EFFECT OF THE HEAT AND SURFACE LASER TREATMENT ON THE CORROSION DEGRADATION OF THE Mg-Al ALLOYS

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Resume
In this paper there is presented the corrosion behavior of the cast magnesium alloys as cast state, after heat and laser treatment. Pitting corrosion resistance of the analyzed alloys was carried out using the potentiodynamic electrochemical method (direct current), based on a anodic polarization curve. On the basis of the achieved anodic polarization curves, using the Tefel extrapolation method near to the corrosion potential, the quantitative data were determined, which describe the electrochemical corrosion process of the investigated alloys: value of the corrosion potential E_{corr} (mV), polarization resistance R_P (kΩ.cm^2), corrosion current density i_{corr} (μA/cm^2), corrosion rate V_{corr} (mm/year) as well the mass loss Vc (g/m^2).

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1. Introduction

During the last few decades the world has seen a rapid growth of application of magnesium and its alloys almost in every field of today's industry. This is due to numerous characteristics of the metal regarded to herein, which permit its use both as a structural element, and as a chemical addition to other metal alloys. It is 35% lighter than aluminium (2.7g/cm^3) and over four times lighter than steel (7.86g/cm^3). Magnesium alloys, beside a low density of (1,7 g/cm^3), have also some other advantages like good ductility, better noise and vibration dampening characteristics than aluminium and excellent castability, high stability of the size and shape, low shrinkage, high strength to weight ratio, as well recyclability, which makes it possible to achieve recycled alloys with quality and properties very close to primary cast alloys, which makes it possible to apply these material instead of new manufactured Mg alloy for constructions of less importance [1-9, 16-18]. Low mass with a very high strength makes it possible to manufacture elements made of this material by casting, by plastic deformation, mechanical treatment or welding.

A lot of light metal applications require the special properties of material surface layer. Method which allows for improvement of the chemical, mechanical and tribological properties of the surfaces is a high power laser treatment. There are several laser surface treatments, namely surface hardening, alloying, cladding and laser melt injection. In surface hardening, the laser beam heats the work piece and changes the microstructure in such a way that the surface properties, for example hardness, of the work piece are changed. In laser alloying the laser beam melts the surface locally while a second material is added to the melt pool. After rapid solidification, the composition, the morphology and properties on the top layer of the workpiece are changed. The aim of laser cladding is the deposition of a cladding onto surfaces of work pieces. The material is deposited by pre-placed powder, powder injection or by wire feeding. The laser beam melts a thin layer of the surface of the work piece together with additional material. After solidification, a small mixture of the top part of the work piece and the coating provides the bonding between substrate and coating. In the laser melt injection process, solid particles are injected in the melt pool, which are trapped after solidification [10-15, 18].

The goal of this paper is to present of the investigation results of the casting magnesium alloys in its as-cast state and after heat and laser treatment.

2. Experimental procedure

The corrosive agent was a 3% NaCl solution. Resistance to electrochemical corrosion was determined on the ground of registered anodic polarisation curves. For potentiodynamic tests system VoltaLab®PGP201 by Radiometer was used. The measurements were carried out in a three-electrode two-chamber glass electrolyser with a volume of 150 cm^3, equipped with a water jacket connected to the thermostat of the UH-4 type ensuring a regulation with accuracy of ±0,1°C. The samples as well the investigated electrodes were made from the cast magnesium alloys. Radiometer was used. Saturated calomel electrode (NEK) of KP-113 type served as reference electrode, whereas platinum electrode of PtP–201 type was used as auxiliary electrode. The measurements were performed at the room temperature after 20 minutes from the first contact of the investigated material with the electrolyte, by a potential change rate of 120 mV/min. The surface area of the tested samples of the cast magnesium alloys was equal 0,5 cm^2.

The investigations have been carried out on test pieces of AZ12, AZ91, AZ61, AZ31 magnesium alloys in as-cast and after heat and laser treatment states (Table 2). The chemical composition of the investigated materials is given in Table 1.

