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CORROSION BEHAVIOUR OF THE AS-CAST AND HEAT-TREATED ZA27 ALLOY

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Abstract: *Corrosion behaviour of the as-cast and heat-treated ZA27 alloy was examined. The alloy was prepared by conventional melting and casting route and then thermally processed by applying T4 heat treatment regime (solutionizing at 370 °C for 3 hours followed by water quenching and natural aging). Corrosion rate of the as-cast and heat-treated ZA27 alloy was determined in 3.5 wt. % NaCl solution through immersion test using both weight loss method and polarization resistance measurements. It was shown that applied thermal treatment resulted in increased ductility of the heat-treatedalloy and had a small beneficial effect on the corrosion resistance of ZA27 alloy.*

Keywords: *ZA27 alloy, corrosion, heat treatment, microstructure, immersion test, polarization resistance*

1. INTRODUCTION

ZA27 alloy belongs to a group of zinc alloys with increased content of aluminium (ZA alloys) which have been used in technological applications for several decades. ZA27 alloy with a nominal aluminium content of 27 wt.% is distinguished with highest strength and lowest density of all ZA alloys [1]. The alloy has been shown to possess favorable combination of physical, mechanical and technological characteristics (low melting point, high strength, good castability, easy machinability) as well as excellent bearing capability, wear resistance and high corrosion resistance [1, 2]. ZA27 alloy has been used for pressure die castings and gravity castings wherever very high strength is required as well as in bearings and bushing applications as a replacement for bronze bearings because of its lower cost and equivalent or superior bearing performances [3].

During past two decades a few different approaches have been taken in order to improve physical, mechanical, tribological and corrosion properties of ZA27 alloy at room temperature: (a) addition of elements like Ni, Ti and Sr [4], (b) using different heat treatment regimes [4-7] and termomechanical treatments [8] (c) improvements in the alloy manufacturing techniques as is the use of thixoforming [9] or unidirectional solidification [10] and (d) production of composites with Al_2O_3, SiC and graphite particles [11-13].

Mechanical properties of ZA27 alloy can be influenced by thermal processing. It was reported [7] that ductility and structural stability of this alloy were markedly improved by applying T4 heat treatment. It was also shown that T4 regime had a beneficial effect on the tribological characteristics of the commercial ZA27 alloy [6], although it resulted in a minor reduction in hardness and tensile strength. In addition, T4 heat treatment is relatively cheap and easy to perform, thus providing time and energy savings.

Upon exposure to the corrosive environment many thermally processed alloys are subject to drastic changes. Possible effects of used heat treatments on the alloy performance in a corrosive medium are essential for a complete understanding of the alloy corrosion behavior [14].

Corrosion characteristics of the as-cast ZA27 alloy have been previously studied and reported in

[15, 16]. Aluminium presence in the alloy has a favourable effect on its corrosion behaviour [15, 16]. The alloy exibits high corrosion resistance in natural atmospheres and natural waters, soil etc. because of zinc ability to form a protective layer of corrosion products at the surface [14, 15], consisting mainly of zinc oxide, zinc hydroxide, simonkolleite or their mixtures. The most common form of corrosion encountered by ZA27 alloy in a variety of natural environments is general (uniform) corrosion [15]. This enables evaluation of the alloy mass loss per unit surface area that is evaluation of corrosion rate. Besides the weight loss method electrochemical polarization measurements have been frequently used in corrosion studies to assess the rate of uniform corrosion [14, 17]. Polarization resistance measurements provide the value of polarization resistance R_p enabling calculation of corrosion current (corrosion rate) according to the well-known Stern-Geary equation [18]. Appropriate values of anodic and cathodic Tafel slope have to be determined in separate experiments [14, 17]. However, it was shown that results of electrochemical measurements were not always in agreement with direct weight loss measurements [19] and weight loss method has been frequently used to confirm the results of electrochemical polarization tests.

Thermally processed (T4) ZA27 alloy is characterized by a good combination of tribological and mechanical properties [6] with ductility twice higher than the as-cast alloy [7] and can be used in producing machine parts where high ductility is required. However, there have been no results reported so far concerning the effect of T4 heat treatment on the corrosion performance of the ZA27 casting alloy. In view of the above, the aim of this work was to examine the influence of T4 heat treatment on the corrosion behaviour of ZA27 alloy. An attempt was also made to establish the correlation between microstructural parameters and corrosion properties of both as-cast and heat treated ZA27 alloy.

