of which (such as modern methods of intensive plastic deformation) are not applicable to cast alloys. There are three main ways to improve their properties: (1) modification of chemical composition (alloying); (2) optimization of casting technology and heat treatment; (3) surface modification (surface treatment, coating, etc.). In this regard, Mg alloys containing a strengthening long period stacking ordered phase (LPSO) that prevents the movement of dislocations and reduces the anisotropy of alloy properties, are considered the most prospective. However, the LPSO phase can significantly increase the corrosion rate of Mg alloys [2], therefore additional surface treatment is necessary to create an anticorrosive layer on the surface of such alloys. This problem can be successfully solved by plasma-electrolytic (microarc) oxidation (PEO or MAO) of Mg alloys [3–5].

2. Experimental
The heat treatment of alloys with rare earth (RE) elements, Mg-2.2Nd-0.6Zr-0.4Zn (ML10), Mg-6.8RE-2.5Zn-0.6Zr and Mg-6.8RE-2.5Zn-0.6Zr systems manufactured by SOMZ LLC (Solikamsk, Russia) was followed by MAO treatment, in the aim to improve their mechanical characteristics and corrosion resistance. For this purpose, standard specimens were manufactured (in accordance with the requirements of GOST 1497-84. "Metals. Tensile testing methods" that were tested on a universal
tensile strength testing machine N50KT in the initial (cast) state and after heat treatment as per the T6 mode (homogenizing annealing at 540°C for 12 hours, quenching in air and complete artificial aging at 200°C for 12 hours). The Brinell hardness of the obtained specimens was also determined using Beijing Time Group HB-3000B hardness tester.

MAO of the alloys after heat treatment was performed in an alkaline-phosphate-aluminate-silicate-fluoride electrolyte (1 g/l KOH, 5 g/l Na₃HPO₄×12H₂O, 5 g/l NaF, 7 g/l Na₂SiO₃×5H₂O and 7 g/l NaAlO₂) at a current frequency of 500 Hz, current density 11.5±0.5 A/dm², duty cycle factor 50%, and current ratio in the cathodic and anodic impulses 0.5 ± 0.05.

Confocal laser scanning microscopy, X-ray diffraction and X-ray fluorescence energy dispersion analysis were used to study the produced specimens of oxide layers on tested magnesium alloys. Confocal laser scanning microscope Olympus LEXT OLS 400 and scanning electron microscope Jeol Neoscope JCM-6000, X-ray diffractometer Shimadzu Maxima XRD-7000S and energy dispersive spectrometer Shimadzu EDX-8000 were used. The specimen corrosion resistance was determined by the method of potentiodynamic polarization in a 3wt% NaCl solution after preliminary holding of specimens in the medium for 20 minutes for the open circuit potential to stabilize using a potentiostat-galvanostat Elins-P45X. Corrosion characteristics were measured on a three-electrode electrochemical cell with a silver-chloride reference electrode and a platinum counterelectrode. All measurements were performed multiple times (at least three times).

3. Results
The microstructures of Mg-2.2Nd-0.6Zr-0.4Zn (ML10), Mg-6.8RE-2.5Zn-0.6Zr and Mg-8.3RE-2.5Zn-0.6Zr alloys before and after heat treatment are shown in figure 1. In the initial state, all alloys are characterized by a non-equilibrium fine-grained structure. After heat treatment, the alloy structure becomes more homogeneous, and a large number of dispersive inclusions of the second phase (in ML10) or formation of a strengthening LPSO phase occurs. For the ML10 alloy, the dispersive phase was identified as Mg12Nd, and for Mg-6.8RE-2.5Zn-0.6Zr and Mg-8.3RE-2.5Zn-0.6Zr alloys, formation of the LPSO phase Mg12YZn, eutectic phase Mg2Zn1Y2, and insignificant amount of dispersive phase Mg24Y5 was identified. Simultaneously, all alloys are characterized by a slight increase in the average grain size after the heat treatment (figure 1). As a result of heat treatment, a significant improvement in the mechanical properties of the alloys was achieved (table 1), namely, yield strength, σy, and tensile strength, σu, are increased, while the duration of the aging in the range of 6-24 hours had almost no effect on them.