Table 1

Chemical composition of investigation alloy (in. wt.%)

Material type	Al	Zn	Mn	Mg	Rest
AZ31	2.96	0.23	0.09	96.65	0.07
AZ61	5.92	0.49	0.15	93.33	0.11
AZ91	9.09	0.77	0.21	89.79	0.14
AZ12	12.1	0.62	0.17	86.9	0.21

Table 2

Parameters of heat treatment of investigation alloy

Sign the state of heat treatment	Conditions of heat treatment		
	Temperature (°C)	Time of heating (h)	Way of cooling
0	As-cast		
	Solution treatment		
1	430	10	Water
2	430	10	Air
3	430	10	Furnace
	Aging after solution treatment with cooling in the water		
4	190	15	Air

Laser alloying was performed by high power diode laser HDPL Rofin DL020 (Table 3) with feeding of hard silicon carbide particles under an argon shielding gas (Fig. 1). Argon was used during laser re-melting to prevent oxidation of the surface layer and the substrate. Particle size of silicon carbide powder was below 75 μm. The process parameters during the present investigation were: laser power – 1,6-2.0 kW, scan rate – 0.5-1.0 m/min and powder injection rate – 1-10 g/min.

Table 3

HPDL Rofin DL 020 parameters

Laser wave length (nm)	808 ÷ 940
Focus length of the laser beam (mm)	82
Power density range of the laser beam in the focus plane (kW/cm^2)	0.8 ÷ 36.5
Dimensions of the laser beam focus (mm)	1.8 x 6.8

The analysis of the investigated samples after the corrosion test was performed using the Zeiss SUPRA 35 scanning electron microscope with the EDAX Trident XM4 dispersive radiation spectrometer at the accelerating voltage of 20 kV.

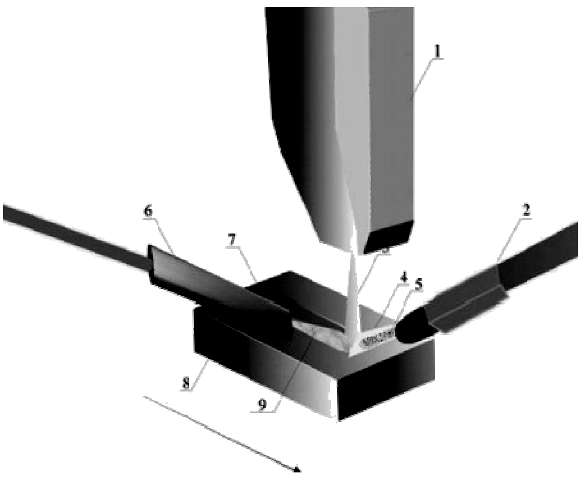


Fig. 1. Laser treatment scheme for casting magnesium alloys: 1 - laser head, 2 - transport gas cylinder and powder feed nozzle, 3 - beam laser, 4 - gas, 5 - powder, 6 - powder feed nozzle, 7 - remelting zone, 8 - base material, 9 - protective gas

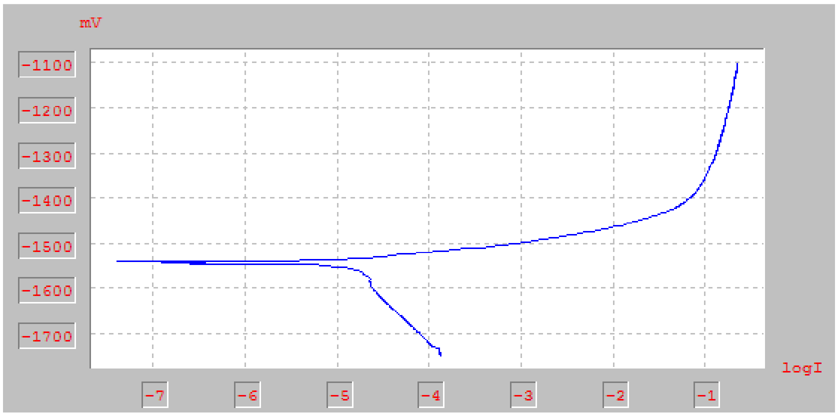
3. Description of achieved results

For the reason to determine the influence of heat treatment and laser treatment using silicon carbide particles as well the influence of laser working parameters, particularly the laser power on corrosion resistance of the investigated Mg-Al-Zn alloys, corrosion tests were performed using the electrochemical potentiodynamic method in 3% NaCl aqueous solution. Based on the results, the corrosion degradation of the surface of the investigated materials was determined in dependence on the aluminium mass content, the heat treatment type, the applied carbide powder and use of laser power.