Within this work corrosion studies were carried out in neutral chloride solutions open to atmosphere because chloride ion is present in many corrosion environments and because of great influence of dissolved oxygen on the corrosion mechanism and kinetics of zinc and zinc alloys [20].

2. EXPERIMENTAL

2.1 Materials

Experiments were performed using zinc-aluminium alloy ZA27. Chemical composition of the alloy is in accordance with EN standard [21]. The alloy was prepared by conventional melting and casting route in Materials Science Laboratory in ″Vinca″ Institute. The alloy casting was performed at 570 °C in the steel mold preheated up to 100 °C. Prismatic castings (20 x 30 x 120 mm) were machine cut and samples for corrosion studies (20 x 30 x 6 mm) and microstructural examinations (4 mm in diameter and 8 mm in height) were obtained. The samples were subjected to heat treatment (T4 regime: solutionizing at 370 ˚C for 3 hours followed by water quenching and natural aging).

2.2 Corrosion tests

Immersion test and polarization resistance measurements were used to access corrosion behaviour of ZA27 alloy as-cast and heat treated. For both ZA27 alloys corrosion rates were determined and expressed as the corrosion penetration rate. All tests were performed in an approximately neutral NaCl solution (pH = 6.7) opened to atmospheric air and with same chloride concentration as in natural seawater (3.5 wt.% NaCl).

In immersion test samples of as-cast and heat treated ZA27 alloy were exposed in stagnant 3.5 wt. % NaCl solution at room temperature. Samples preparation and exposure were performed in accordance with ASTM G31 [22]. After dry ground samples were wet ground using progressively finer abrasive SiC paper (240, 360, 600 and 800 grit), washed in warm running water, rinsed with acetone and dried in the air. After weighing, the samples (in triplicate) were vertically exposed in the test solution. After 30 day exposure the samples were withdrawn from the test solution and rinsed with distilled water. Corrosion products were removed from the samples by chemical cleaning according to ASTM G1 [23]. The samples were then reweighed to determine their mass loss during exposure to NaCl solution.

Measurements of polarization resistance were carried out at room temperature using a cell for flat specimens with a contact area of 1 cm^2 between working electrode and electrolyte (3.5 wt. % NaCl, $pH = 6.7$). Platinum electrode was used as a counter electrode while saturated calomel electrode (SCE) was a reference electrode. Working electrode (as-cast and heat treated ZA27 alloy, respectively) was washed with acetone and distilled water before electrochemical polarization test. The test was conducted using Gamry Reference 600 Potentiostat and three measurements were performed for each working electrode, with good reproducibility. Prior to each polarization test, the electrode was permitted to stabilise for approximately 30 to 60 min in the test solution to make sure that steady state has been reached. The working electrode was then cathodically polarised from its open circuit potential *OCP* by 15 mV, which was immediately followed by a cathodic sweep over a 30 mV range at the 0.2 mV/s sweep rate.

2.3 Microstructural examination

Surface morphology and microstructure of the as-cast and heat treated samples of ZA27 alloy were examined before immersion test and after 30 day exposure in the test solution. The samples were analyzed by optical microscopy (OM) using Carl Zeiss optical microscope.

The samples for microstructural studies were prepared by wet grinding on progressively finer abrasive paper (240, 360, 600 and 800 grit SiC), with subsequent polishing with diamond paste (up to 2 µm particles size) on polishing cloth. Before their exposure to test solution (3.5 wt. % NaCl) the samples were rinsed with acetone and dried in the air. After exposure, the samples were wet ground and polished. Etching in 9 % v/v nitric acid was applied to reveal the samples microstructure.

3. RESULTS AND DISCUSSION

3.1 Corrosion rate

Immersion test. After 30 day exposure to quiescent NaCl solution surfaces of the test samples were covered with white powdered corrosion products. Corrosion has occured uniformly over the surface of exposed as-cast and heat treated samples. Corrosion products were removed by chemical cleaning and the samples were then reweighed to determine their mass loss during exposure to NaCl solution. On the basis of the samples mass loss the average penetration rate of corrosion (corrosion rate) was calculated using the following expression [23]:

$$C_R = \frac{K \cdot W}{A \cdot T \cdot D} \tag{1}$$

where C_R is corrosion rate (mm/year), K is a constant [22], W is sample mass loss (g), A is sample area (cm^2), T is time of exposure (hours) and D is density of ZA27 alloy (g/cm^3).

