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Corrosion properties of selected products made of alloy AZ91*

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The paper compares and evaluates corrosion resistance of supplied products made of the alloy AZ91 (castings of car wheels, cast plates and cold formed bars) on the basis of test made in condensation chamber with sulphur dioxide and electro-chemical potential-sweep method with use of water diluted solution of sulphate and chloride. Character of corrosion attack on all the samples was uneven, mainly pitting corrosion. Electro-chemical test did not find any significant differences between values of potentials of de-passivation and re-passivation of tested samples and products. Considerable differences were observed in morphology of corroded surface in relation with segregation and dissociation of cathodic phase γ ($Al_{12}Mg_{17}$).

1. INTRODUCTION

Magnesium alloys of the type AZ91 ($MgAl_9Zn_1$) with good machinability and castability have comparatively high values of specific strength properties. However, they have low corrosion resistance in aqueous environments containing chlorides, sulphates, etc. in comparison with other technically important materials.

Increase of contents of Al (2 up to 8%) in castings improves resistance to uniform corrosion, but at the same time resistance to corrosion cracking decreases [1]. Aluminium moreover increases detrimental effect of Fe, while Mn and Zn have the opposite effect. Alkaline environment supports growth of film and restricts corrosion, however in case of excessive thickness defects or cracks are formed on the interface $Mg(OH)_2/Mg$, which can act as spots of initiation of corrosion [2]. Corrosion of Mg is manifested by specific processes, such as negative differential phenomenon [3], corrosive creep [4]. Creep rate in corrosion environment increases with Al contents, and at the same time creep service life decreases in the order AS21 ($MgAl_2Si_1$), AM50 ($MgAl_5Mn$), AZ91D [4].

Electrochemical polarisation methods are often used for investigation of corrosion behaviour of Mg alloys of the type AZ91. They can be used also at forming of protective anodic or conversion layers in certain environments (chromates, phosphates, fluorides). For example tests of penetration of foil with thickness of 1 mm made of alloy AZ91 in solutions 0.01; 0.1 and 1.0 M NaCl at potential of $-1.4V$ were performed within the frame of the work [2]. Mechanical-chemical effect for explanation of corrosion cracking of alloys AZ91, AM50

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and AZ31 was investigated with use of potentio-dynamic polarisation method and electrochemical impedance spectroscopy [5].

The paper issues from the works [6,7] and its objective is comparison and evaluation of corrosion resistance of selected products (cars car wheels, cast plate, formed bar) made of the alloy AZ91 on the basis of exposition test in condensation chamber and potentio-dynamic polarisation method.

2. EXPERIMENTAL PROCEDURES AND RESULTS

2.1 Selected samples made of alloy AZ91

For accelerated corrosion tests we used samples taken from the cast car wheel (hereinafter marked as C, D, with dimensions 150x25x10mm), samples made from the cast plate (BTZ, TZT4, 150x20x10mm) and also samples (ϕ 6x160mm) taken from the round cold formed bar with the following mechanical properties: $R_m=340$ MPa, $R_{p0.2}=190$ MPa, $A_5=15\%$. Chemical composition of samples is given in the Table 1. Sample of the plate BTZ was tested in initial state as supplied without thermal treatment. The samples marked C, D and TZT4 underwent basic thermal treatment T4: 375°C/3h + 415°C/20h/air.

Table 1. Chemical composition of tested products (in weight %)

sample	Al	Zn	Mn	Si	Cu	Fe	Zr	Be
car wheel C, D	9.15	0.6	0.24	0.029	0.01	0.014	-	0.0001
plate BTZ, TZT4	8.25	0.63	0.22	0.035	0.003	0.014	0.002	0.0002
bar I, II	8.7	0.7	0.13	-	-	0.005	-	-

2.2. Methodology of corrosion testing

Accelerated test in condensation chamber with addition of SO₂ was made in accordance with the standard [8] in 24-hour cycles. In the first part of the cycle the samples were exposed to corrosive environment of the chamber at temperature of 40±2°C and relative humidity of 100% during 8 hours with addition of SO₂ in the form of H₂SO₃. In the second part of the cycle the samples were situated in laboratory environment at the tem of 22±2°C for 16 hours. The samples were ground before the tests with fine SiC paper, cleaned and weighed on analytical scales. After certain number of cycles (1, 3, 7, 9, 16, 30) dried samples were visually inspected and weighed again. After completion of the test corrosion products were removed from the samples according to the standard [9] and the samples were assessed in respect with the standard [10] from the viewpoint of pitting corrosion. Scope and character of corrosion attack was evaluated also on the basis of gravimetric method, visual inspection with use of digital colour macro-photography and metallographical inspection.