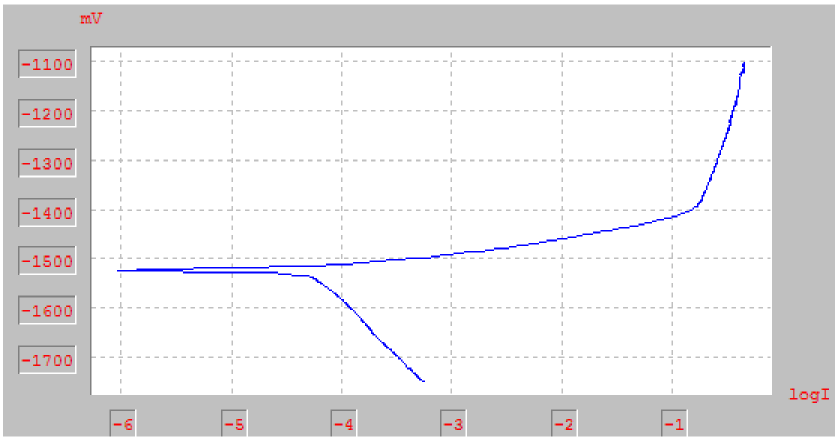
As a result of this study, polarization curves were obtained (current density dependence of the changed potential) for the analyzed samples (Fig. 2). Polarization curves of the tested materials are composed of anode branches, which correspond to the corrosion reactions, and cathodic branches, corresponding to the hydrogen depolarization.

On the basis of polarization curves, using the extrapolation Tefel method near the corrosion potential, the quantitative data describing the phenomenon of electrochemical corrosion of the material was determined: corrosion potential values E_{corr} (mV), corrosion current density i_{corr} (mA/cm^2) and the polarization resistance Rp (Ω.cm^2) (Table 4, 5). Polarization curves and corrosion current density values indicate the speed of dissolution of test surface. Analysis of the polarization curves, corrosion potential, corrosion current density – corrosion rate and polarization resistance confirms that the best corrosion resistance in as cast state is achieved for the sample with 3% aluminum content - AZ31, with a corrosion resistance potential of -1573.67 mV, with a corrosion resistance of 1.29 kΩ.cm^2, and a corrosion current density of 3.43 μA/cm^2. During the anodic scan for the AZ31 alloy, the corrosion current density i_{corr} is lower in most cases (except for the state after aging) compared to the alloys with higher concentrations of Al, which shows the good corrosion resistance of this material. A slight decrease of the corrosion parameters for samples of AZ31 alloys is also characteristic for the AZ61 alloy. However, a clear deterioration of the corrosion resistance, when the polarization resistance decreases with increasing current density was found in case of the AZ12 and AZ91 alloys (Table 4).

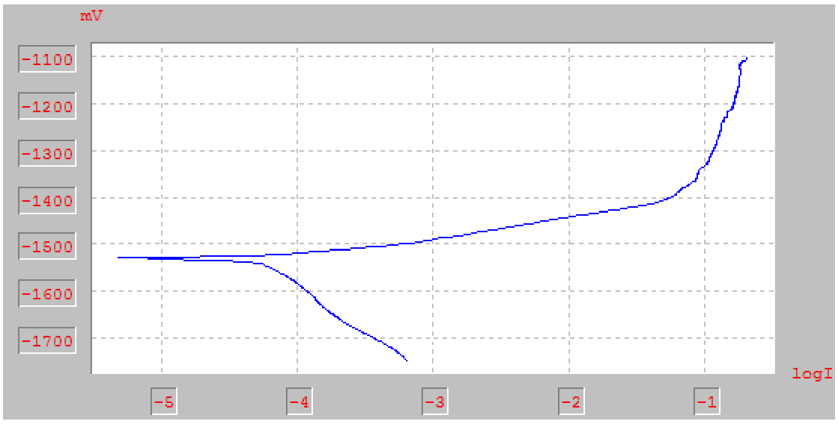
Similar investigations of the corrosion resistance of magnesium cast alloys were performed after heat treatment. The lowest corrosion current density i_{kor}, and so the smallest anodic dissolution of cast magnesium alloy with varying concentrations of aluminum and related best corrosion resistance after heat treatment reveals the AZ61 and AZ31 alloys - respectively 1.30 and 1.41 (μA/cm^2) (Table 4). However the lowest resistance against the effects of the aggressive agent, which is related to the damage propagation both inside and on the material surface show of the AZ12 alloys (Table 4).