Calculated values of corrosion rate were 0.118 mm/year for the as-cast and 0.095 mm/year for the heat treated ZA27 alloy.

Polarization resistance measurements. Polarization curves in a small potential range near to *OCP* were obtained in the electrochemical polarization test for both as-cast and heat treated ZA27 alloy. Polarization resistance R_p was determined from the slope of experimental curve ($\mathrm{d}E/\mathrm{d}j$) at corrosion potential E_{corr} (Fig. 1a, b).

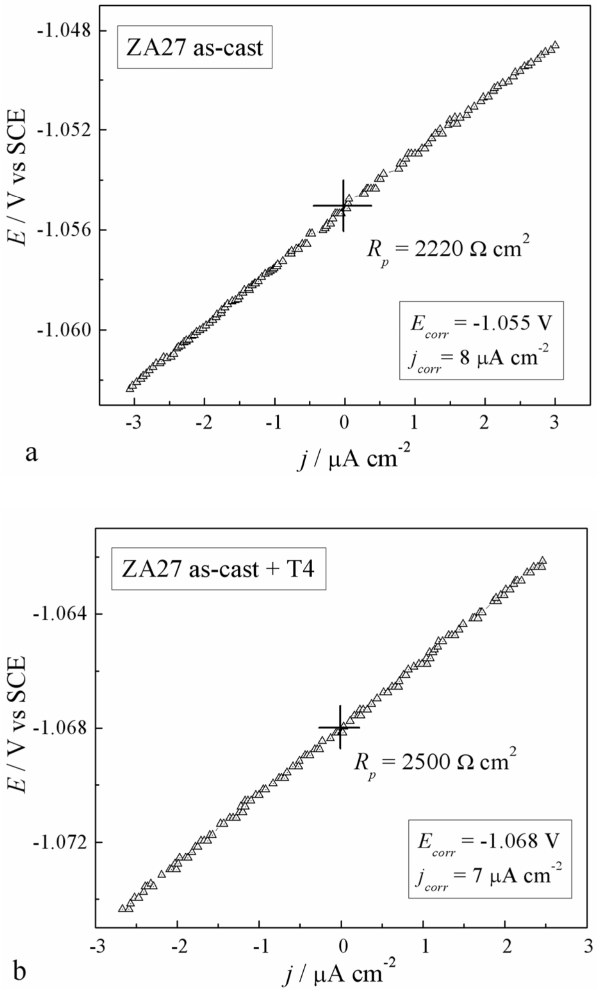

Figure 1. $E-j$ curves in 3.5 wt.% NaCl. (a) ZA27 alloy as-cast, (b) ZA27 alloy heat treated.

It can be seen that applied heat treatment resulted in increased value of R_p. Polarization resistance can be converted to corrosion current density j_{corr} using the Stern-Geary equation [18]:

$$j_{corr} = \frac{B}{R_p} \tag{2}$$

where B is a parameter dependent on the values of anodic b_a and cathodic Tafel slope b_c:

$$B = \frac{b_a \cdot b_c}{2.303 \cdot (b_a + b_c)} \tag{3}$$

Accordingly

$$j_{corr} = \frac{b_a \cdot b_c}{2.303 \cdot (b_a + b_c) \cdot R_p} \tag{4}$$

This expression was derived on the assumption that both anodic and cathodic reactions were charge-transfer controlled [14]. For a process that is controlled by diffusion of the cathode reactant and in which the anodic process is under activation control the modified Stern-Geary equation applies [14]:

$$j_{corr} = \frac{b_a}{2.303 \cdot R_p} \tag{5}$$

It has been recently reported [24] that corrosion of ZA27 alloy in chloride solutions takes place with charge-transfer controlled anodic reaction (alloy dissolution, with anodic Tafel slope b_a = 40 mV/dec), while cathodic reaction is under diffusion control of oxygen reduction. The value of anodic Tafel slope (b_a = 40 mV/dec) corresponds closely to values reported in literature for anodic dissolution of zinc [25]. Low solubility of oxygen (about 10^{-3} mol/dm^3) [14] in the test solution limits the transport of oxygen to the electrode surface and the cathodic reaction is under dominant diffusion control of oxygen reduction. When the reaction rate is entirely controlled by the rate of mass transport it no longer depends on potential [17] and the value of cathodic Tafel slope $b_c \rightarrow \infty$. Accordingly, the Eq. (5) was used to calculate corrosion current density. Calculated values were 8 μA/cm^2 for the as-cast and 7 μA/cm^2 for the heat treated ZA27 alloy.