Potentio-dynamic polarisation measurement was performed in accordance with the [3, 11] with use of potentiostat (PGP201) and computer, with use of special corrosion cell and aerated water solutions of 0.05M Na₂SO₄ and 0.1 M NaCl under normal temperature. After measurement of initial corrosion potential (E_{cor}) polarisation tests were started at potential of -1800 mV (to saturated calomel electrode SCE) with polarisation rate of 1mV/s up to reversible potential (E_v) at current density of 5.0 mA/cm² and then back to the final potential at -10µA/cm². On the basis of the measured polarisation curves there were determined values of de-passivation potential E_d (forming of stable pitting), and also values of re-passivation potential E_r (for 10µA/cm², stopping of pitting) and also potential $E_{\text{cor}}=E(i=0)$ at $dE/di > 0$.

Every polarisation measurement was repeated at the same place twice and after completion of test the exposed surface was inspected and photographed with use of microscope.

3. DESCRIPTION AND DISCUSSION OF RESULTS

On the basis of measured corrosion weight gains or losses in dependence on time there were plotted the corresponding graphical dependencies for comparison of corrosion resistance of tested samples and products made of the given alloy of the type AZ91 (Fig.1). Average value of measured proportions of weight gains to losses was 5.10 (from 4.7 to 5.5), which corresponds to formation of sulphate $MgSO_4$ (relation of molar masses $MgSO_4: Mg = 4.95$) or hydrated magnesium sulphite.

Higher changes of mass were recorded in formed bars in comparison with castings, the differences between which are practically insignificant (random). Derived corrosion rates are also approx. twice higher in formed bars (for the time interval from 50 to 300 hours), however, in longer time periods these corrosion rates got equal for both groups of samples.

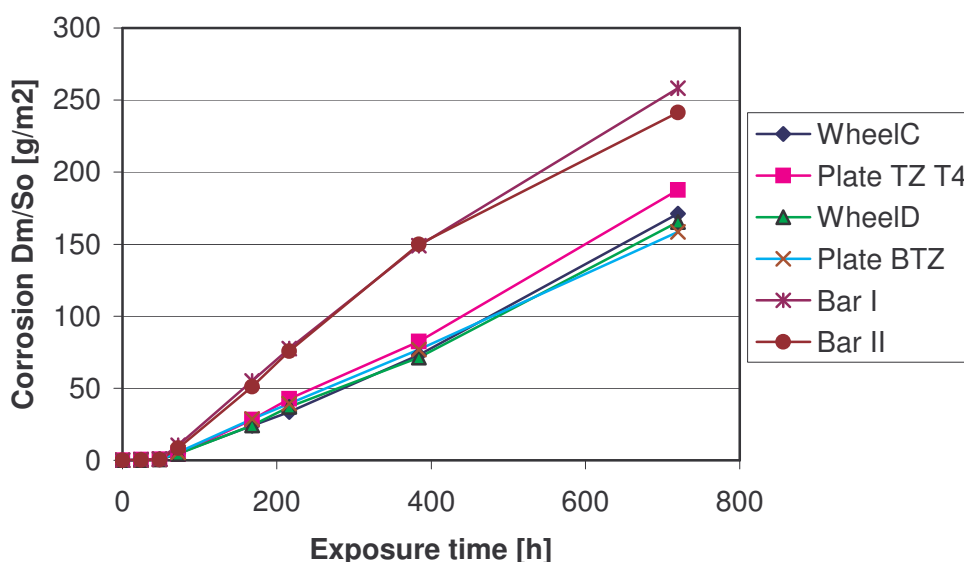


Fig. 1. Changes of mass in dependence on exposure time in condensation chamber with addition of SO_2

Corrosion products were light grey with low adhesiveness. Corrosion attack was higher on side and bottom parts, where corrosion products started to fall off by the end of exposure.

Corrosion of samples in condensation with SO_2 (simulation of polluted industrial atmosphere) was in majority of samples of uneven character with average depths of corrosion attack given in the Table 2, from which it is obvious, that attack was bigger on wheels.

