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Intergranular Corrosion of the as Cast Hypoeutectic Zinc-Aluminium Alloy

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Abstract

The paper presents the research results of the solenoid housing made of the Zn4Al1Cu alloy that was destroyed as a result of corrosion. Surface of the tested part showed macroscopically the features typical for white corrosion, and the resulting corrosion changes led to a disturbance of the alloy cohesion. The research performed have shown that the tested solenoid valve has intergranular corrosion as a reaction of the environment containing road salt. The corrosion was initiated in the areas of the alfa phase existence appearing in the eutectic areas which propagated over dendritic areas of the alloy. Initiation of the corrosion followed as a result of the galvanic effect of the alfa phase reach in aluminium showing higher electrochemical potential, in contact with the eta phase reach in zinc. The impact of the phase reach in lead present in the microstructure on the corrosion processes run was not found.

Keywords: Metallography, Corrosion resistance, Intergranular corrosion, Zinc alloy, ZnAl4Cu1 alloy

1. Introduction

Alloys of zinc and aluminium found wide application in the automotive and electronics industry and in the products of daily use. Due to their very good tribological properties they are applied, among others, as alternative for the traditional bearing alloys [1,2]. Particularly well they are suited for large loads appearing at low speeds of the bearing work [1]. The remaining favourable features of these materials are: relatively high static and fatigue strength as well as hardness, good castability, low melting temperature, and low material density [1,3,4]. The problem is the low structural stability over long time after casting [5]. Studies show that composition and structural modification can significantly improve the properties of the zinc alloys [2,5,6].

The materials are frequently tested in the context of their use as the coating material [3,7-13], but also the welding applications

[14]. Despite many advantages of the materials, the defects of machines and equipment are recorded caused by their corrosion wear [15].

The equilibrium microstructure of these alloys depends on content of aluminium. The ZnAl4Cu1 alloy belongs to hypoeutectic alloys in terms of microstructure. The alloy is characterised by low crystallisation temperature amounting to about 400 °C (Fig.1). After the eutectic transformation in temperature of 382 °C the alloy consists of dendritic precipitations of the η solid solution with the hexagonal close-packed (hcp) and the $(\eta+\gamma)$ eutectic. The first form of the eutectic is coarse-grained. The eutectoid transformation taking place in temperature of 275°C leads to disintegration of the γ phase into the $(\alpha+\eta)$ eutectoid, as a result of which the fragmentation of the eutectic components into $(\eta + \text{eutectoid } (\alpha+\eta))$ follows. Copper of content up to 1% by weight dissolves in the solid solution η , which causes increase in strength, hardness and resistance to general corrosion of the alloy

[16÷18]. In case of the higher content, because of low solubility in zinc, presence of copper in the alloy leads to precipitation in the alloy of the CuZn_4 (ϵ) phase creating also the ($\epsilon+\eta$) eutectic [17,18]. Addition of copper influences also lowering of eutectic transformation temperature and increasing the liquidus temperature [17,18]. Authors of paper [5] show that good results are obtained by partially replacement of copper with titanium.

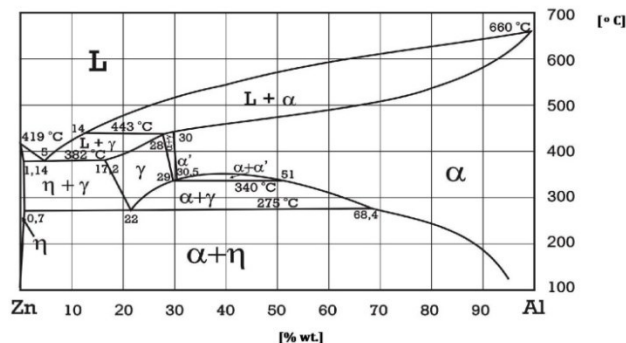


Fig. 1. The two-component phase diagram of the Zn-Al system [after 1,7,17]

