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On the quantitative assessment of corrosion damages of aluminum at the early stages using confocal laser scanning microscopy

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Despite being widely used in such industries as chemical, aviation and food ones, aluminum and its alloys are known to be prone to localized corrosion, and this remains a problem to be solved, especially when it comes to pitting corrosion. Therefore, there is a necessity to detect traces of corrosion at the earliest stages and to quantify the extent of corrosion damage. The simplest solution for assessing the overall corrosion rate is to use the gravimetric method, which, however, does not provide information for assessment of localized corrosion. This paper is devoted to the consideration of the possibilities of using the method of confocal laser scanning microscopy (CLSM) for assessing corrosion resistance using high-purity aluminum. The CLSM method, due to its high resolution (especially along the vertical axis), enables to obtain quantitative data on the volume of corroded metal, determine the depth of corrosion damage including building their profilograms, and analyze the morphology of the surface damaged by corrosion. Owing to the high sensitivity of the CLSM method, corrosion losses were detected within 21 days, contrary to the standard gravimetric method, which failed to determine the loss of metal even after 160 days of corrosion testing.

Keywords: confocal laser scanning microscopy, corrosion morphology, corrosion rate, corrosion of aluminum, pitting corrosion, corrosion test, corrosion detection, accelerated corrosion testing.

1. Introduction

The contemporary development of industry as well as the development of new technological processes occurring in aggressive environments, necessitate the appearance of highly-qualitative structural materials. The most important structural materials are metals and their alloys. However, due to the chemical and electrochemical interaction of products with the environment in the course of exploiting them corrosion occurs [1].

Aluminum alloys are widely used in the aviation and automotive industries, shipbuilding and instrumentation, rocket technology and construction [2], for example, aluminum alloys make up to 30 – 35% of aircraft materials. In modern aircraft, aluminum is used literally everywhere: in the fuselage, flaps, wing and tail structures, etc. [3].

Due to the formation of a thin oxide film, aluminum alloys exhibit high corrosion resistance at pH 4 to 8 [4]. However, with a pH deviation of less than 4 and more than 8, aluminum is prone to localized types of corrosion, namely pits and pitting. The pH level (less than 4 and more than 8) is typical for almost all natural environments, such as fresh and sea water, humid air and, in some cases, soil. The listed types of corrosion are among the most dangerous [4].

The propagation of localized corrosion in constructions and their parts leads to more serious consequences than the loss of metal mass, among them can be mentioned the loss of strength [5] and ductility [6], fatigue life [7], reflectivity [8], etc. Therefore, the quantitative assessment of the corrosion process of aluminum alloys and the development of recommendations for its prevention appear in priority.

The main standards used in assessing the corrosion rate of aluminum and its alloys (GOST 9.913-90, ASTM G31, ISO 11130:2017) involve assessing the corrosion rate of metals and alloys by immersing samples into a corrosive solution with measuring the mass of the samples before and after corrosion testing. To compute the corrosion rate, it is necessary to calculate the mass loss of the sample and to know the time and surface area of the sample. A significant disadvantage of this technique is that only the average (general) corrosion rate is calculated and there is no information about localized types of corrosion. Another downside of the method is its low sensitivity. So, for example, according to GOST 9.913-90, tests of aluminum and its alloys are carried out from 30 to 180 full days, and what concerns more corrosion-resistant ones, testing may last up to a year or more.

Thus, the priority task should be the development of methods for assessing the corrosion rate, capable of determining corrosion damage at the early stages and calculating not only the uniform corrosion rate, but also the most widespread and more dangerous — localized one. Many authors note the difficulties that researchers face when trying to quantitatively describe pits and pittings, especially small ones [9,10].

Our previous studies on the surface of destruction of low-carbon steel [11] and corrosion damage of magnesium [12] using the method of confocal laser scanning microscopy (CLSM) showed the high efficiency of this method in analyzing the morphology of a damaged surface. Owing to the high resolution along the horizontal axes of 100 – 120 nm and along the vertical axis — 10 nm, in particular, the use of the CLSM method is a promising tool for identifying and quantifying corrosion damage at the early stages of such corrosion resistant materials as aluminum and its alloys.