Size of surface of corrosion pits was also the biggest (2 mm^2) in samples of the wheel C and D, and also in bars. The smallest surfaces (0.5 mm^2) were on the contrary found on plates. Density of pitting corrosion attack was on all samples approx. 50 points per cm^2 ($5 \cdot 10^5 \text{ m}^{-2}$, No. 5) according to the standard [10].

Tab. 2. Average depth (in mm, out of 10 the most deepest observed) points of corrosion

place	Wheel C	Wheel D	Plate BTZ	Plate TZT4	Bar I	Bar II
Top	0.333	0.233	0.133	0.093	0.050	0.061
Bottom	0.367	0.467	0.117	0.133	0.103	0.125
Side jacket	0.402	1.27	0.200	0.250		

Structures of products made of the alloy AZ91 and profile of corrosion attack of individual samples showed, that corrosion attacks preferentially grains of solid solution δ and is limited to grain boundaries, where electro-chemically more stable phase γ has precipitated.

Typical potentiodynamic polarisation curves for 0.05 M Na_2SO_4 are documented in Fig. 2 and values of potentials of de-passivation E_d and re-passivation E_r , as well as values of corrosion potentials (E_{cor}) are for comparison represented in bar graphs, see Fig. 3 for 0.05 M Na_2SO_4 and Fig. 4 for 0.1 M NaCl . The following is generally true: the higher the values E_d and E_r and differences $E_d - E_{\text{cor}}$, or smaller $E_d - E_r$, the higher resistance to pitting or crevice corrosion. The values E_d are subject to composition and cleanness of the surface, related to its preparation or modification, quality of passive layer, etc. That's why they show higher scatter in comparison with the values E_r , related more to composition of the alloy in volume (in the area of material dissolution) and solution in points of corrosion or in pits. At the same time the values E_r can delimit area for cathodic protection ($E_{\text{ochr}} < E_r$) or they can be assessed as ultimate threshold stress for propagation of point corrosion. During repeated measurement at the same place influence of surface is eliminated at easier re-initiation at points of corrosion, so the values E_d can relate better with composition and structure of material itself.

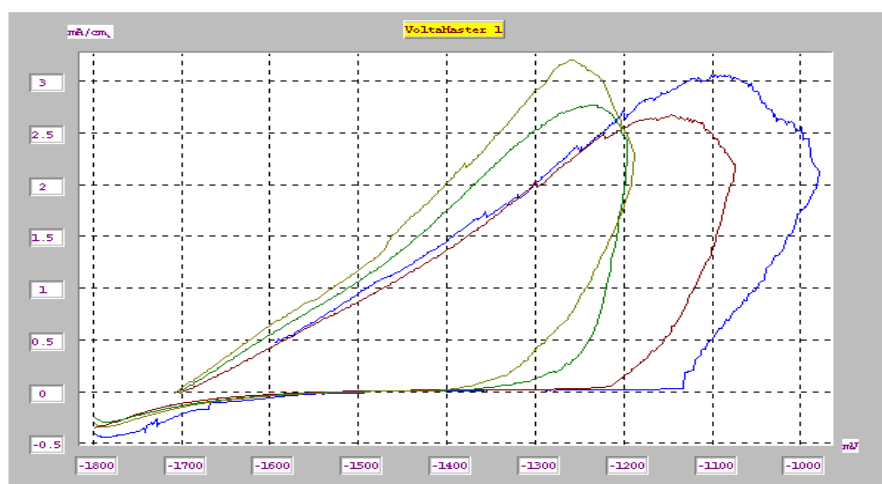


Fig. 2. Cyclic polarisation curves of selected samples made of the alloy AZ91 (ordered by E_d : wheel C, wheel D, plate BTZ, plate TZT4) in environment of 0.05 M Na_2SO_4 .

Comparison of values of the mentioned potentials of the samples tested in the same environment (0.05 M Na_2SO_4 or 0.1 M NaCl) did not find any significant differences. In sulphate solution plates had at the average higher values E_d and $E_d - E_r$ as compared with wheels, while values E_r were approximately at the same level. In sulphate solution the values E_r were slightly lower (at the average by 60 mV) in comparison with E_r in chloride solution. The values of de-passivation potentials measured in chloride environment were generally lower.

It is difficult to compare the order of resistance determined in the chamber with addition of SO_2 and formation of sulphates according to corrosion kinetics with the order of resistance according to the measured values of potentials in sulphate environment, i.e. according to thermo-dynamic viewpoint.