The corrosion resistance of zinc alloys is close to aluminium alloys. In the normal atmospheric conditions the surface of zinc and its alloys are coated with a layer of protective products of corrosion, containing mainly zinc oxide ZnO , zinc hydroxide Zn(OH)_2 and basic zinc carbonates: $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$, $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2 \cdot \text{H}_2\text{O}$. They are creating within the range of pH from 7 to 12, instead, but the minimum of corrosion is observed within the range of pH from 9 to 11. In the remaining range of pH zinc is extensively corroded, as its surface is free of corrosion products or they are porous [1,19,20]. In presence of chlorine zinc creates highly hygroscopic products of corrosion ZnCl_2 . It was found that in case of Zn-Al alloys the dominating components of corrosion products in the environment containing chlorine ions are hydrozincite $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$ and simoncolleite $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ [11].

Besides the electrochemical nature of metals, the essential influence also have the microstructural factors, such as type of coexisting phases or the way of distribution. The microstructure of two phases leads to occurrence of galvanic micro cells favouring electrochemical corrosion and selective dissolution of the phase with lower electrochemical potential [3,7,21]. The research was undertaken on evaluation of the microstructure impact on mechanical properties and the corrosion resistance of the casting zinc alloys [22-24]. The relationship was found between morphology and the grain size and the corrosion resistance of a material [1,7,25-27]. Coarse dendritic macrostructure favours better corrosion resistance of the Zn-Al alloys [1].

The intergranular corrosion belongs to the most dangerous types of corrosion. It leads to lowering the plastic and strength properties of materials involved in it, and in the extreme cases even to total destruction of the material. It is conditioned by microstructure of the material. It is caused by segregation of chemical composition related to creation at grain boundaries of phase or the structural component of the chemical composition

richer in the alloy element. If the structure component appearing on grain boundaries shows the different electrochemically character in relation to the matrix, then the corrosion processes are taking place over grain boundaries disturbing their consistency and leading to destruction of a component. The schematic diagram of intergranular corrosion in case of occurrence of precipitations on the grain boundaries is shown after [21] in Figure 2.

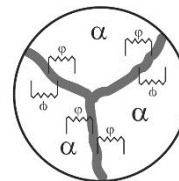


Fig. 2. Schematic diagram of galvanic micro cell leading to intergranular corrosion [after 21]

2. Materials and methods

The tests were performed in the research laboratory of the Machinefish Materials&Technologies Ltd. at the sample taken from the solenoid housing made of alloy of the ZnAl_4Cu_1 grade according to PN-EN 1774, which corroded during operating with exposure to the impact of road salt. Macroscopic tests were performed with the use of Leica M205 C stereoscopic microscope. The microscopic tests were accomplished using the Leica CTR 6000 microscope, as well as the Phenom World ProX.

3. Results and discussion

The macroscopic observation of the corroded part have shown that its surface is covered with products of white corrosion typical for zinc alloys (Fig. 3).

Microstructure of the tested material was characteristic for the hypoeutectic alloys and is composed of dendrites of the η phase and the eutectic ($\alpha+\eta$) (Fig. 4, 5). In dendrites the minor spot inclusions of the α phases precipitating as a result of transformations in the solid phase were observed.

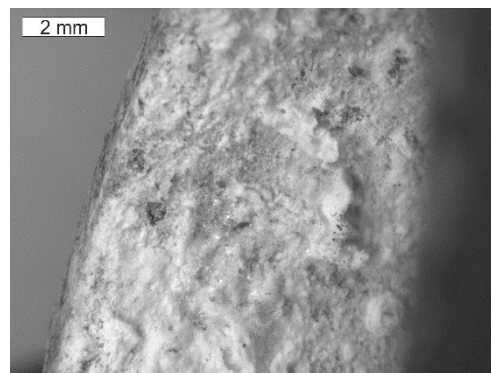


Fig. 3. General view of the tested component corroded surface. Stereoscopic microscopy