2. Materials and experimental methods

For corrosion testing high-purity aluminum A95 (99.95 wt.%) was used as a model material. Samples were prepared using an electric spark machine (Sodick AG 400L LN2W). Samples of two types were used in the work: 3 mm in diameter for determining the corrosion rate using CLSM [12] and 5 mm in diameter for the gravimetric method. The low sensitivity of the gravimetric method necessitated enlargement of the sample size. The samples were pressed into polyethylene using a Buehler SIMPLIMET 1000 machine. The samples were prepared according to the procedure developed in [12]. The section was grinded and polished with sandpaper up to 4000 grit under running water on Struers LaboPol-25 to obtain a flat metal surface with a frozen fill. After grinding, the samples were washed in isopropyl alcohol, degreased for 3 minutes in an ultrasonic bath, and quickly dried under a stream of air.

Corrosion testing of samples was carried out by full immersion into a solution of 3% sodium chloride and 0.1% hydrogen peroxide (H_2O_2) at a temperature of 20 – 25°C in accordance with GOST 9.913-90 and every 5 days 0.1% H_2O_2 was added to the solution. The corrosive solution was changed to a fresh one the moment it became too contaminated with corrosion products (once a month). The tests lasted 160 full days. In the course of the experiment, some of the samples were taken (about once a week) from the corrosive solution and examined using CLSM, the rest of the samples were examined using the gravimetric method. After testing, corrosion products were removed in a solution of nitric acid and distilled water in a ratio of 1:1 using an ultrasonic bath (GOST 9.907-2007). The samples were weighed before and after corrosion tests using an analytical balance with an accuracy of 0.0001 g. The surface of the samples after corrosion tests was studied using a confocal laser scanning microscope (Olympus LEXT OLS 4000). Quantitative assessment of corrosion damages and corrosion rate was conducted according to an earlier developed method using CLSM [12]. The depth of the pittings was measured using ASTM G46-94 and was taken as an average of the ten deepest pittings.

3. Results and discussion

3.1. Weight loss measurements

Unfortunately, it was not possible to reveal the mass loss of the samples and, consequently, to calculate the average corrosion rate after corrosion tests using the gravimetric method throughout the tests, up to 160 full days. The reason for this was that, despite the high accuracy of laboratory analytical balances and the enlarged size of the samples compared to the samples for CLSM, the loss of metal turned out to be lower than the sensitivity of the analytical balance (0.0001 g).

3.2. Corrosion rate measurement using the CLSM method

Average corrosion rate measurement. The dependence of the average corrosion rate from the exposure time into a 3% sodium chloride solution and 0.1% hydrogen peroxide after the removal of corrosion products is shown in Fig. 1. Using the corrosion rate assessment method developed in the course of our previous studies [12], the average corrosion rate was calculated from the volume of lost metal using CLSM. Despite small corrosion damage and the impossibility of assessing the corrosion rate by the standard gravimetric method, calculation of the corrosion rate by the CLSM method became possible after 21 days. At the same time, the maximum average corrosion rate of the samples was recorded and the result was 0.045 μm/year. The trend shows an initial steep rise in the corrosion rate, corresponding to the active region, until reaching a peak value (0.045 μm/yr.), next, due to the adhesion of oxides formed in the corrosion process to the metal surface (corrosion products), the corrosion rate gradually decreases as a result of passivation. The slight increase in the corrosion rate after the decrease was associated with the transpassive region (repassivation).

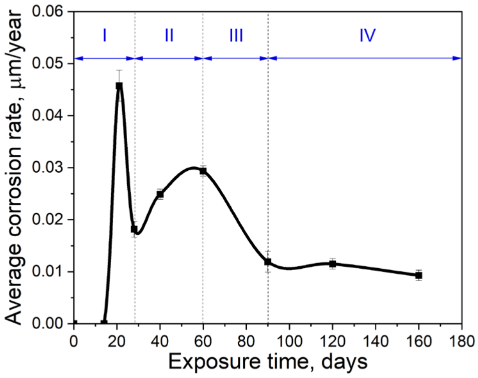

Fig. 1. The rate of general corrosion depending on the exposure time into a corrosive solution according to CLSM after removal of corrosion products.