Values of j_{corr} obtained on the basis of polarization resistance measurements (section 3.1) were converted into penetration rate C_R. Corrosion current density j_{corr} (μA/cm^2) and corrosion rate C_R (mm/year) are related by the following equation [23]:

$$C_R = K_i \cdot \frac{j_{corr}}{D} \cdot E_W \tag{6}$$

where K_i is a constant, E_W is equivalent weight of ZA27 alloy and D is as in Eq. (1). Calculated values of penetration rate were 0.099 mm/year for the as-cast alloy and 0.087 mm/year for heat treated ZA27 alloy. These results as well as the results of immersion test indicate to somewhat lower value of corrosion rate of heat treated ZA27 alloy in comparison to the as-cast alloy which means that applied heat treatment resulted in increased corrosion stability of ZA27 alloy. In addition, results of electrochemical measurements are in a very good agreement with results of gravimetric measurements.

Low values of corrosion rate obtained for as-cast and heat treated ZA27 alloy indicate to high corrosion resistance of both ZA27 alloys in neutral chloride solutions open to atmospheric air.

3.2 Microstructures

Corrosion behaviour of ZA27 alloy is determined by the alloy microstructure that is by chemical composition and distribution of the alloy phases [10, 19].

General surface appearance of the as-cast alloy is presented in Fig. 2a. Inclusions can be noticed in the alloy sample while porosity was not observed at this level of examination. The alloy was casted in metal mold (section 2.1) and hence subjected to rapid cooling. Solidification of the alloy in these conditions resulted in the alloy with dendritic microstructure as can be seen in Fig. 2b.

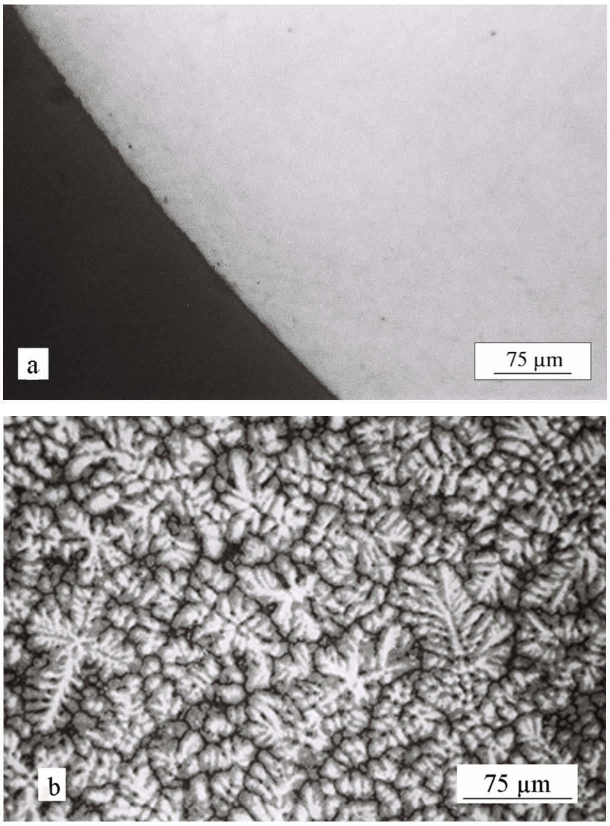

Figure 2. Microstructure of ZA27 alloy as-cast. (a) OM, polished, (b) OM, etched

Developed dendrites are complex (Fig. 2b), consisting of a core (α phase) and a periphery (a mixture of α phase and hexagonal η phase). The η phase is located into interdendritic regions. It was shown by SEM/EDS analysis [24] that dendritic cores are rich in aluminium; interdendritic phase is rich in zinc, while the composition of dendritic periphery is approximately equal to the chemical composition of ZA27 alloy. The SEM/EDS analysis has also indicated presence of intermetallic compound $CuZn_4$ (ε-phase) in interdendritic regions. It was reported that presence of ε phase had a beneficial effect on mechanical and wear properties of ZA27 alloy, particularly after certain heat treatment regimes [6].