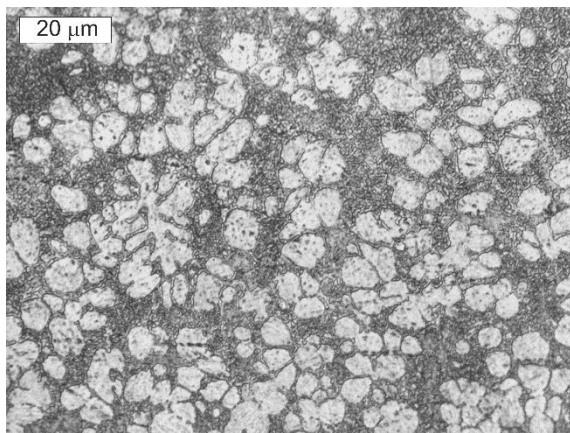


Fig. 4. Microstructure of the ZnAl4Cu1 alloy. Visible dendritic precipitations of the η phase characteristic for casting alloys and the $(\alpha+\eta)$ eutectic. Light microscopy

Theoretically the η phase should contain about 1,14% wt. of Al. The research accomplished with the use of EDX method have shown that areas of the dendrites of the η phase contain about 1,44% aluminium and are enriched in copper (Fig. 5, location 1). Precipitations rich in aluminium, which appear in the eutectic areas show content of Al close to theoretical eutectoid transformation (Fig. 5, location 2). In microstructure of the component also the presence of bright precipitations rich in lead was found (Fig. 5, location 3). Copper was observed exclusively in the solid solution η . The phase rich in copper was not found in the alloy.

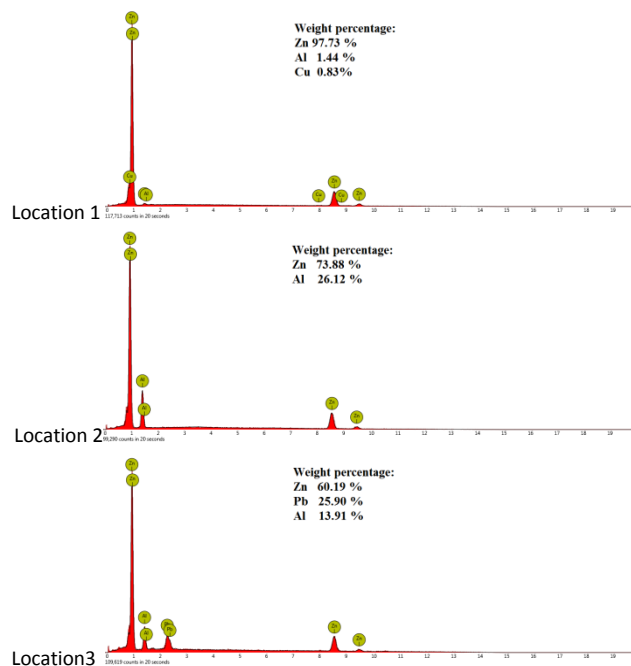


Fig. 5. Spectra of the characteristic X-ray radiation obtained for locations indicated in Figure 6