3.3. Corrosion morphology

The morphology of the aluminum surface after immersion into the test solution for various times is shown in Fig. 2 a, d, g as general panoramas, and in Fig. 2 b, e, h — as height maps of the selected areas of the biggest corrosion damage When the samples were removed after 14 days, there was no obvious evidence of corrosion on the surface of the samples. The first spots of corrosion were identified after 21 days (Fig. 2 a, b) and were presented in the form of small corrosion pits, round or almost round pittings with an increase in the immersion time up to 90 days (Figs. 2 d, e), some of the pittings cease growing, while others continue

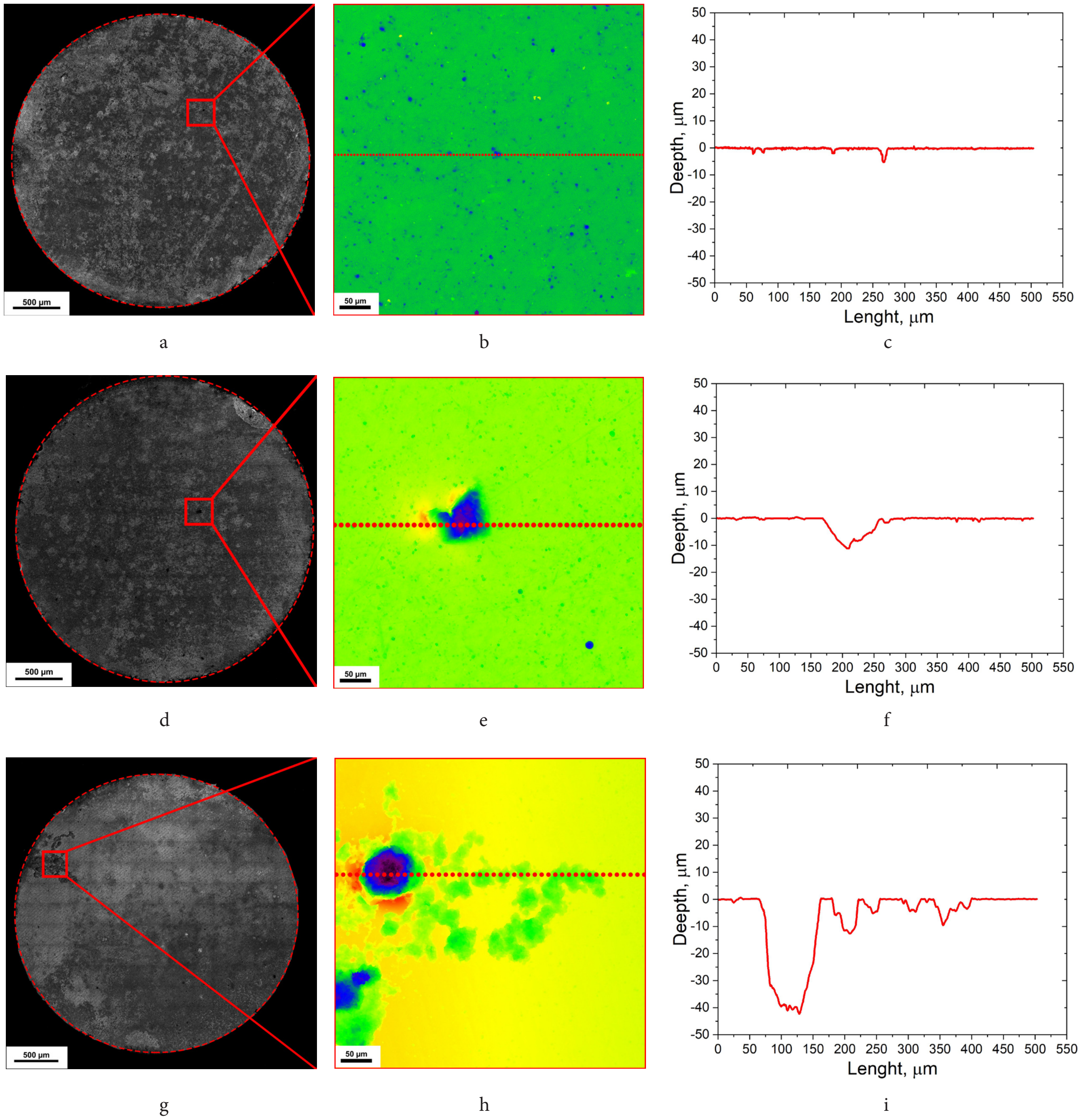

Fig. 2. (Color online) Panoramic images of high-purity aluminum after corrosion testing and removal of corrosion products after 21 (a), 90 (d) and 160 days (g) and the corresponding height maps of the selected areas of the biggest corrosion damage (b), (e), (h) and profilograms of the deepest pits obtained along the dashed lines (c), (f), (i).

to increase in depth and width. As the immersion time increases, the depth and width of the pits continue to grow, and adjacent pits begin to merge, forming larger corrosion damage, expressed as corrosion pits (Fig. 2h).