Significant differences appeared in morphology of attack of surface subject to material structure. In sulphate solution there were formed white-grey shallow pits, in chloride solution there were formed grey-black corrosion stains created by connection of points of corrosion or by zones of points of corrosion in direction of grinding.

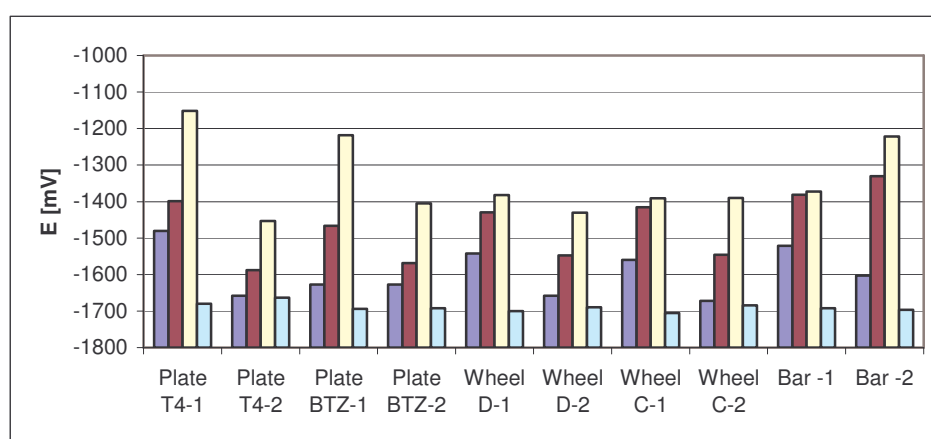


Fig. 3. Measured values of corrosion potential of the samples made of the alloy AZ91 in solution of 0.05M Na_2SO_4 .

There are progressively shown the values E_{cor} , E_{cor} , E_{d} and E_{r} and sequence of measurement (1,2) for each sample

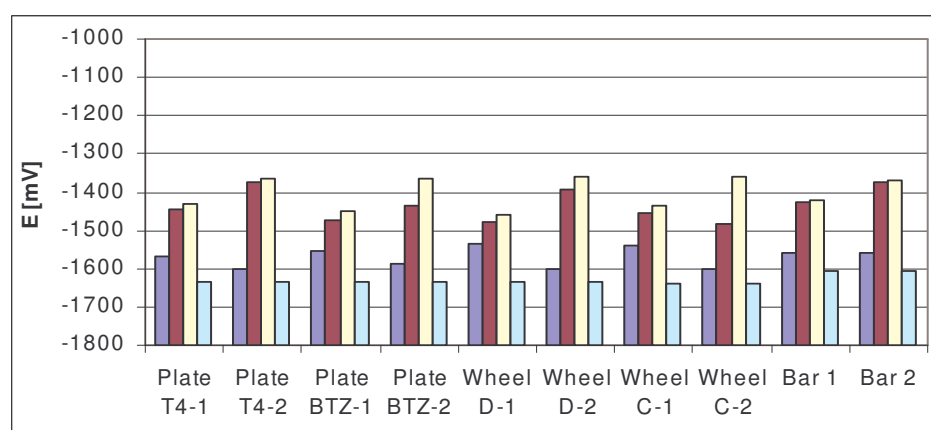


Fig. 4. Measured values of corrosion potentials in the order E_{cor} , E_{cor} , E_{d} and E_{r} for the Samples made of the alloy AZ91 in solution of 0.1M NaCl .

4. CONCLUSIONS

On the basis of testing and comparison of corrosion resistance of selected products made of the alloy AZ91 in condensation chamber with addition of sulphur dioxide and potentiodynamic polarisation method it is possible to formulate the following conclusions:

- In condensation chamber according to the measured changes of weight there occurred uneven corrosion attack, which was in case of cold formed bars twice higher in comparison with castings (car wheels and plates), however, corrosion pits were deeper (at the average 2-4x) on cast wheels in comparison with bars or plates. Metallographic investigation has confirmed point corrosion, penetrating more easily inside the grains with homogenous solid solution (δ).

- Electro-chemical tests in diluted neutral solutions of sulphate and chloride (0.05M Na₂SO₄ and 0.1M NaCl) have ascertained certain differences in values of corrosion potentials and potentials of de-passivation, however, only minimum differences in values of re-passivation potential were established at comparison of resistance of products. There were observed bigger differences in morphology of exposed surface, reflecting structural states of material.

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