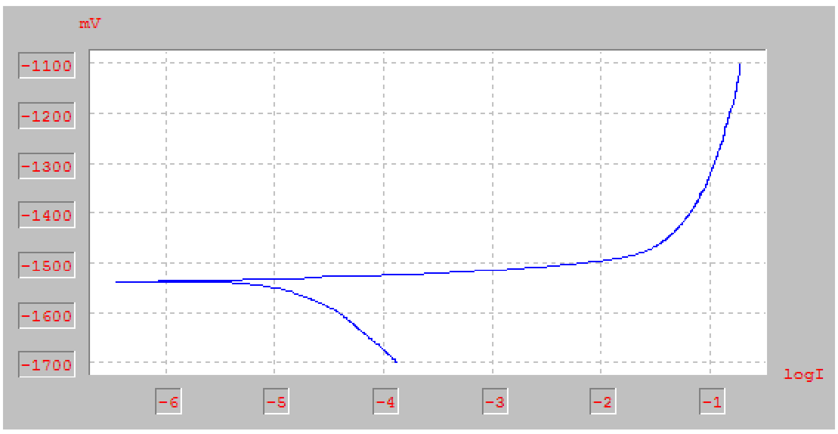
a) in as-cast state



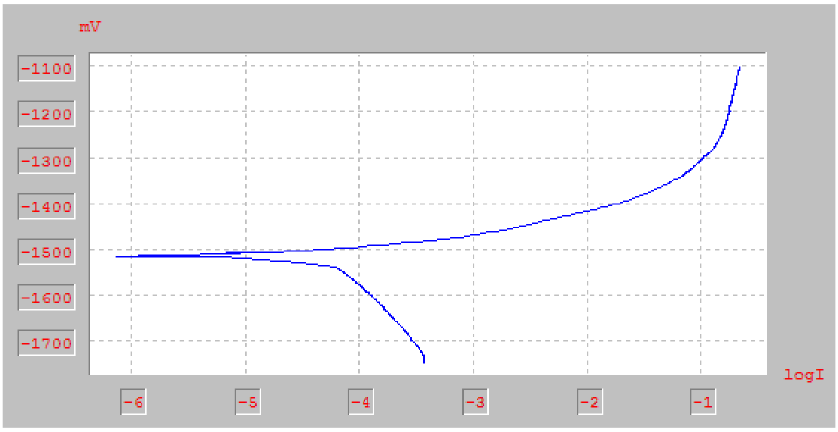
b) after solution heat treatment with cooling in the water



c) after solution heat treatment with cooling in the air



d) after solution heat treatment with cooling in the furnace



e) after aging treatment

Fig. 2. Polarization curves of the magnesium cast alloys AZ12

Table 4

The parameters measured during the corrosion tests for the magnesium alloys in as-cast state and after heat treatment

Investigated alloys	Sing the state of heat treatment	Corrosion potential E_{cor} (mV)	Polarisation resistance Rp (kΩ.cm^2)	Corrosion current density i_{cor} (μA/cm^2)
AZ31	0	-1573.67	1.29	3.43
	1	-1560.02	2.42	1.83
	2	-1554.12	2.54	1.30
	3	-1586.77	1.25	4.00
	4	-1524.02	2.26	1.41
AZ61	0	-1621.20	0.83	4.59
	1	-1609.20	1.19	3.27
	2	-1586.80	1.56	3.09
	3	-1642.80	0.94	6.09
	4	-1555.20	3.4	1.30
AZ91	0	-1548.27	0.36	14.30
	1	-1561.10	0.29	17.40
	2	-1539.25	0.17	22.10
	3	-1577.72	0.16	23.80
	4	-1518,38	0.40	9.60
AZ12	0	-1551.65	0.40	13.75
	1	-1555.55	0.31	15.80
	2	-1537.35	0.27	18.90
	3	-1573.25	0.21	21.10
	4	-1522.55	1.13	8.00