3.4. The depth of the pittings and localized corrosion rate

As for aluminum alloys, general or average corrosion is negligible. As for the predominant corrosion mechanism, it turned out to be pitting corrosion, so the most informative parameters for aluminum pitting corrosion were the maximum pitting depth and localized corrosion rate [13].

The profilograms of the deepest corrosion damage were obtained according to 3D scans using CLSM. The first pockets of corrosion damage in the form of small pits were recorded after 21 full days after the tests were conducted (Fig. 2c). The maximum pitting depth was 1.9 μm. After 90 days, the maximum pitting size reached 11.5 μm (Fig. 2f) and after 160 days due to the exposure to a corrosive environment the size reached 41.0 μm (Fig. 2i).

In Fig. 3 the dependence of the maximum pitting depth on the exposure time is presented. The curve is characterized by a bimodal trend and several stages can be distinguished on the curve:

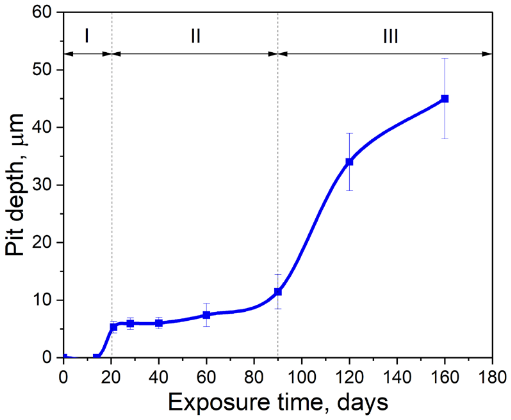

Fig. 3. Trend of the maximum pitting depth on the exposure time in a corrosive solution.

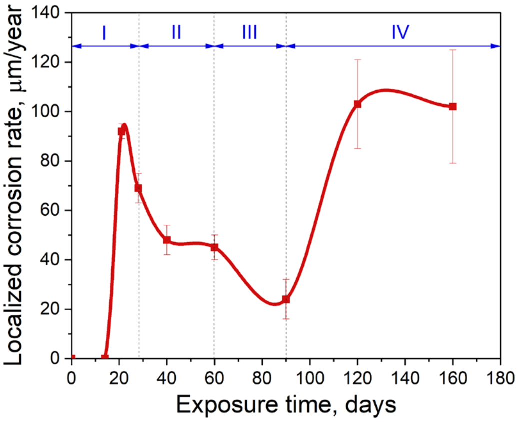

Fig. 4. Localized corrosion rate versus exposure time.