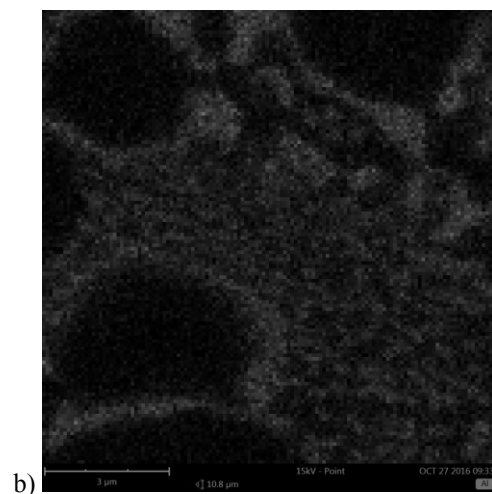
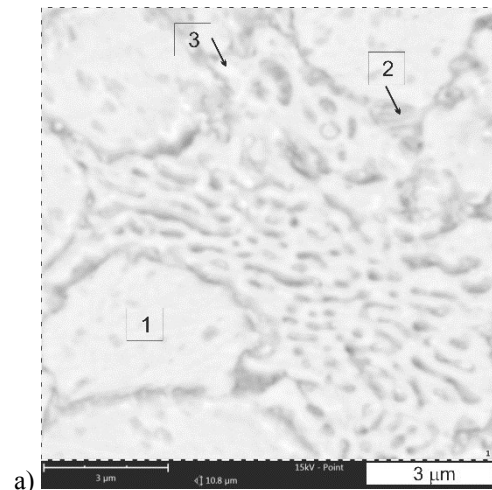


Fig. 6. Microstructure of the tested ZnAl4Cu1 alloy (a) and distribution of aluminium in the analysed area (b). Visible precipitations of the η phase and areas of the $(\alpha+\eta)$ eutectics rich in aluminium. Locally visible the phase rich in lead in the form of bright precipitations. SEM

The correlation between microstructure of alloys from the Zn-Al system and the corrosion resistance is undertaken in numerous publications, however with the incomplete description of the course of corrosion [1,3,7-13,22,23,25-27]. The performed microscopic tests have shown appearance of the intercrystalline corrosion leading to disturbing the alloy consistency and its pulverisation (Fig.7÷10). It has been found that the resulting corrosion propagates over the grain boundaries and the interdendritic areas. It is initiated in the areas of the α phase existence appearing over grain boundaries and in the areas of eutectic as a result of galvanic effect of the phase rich in aluminium α in reference to the phase rich in zinc η . Appearance of the isolated precipitations of the α phase over grain boundaries promotes the loss of consistency in the alloy. This indicates for occurrence of essential differences in electrochemical potentials of both phases. Observed selective dissolution of η phase indicates for the cathodic nature of the α phase. It is known that

aluminium is characterised with lower normal potential than zinc, amounting to $-1,66$ V. In case of zinc it amounts to $-0,76$ V. In the subject literature it did not work out to find data concerning values of corrosion potentials of the α and η phase. However, it could not be expected that solid solutions created at the base of these elements will be characterised with similar values of electrochemical potentials to those obtained for pure elements.

The observations are confirmed by the research of other Authors. The preferential attack of corrosion was also observed by Authors of the work [1]. In the work [22] it has been stated that in the hypoeutectic Zn-Al alloys the increased susceptibility to corrosion is observed with the increase of aluminium content in the alloy, which is related to the increasing share of eutectic. As a consequence, with increase of aluminium content in the alloy a shift in corrosion potentials in the direction of lower values is observed, and the increase in the rate of corrosion processes run [12,22]. The opposite situation is observed in the hypereutectic alloys, where the corrosion resistance drops with the growing content of aluminium [1]. It has also been found that occurrence of the lamellar eutectic, where both phases are mutually separated, lowers the rate of corrosion processes, in contrast to the separated precipitations [27].

The relevant literature data indicate that increase in predisposition of the alloy to intergranular corrosion is affected by increased content of lead in the alloy, which leads to its segregation and appearance in grain boundary areas [15]. The performed microscopic tests have not shown the impact of presence of the singular, isolated precipitations rich in lead on accelerated dissolution of the alloy in their vicinity.