The effect of corrosion on the microstructure of the as-cast sample after 30 days exposure in the test solution is shown in Fig. 3.

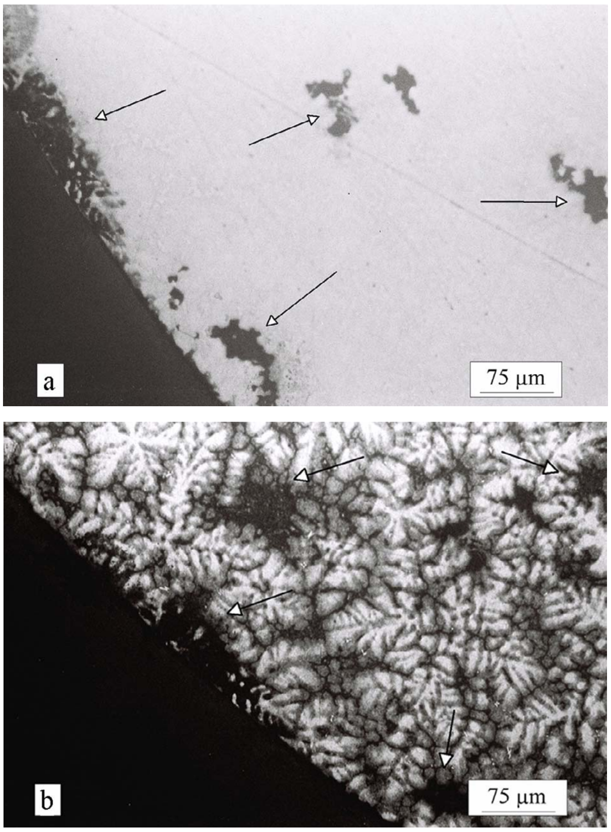

Figure 3. Microstructure of ZA27 alloy as-cast after 30 day exposure in 3.5 wt.% NaCl. (a) OM, polished, b) OM, etched.

It can be seen that corrosion has started on the edge of the sample and around inclusions (Fig. 3a). It was noticed [25] that corrosion of zinc and zinc alloys in salt solutions usually started at places where defects (scratches) or impurities were present. Corrosion process around inclusions in the as-cast sample mainly takes place laterally over the sample surface, which can be also seen on the etched sample (Fig. 3b). Destruction of η phase and $\alpha + \eta$ phase mixture regions has occured during corrosion process (Fig. 3b).

The T4 heat treatment that was applied within this work differs from the heat treatment regime recommended by standard [21] where furnace cooling instead of water quenching has been prescribed. It was shown earlier [7] that structure coarsening and appearance of T' phase ($Al_4Cu_3Zn_2$) took place during furnace cooling of ZA27 alloy. The T' phase is brittle and has a bad influence on ductility of ZA27 alloy. By using T4 regime within this work the appearance of T' phase in the heat treated samples was avoided which resulted in increased ductility of heat treated ZA27 alloy as was reported in [7].

Chemical composition of ZA27 alloy did not change after thermal processing while microstructure of heat treated ZA27 alloy remained dendritic although a significant morphological change took place as a result of T4 heat treatment. Solutionizing time (3 hours) was not enough for a complete homogenization i.e. for a complete destruction of dendritic cores and interdendritic η phase. The regions of $\alpha + \eta$ phase mixture were extended while dendritic cores (α phase region) and interdendritic regions (η phase) were reduced as can be seen in Fig.4b. A decrease in size of dendritic cores (α phase) and rounding off their edges happened, as well as the separation of individual dendritic cores into several smaller segments. Smaller dendritic cores were transformed into $\alpha + \eta$ phase mixture. During heating at 370 °C for 3 hours, there was an expansion of β phase at the expense of supersaturated α and η phases. After cooling, the newly created β phase was transformed into $\alpha + \eta$ phase mixture. According to the results presented in [7] the lattice parameter of α phase in the heat treated alloy was reduced comparing to the lattice parameter of α phase in the as-cast alloy as a consequence of zinc diffusion from the metastable α phase. Besides, it was shown by quantitative metallographic analysis [26] that volume fraction of $\alpha + \eta$ phase mixture was increased while both volume fractions of α and η phase were reduced in the heat treated ZA27 alloy in relation to the as-cast alloy. The effect of corrosion on the microstructure of heat treated ZA27 alloy is shown in Fig. 4a, b.