1. Initial stage of corrosion. In the area of observation from the onset of testing up to 14 days inclusively, there were practically no damages. At this stage, the natural oxide film ruptures in "weak" spots [14] and then a large number of pittings appear (Fig. 2 b). After the 21st day the development of pittings resulted in a sharp increase in the localized corrosion rate up to 93 μm/year (Fig. 4);

2. Pitting growth stage. Only a small part of the previously formed corrosion pits can continue to grow as a result of electrochemical reactions on the anode and cathode. The anode is the bottom of the corrosion pit, and the cathode is the aluminum surface around the pit. As a result of electrochemical reactions, corrosion on the anode "digs" a hole deep into aluminum by forming Al^{3+} ions. These ions diffuse to the surface from the hole and out to alkaline region in the form of OH^- ions. A result of this aluminum hydroxide $Al(OH)_3$ is released on the cathode [4]. The accumulation of corrosion products in the form of white, voluminous and jelly-like formations of $Al(OH)_3$ leads to clogging of the corrosion pits and slows down the growth of pittings. In the period from 20 to 80 days, an almost unchanging state of the reaction is observed. Owing to this, the localized corrosion rate is noticeably reduced to a level of 23 μm/year.

3. Corrosion products on the surface and especially above the pits contribute to the existence of more anoxic processes inside the pits, as well as to the development of the scenario for pitting corrosion of aluminum proposed by Wranglen [4], and also mentioned by Shreir [15], who noted the similarity with the mechanism of pitting corrosion of steel. Further corrosion probably occurs predominantly under local anoxic conditions, with the cathodic reaction changing to water dissociation with hydrogen release. Low pH is established in corrosion pits [16]. In turn, this leads to the release of gaseous hydrogen and subsequent rupture of the corrosion products. Corrosion propagation to the walls of the pit, which are still within the potential, due to their proximity to the surface. As a result, corrosion begins to develop in a horizontal direction, which is expressed in an increase in the diameter of the pittings and eventually leads to merging with other pittings, forming deeper and wider corrosion pits (Fig. 2 i).

Resulting from the processes described above, the pitting depth in the area from 90 days onwards rapidly increases to 45 μm (Fig. 3), and the localized corrosion rate increases again to 105 μm/year (Fig. 4).

The mechanisms discussed are consistent with the well-established theory of pitting corrosion of metals, which has been found on various materials with long-term exposure in a corrosive environment, including cast irons [17], low-carbon steels [18], copper alloys [19] and under various test conditions [20, 21, 22].

3.5. Kinetics of development of general and localized corrosion rates

It is of interest to compare the kinetics of the general (Fig. 1) and localized (Fig. 4) corrosion rates. At the initial stage of testing (up to 28 days), the change of both rates occurs almost identically: at first, a sharp increase in speed is observed, and then the same sharp decrease. The growth of general corrosion rate is associated with the appearance of a large number of small pittings, and the decline in rate is associated with their passivation due to the formation of corrosion products. At the next stage (28 – 60 days), the general corrosion rate begins to grow again, and the localized one stabilizes. This fact is explained by the emergence of a large number of new pittings, which contribute to general corrosion, but practically do not affect localized corrosion due to their small depth. At the third stage (60 – 90 days), both rates again decrease quite sharply due to the passivation of a new portion of pittings. After 90 days, the general corrosion rate stabilizes (the equal volume of metal corrodes per unit time), but at first (in the period from 90 to 130 days) this occurs solely due to the deepening of the deepest pittings, and after 130 days it occurs due to uniform growth in depth and in the width of all existing pittings.

4. Conclusions

1. According to the results of this study, it has been established that the CLSM method is effective for assessing the morphology of localized aluminum corrosion damage and allows one to quantify not only the average corrosion rate, but also the maximum pitting depth, as well as the localized corrosion rate.

2. The sensitivity of the CLSM method turned out to be significantly higher than the standard gravimetric method: CLSM allows one to identify the first corrosion pockets and to give them a quantitative assessment within 21 days, while the weight method was not able to register significant weight changes even after 160 days.

3. The use of CLSM to obtain data on the maximum depth of pitting caused by aluminum corrosion indicates a bimodal trend in the change in the localized corrosion rate in time, contrary to the classical concepts of a law function.

4. It is most likely that the corrosion process in pure aluminum develops cyclically according to the following scheme: nucleation of pittings → their passivation → stabilization of pittings growth → nucleation of new pittings, etc. in the cycling manner.

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