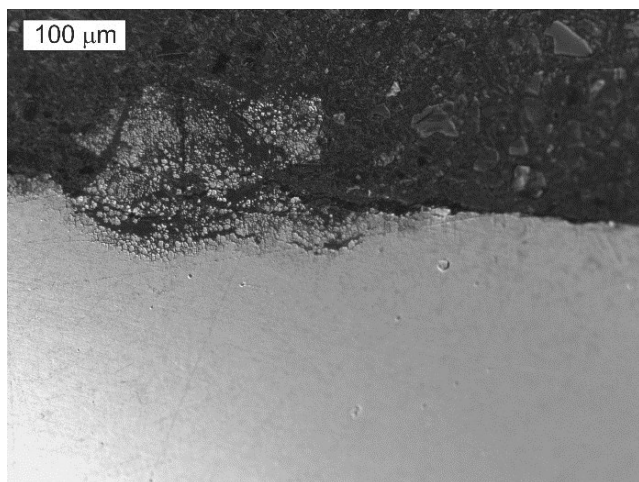


Fig. 7. Near-surface area of the tested material. Visible intergranular corrosion of the tested component leading to a loss of cohesion in the material.
Light microscopy, DIC, non-etched state

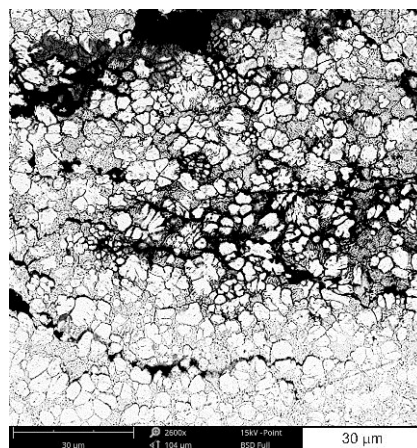


Fig. 8. Intergranular corrosion of the tested component. Visible dissolution of the eutectic areas. SEM

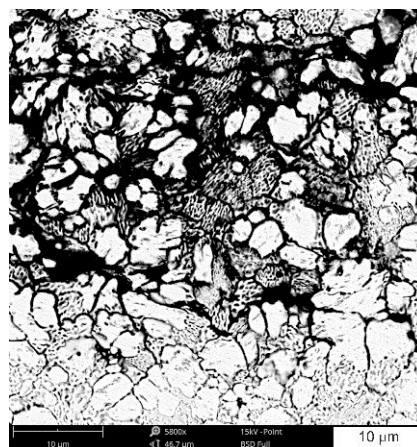


Fig. 9. Magnified fragment of the area from Figure 8. Visible selective dissolution of η phase rich in zinc separated by the α phase being a part of the eutectic leading to a loss of cohesion of the material. SEM

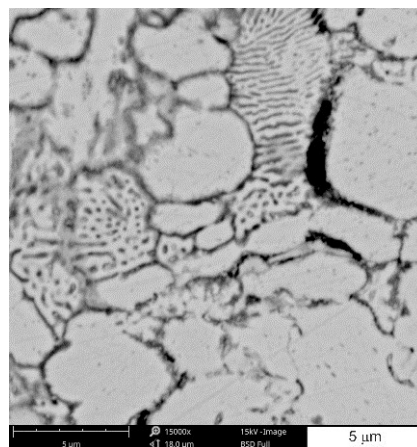


Fig. 10. The loss of the material consistency running over grain boundaries and dissolution of η phase occurring in the area of eutectic. SEM

4. Conclusions

The purpose of the accomplished tests was determining the nature of corrosion, which occurred in the solenoid valve housing made of the ZnAl4Cu1 alloy. It has been stated that the formed corrosion displayed the intergranular nature propagating over the grain borders and the interdendritic areas. The corrosion is initiated in the areas of the α phase existence as a result of the galvanic effect of the solid solution of zinc in aluminium (α) in reference to the solid solution of aluminium in zinc (η). This leads to disturbing the alloy consistency and its pulverisation stage over grain boundaries in the first, and next in the eutectic areas. A consequence of this is decrease in the active cross-section of the part covered by corrosion, which leads to lowering the plastic and strength properties of the corroding material.

The creating corrosion is conditioned by the existing microstructure of the alloy and there is no possibility of reducing its occurrence by heat treatment. For that reason the only way of preventing that type of corrosion is to limit contact of the parts made of such material with the corrosive environment.

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