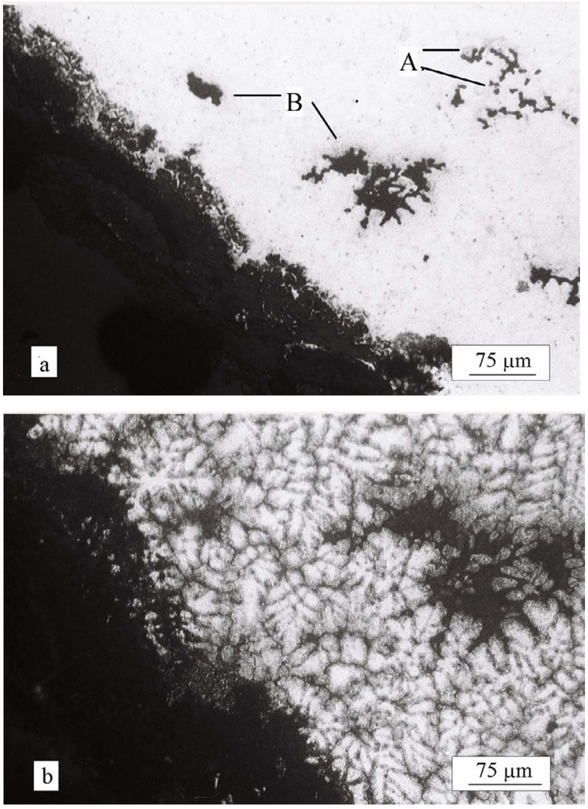

Figure 4. Microstructure of heat treated ZA27 alloy after 30 day exposure in 3.5 wt. % NaCl.
(a) OM, polished, (b) OM, etched.

Corrosion attack is observed on the sample edge (area of mechanical damage) and around some inclusions (Fig. 4a). As can be seen in Fig. 4b corrosion has occured in the region of $\alpha + \eta$ phase mixture and in the interdendritic η phase. Bright islands of α phase are surrounded by dark corrosion products. Appearance of microcracks in the heat treated samples was not observed after one month of exposure in corrosion environment which indicates increased ductility and thus, greater corrosion stability of heat treated ZA27 alloy.

Based on all results presented it could be concluded that applied heat treatment (T4) affected the microstructure of ZA27 alloy, as well as its corrosion resistance The alloy morphology was changed so that regions of $\alpha + \eta$ phase mixture were extended while dendritic cores (α phase region) and interdendritic regions (η phase) were reduced (Fig. 4b). The presence of microcracks was not observed in thermally processed ZA27 alloy neither before exposure to NaCl solution nor after 30 day exposure to this solution. This indicates an increase in ductility of the heat treated alloy. All these resulted in greater R_{p} value (Fig. 1b) and lower j_{corr} value of theat treated ZA27 alloy, namely in reduced corrosion rate. These results allow us to conclude that T4 heat treatment of ZA27 alloy has a small beneficial effect on its corrosion resistance which was the aim of this work.

4. CONCLUSIONS

On the basis of the results presented the following conclusions can be made:

1. Microstructure and corrosion resistance of ZA27 alloy was affected by T4 heat treatment.
2. Microstructure of heat treated ZA27 alloy remained dendritic after T4 heat treatment while corrosion process takes place through η phase and $\alpha + \eta$ phase mixture like in as-cast ZA27 alloy.
3. T4 heat treatment has shown small beneficial effect on the corrosion resistance of ZA27 alloy.
4. Low values of corrosion rate obtained for as-cast and heat treated ZA27 alloy ipoint out to high corrosion resistance of both ZA27 alloys in neutral chloride solutions open to atmospheric air.
5. Increased ductility and favourable corrosion properties of heat treated ZA27 alloy indicate its potential use in manufacturing machine parts like gears and worm gears.
6. Values of corrosion rate obtained in electrochemical polarization test are in accordance with results obtained by the weight loss method.

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