However, the heat treatment hardening caused by precipitation of dispersive inclusions or LPSO phases resulted, at the same time, in significant decrease of corrosion resistance of the investigated alloys (by 10 times or more). To resolve this issue, these alloys were subjected to MAO, and the effect of such treatment was evaluated. On all alloys, the thickness of oxide layers was about 40 microns, with a relatively small variation for all alloys – the dispersion coefficient is 10-15%. Concurrently, all the obtained oxide layers are characterized by a pronounced two-layer structure: an outer porous layer with separate craters and transverse cracks, and an inner less defective and denser layer directly adjacent to the magnesium substrate (figure 2).

The dominant phase of all oxide layers is magnesium oxide MgO (periclase mineral) produced as a result of direct oxidation of the treated substrate by micro-arc discharges which is similar to [6]. Magnesium oxide content in the layer for all specimens is 98-99 wt%. The magnesium aluminate phase – MgAl2O4 with the content of 1-2 wt% was also detected. All specimens are characterized by a sufficiently high crystallinity degree – 83-92 vol.% which is in good agreement with [7]. Concurrently, it should be noted that phosphorus and silicon were found in the oxide layers in the amount of 3.5 wt% and 1.8-2.8 wt%, respectively, which are not part of the detected crystalline phases. Apparently, these elements are part of the amorphous phase formed in the oxide layers [6].

The PEO treatment of alloys allowed to significantly increase their corrosion resistance. It was found that after PEO, corrosion current densities decreased by 1-3 orders of magnitude - from 14-19 µA/cm² in the initial alloys to 0.016-0.7 µA/cm² in the alloys after PEO. The Mg alloy with
neodymium experienced the least effect of PEO treatment – a decrease in the corrosion current density by ~ 22 times. For Mg-6.8RE-2.5Zn-0.6Zr and Mg-8.3RE-2.5Zn-0.6Zr (with Gd) alloys, the effect was much more significant - 240-1200 times. Besides, there is no obvious corrosion potential offset as a result of PEO treatment compared to alloys in the initial state.

Figure 1. Microstructures of the alloys (from left to right) Mg-2.2Nd-0.6Zr-0.4Zn (ML10), Mg-6.8RE-2.5Zn-0.6Zr and Mg-8.3RE-2.5Zn-0.6Zr before (top row), and after (bottom row) heat treatment in the mode: homogenization 540±10°C, 12 h + air quenching + aging 200±5°C, 12 h.

Table 1. Mechanical properties of alloys Mg-2.2Nd-0.6Zr-0.4Zn (ML10), Mg-6.8RE-2.5Zn-0.6Zr and Mg-8.3RE-2.5Zn-0.6Zr before and after heat treatment in the T6 mode.

| Alloy, state         | σT, MPa | σv, MPa | ε, % | HB  |
|----------------------|---------|---------|------|-----|
| ML10, cast           | 108     | 174     | 6.9  | 55  |
| ML10(T6) (GOST 2856-79) | 140     | 238     | 3    | 70.5|
| Mg-6.8RE-2.5Zn-0.6Zr, cast | 126.7   | 197.3   | 6.2  | 63.5|
| Mg-6.8RE-2.5Zn-0.6Zr (T6) | 132.6   | 241     | 7.9  | 69.5|
| Mg-8.3RE-2.5Zn-0.6Zr, cast | 133     | 201     | 4.0  | 66.1|
| Mg-8.3RE-2.5Zn-0.6Zr (T6) | 138     | 259     | 13.6 | 74.7|

Figure 2. The structure of oxide layers (cross-sections, SEM) on the alloys Mg-2.2Nd-0.6Zr-0.4Zn (a), Mg-6.8RE-2.5Zn-0.6Zr (b) and Mg-8.3RE-2.5Zn-0.6Zr (c).
Figure 3. OCP change (a) and Tafel (b) curves for alloy specimens in the initial (bare) state and after surface modification by PEO method in 3.5% NaCl solution.