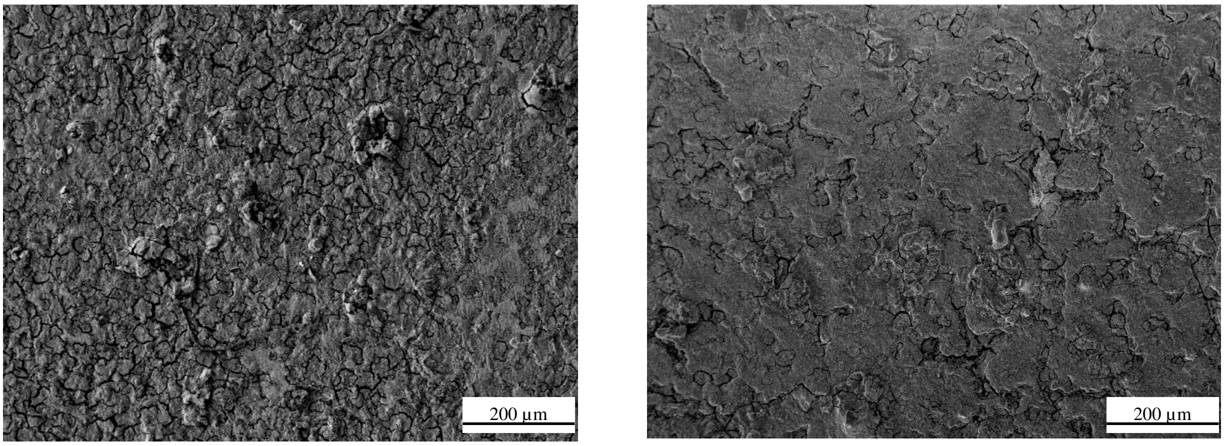
Table 5

The parameters measured during the corrosion tests for the magnesium alloys after alloying process with SiC powder

Investigated alloys	Laser power (kW)	Corrosion potential E_{corr} (mV)	Polarisation resistance Rp (kΩ.cm^2)	Corrosion current density i_{corr} (μA/cm^2)
AZ31	1.6	-1515	44.81	0.582
	2.0	-1524	341.43	0.091
AZ61	1.6	-1481	48.19	0.543
	2.0	-1435	222.48	0.141
AZ91	1.6	-1541	308.09	0.086
	2.0	-1420	192.25	0.135
AZ12	1.6	-1541	146.50	0.180
	2.0	-1462	165.74	0.157

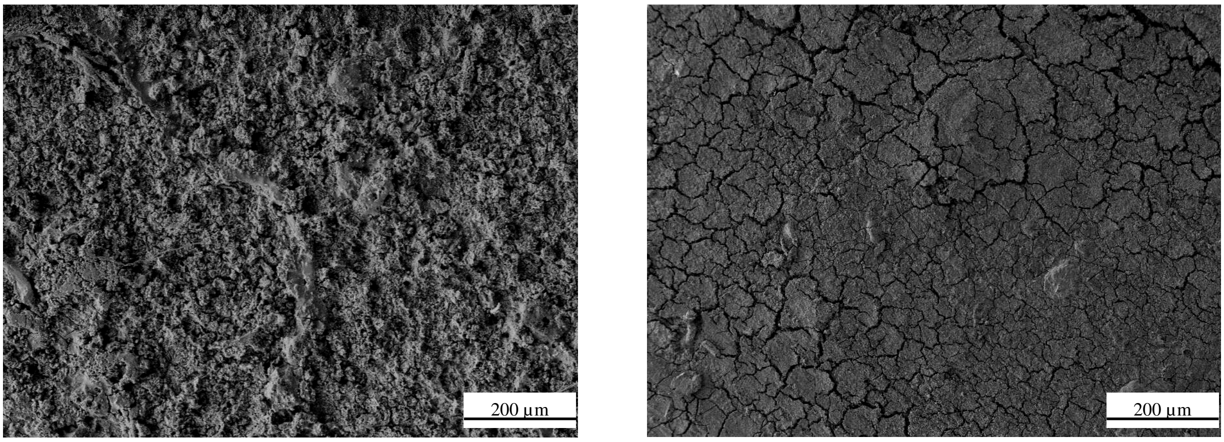
Analysis of the results obtained for alloys with 12, 9 and 6% aluminum concentration confirms the corrosion resistance increase of materials after precipitation hardening compared to cast alloys, as well as alloys after performed solution heat treatment. The lowest parameters describing the phenomenon of pitting corrosion in all analyzed cases are characteristic for samples after solution heat treatment and cooling with furnace (Table 4). For investigation of the corrosion processes after laser alloying with WC, TiC, Al_2O_3 and SiC powders the surface layer of the material after alloying with SiC was selected for the reason of their proper quality and morphology (shape and continuity of the surface).