Table 2. Basic electrochemical corrosion indicators (ASTM G102-89) of the investigated magnesium alloys.

| Specimen                  | Ecorr, mV   | icorr, μA/cm² | Rp, Ω·cm²     | CR, mm/yr | MR, g/(m²·d) |
|---------------------------|-------------|---------------|---------------|-----------|--------------|
| ML10(T6)                  | -1692±17    | 16.68±0.34    | (1.78±0.04)·103 | 0.348     | 1.825        |
| ML10(T6)+PEO              | -1575±3     | 0.732±0.138   | (5.60±1.27)·104 | 1.4·10-2  | 7.1·10-2     |
| Mg-6.8RE-2.5Zn-0.6Zr(T6)  | -1663±21    | 18.96±2.10    | (1.72±0.16)·103 | 0.354     | 2.026        |
| Mg-6.8RE-2.5Zn-0.6Zr(T6)+PEO | -1634±5    | 0.016±0.002   | (3.07±0.01)·106 | 0.3·10-3  | 1.6·10-3     |
| Mg-8.3RE-2.5Zn-0.6Zr(T6)  | -1677±31    | 14.01±4.15    | (1.69±0.47)·103 | 0.349     | 2.081        |
| Mg-8.3RE-2.5Zn-0.6Zr(T6)+PEO | -1715±18   | 0.058±0.021   | (1.94±0.82)·106 | 0.9·10-3  | 5.2·10-3     |

*±σ is given as an error

It should be noted that localized pitting corrosion is typical for all the investigated alloys, therefore, calculation of the corrosion rate and mass loss may yield some error and, most likely, the CR and MR values in table 2 are somewhat underestimated [8]. However, comparative tests of alloys can be carried out using the Tafel curves, both between the alloys, and to evaluate the efficiency of treatment of each alloy by PEO method.

4. Conclusions

It can be concluded that the heat treatment of cast magnesium alloys with RE additions results in an increase in yield and tensile strength by ~ 5-20%, and in plasticity by almost 2 times, the effect mainly provided by the presence of the LPSO phase. The Mg-8.3RE-Y2.5Zn0.6Zr alloy after the applied heat treatment has the best mechanical properties among the investigated alloys (elongation ~12% and hardness ~75 HB). In addition, this alloy has additional potential for increasing strength by optimizing...
heat treatment modes. At the same time, the alloy chemical composition has almost no effect on the oxidability and phase composition of the oxide layers produced by MAO.

Treatment of alloys by MAO method improves the corrosion resistance of the investigated alloys due to formation of the barrier oxide layer. The oxide layer prevents the access of corrosive medium to the substrate metal and by this way prevents the dissolution of metal during prolonged holding in a corrosive medium. This also reduces the corrosion currents (when specimens are polarized) by about 3 orders of magnitude.

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References
[1] Czerwinski F 2012 Magnesium Alloys - Corrosion and Surface Treatments (InTech)
[2] Li C Q, Xu D K, Zeng Z R, Wang B J, Sheng L Y, Chen X B and Han E H 2017 Mater. Des. 121 430–41
[3] Sikdar S, Menezes P V, Maccione R, Jacob T and Menezes P L 2021 Nanomaterials 11 1375
[4] Lu X, Mohedano M, Blawert C, Matykina E, Arrabal R, Kainer K U and Zheludkevich M L 2016 Surf. Coatings Technol. 307 1165–82
[5] Polunin A V, Cheretaeva A O, Borgardt E D, Shafeev M R, Katsman A V and Krishtal M M 2020 J. Phys. Conf. Ser. 1713 12036
[6] Lu X, Blawert C, Huang Y, Ovri H, Zheludkevich M L and Kainer K U 2016 Electrochim. Acta 187 20–33
[7] Curran J A and Clyne T W 2005 Surf. Coatings Technol. 199 177–83
[8] Shi Z, Cao F, Song G L and Atrens A 2014 Corros. Sci. 88 434–43