Analysis of the polarization curves (corrosion potential, corrosion current density and corrosion resistance) confirms that the best corrosion resistance after alloying with SiC powder reveals samples with a concentration of 3% aluminum - AZ31 with the corrosion potential of -1524 mV, palarization resistance of 3.41 kΩcm^2 and the current density of 0.091 μA/cm^2. During the anodic scan for most types of tested laser alloyed surfaces - with the exception of the alloy AZ91 - the highest value of polarization resistance, and therefore the best corrosion resistance was obtained for SiC alloyed materials with a laser power of 2.0 kW (Table 5), which is directly connected to the quality of the obtained remelted surface (homogeneously distributed particles in the whole remelting zone, a homogeny thickness and roughness, better than the roughness obtained for samples alloyed using lower laser power, i.e. 1.0 ÷ 1.6 kW). Surface morphology of the investigated samples after corrosion test performed before and after heat and laser treatment (Fig. 3, 4, 5) shows irregular shaped pinholes and numerous cracks in the surface layer of the material. The majority of the defects after heat treatment is present in case of solution heat treatment with furnace cooling and they are coming into existence in neighborhood to the occurred precipitations, what causes discontinuity of the surface and therefore a significant mass loss. The smallest visible surface layer destruction after heat treatment is characteristic for magnesium cast alloys after ageing (Figs. 3, 4). On the surface of the samples there are present also corrosion products, which builds compact conglomerates with characteristic needle shape formed in the majority of the cases inside of the pinholes (Fig. 5).



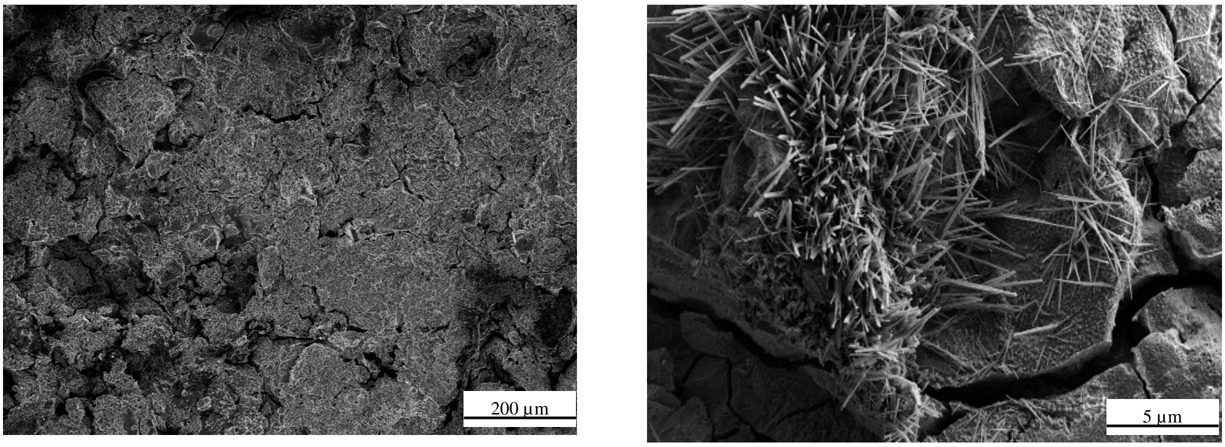
a) in as-cast state *b) after aging -after corrosion tests*

Fig. 3. Surface morphology of the AZ31 magnesium alloy



a) in as-cast state *b) after aging -after corrosion tests*

Fig. 4. Surface morphology of the AZ12 magnesium alloy



a) after solution heat treatment with cooling in the furnace *b) after solution heat treatment with cooling in the air*

Fig. 5. Surface morphology of the AZ91 magnesium alloy after corrosion tests

4. Conclusions

Analysis of the polarization curves, corrosion potential and current density and polarization resistance confirms that the best corrosion resistance in as cast state and also after heat and laser treatment is achieved for the sample with 3% aluminum content - AZ31. During the scan in anodic direction for most types of tested laser alloyed surfaces - with the exception of the alloy AZ91-the highest value of polarization resistance, and that fore the best corrosion resistance was obtained for SiC alloyed materials with a laser power of 2.0 kW, which is directly connected to the quality of the obtained remelted surface. Surface morphology of the investigated samples after corrosion test performed before and after heat and laser treatment show irregular shaped pinholes and numerous cracks in the surface layer of the material. The majority of the defects after heat treatment is present in case of solution heat treatment with furnace cooling and is coming into existence in neighborhood to the occurred precipitations, what causes discontinuity of the surface and that fore a significant mass loss.

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