Electrochemical studies of the composite polymer-containing coating on the 1579 aluminium alloy with welded joint

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Abstract. The features of corrosion process on the surface of the 1579 Al alloy with welded joint area were investigated using SIET (scanning ion-selective electrode technique) and SVET (scanning vibrating electrode technique) in 3\% NaCl. The development of corrosion was realized along the weld interface. Methods of composite polymer-containing layer generation based on plasma electrolytic oxidation (PEO) sufficiently improve the anticorrosion behavior of the Al alloy. Corrosion of Al alloy with protective layers are described in details. Composite coatings have the best anticorrosion properties and increase the stability of material in the corrosive medium.

1. Introduction

Al alloys are attractive material to be used in such fields as automobile, aerospace and marine technology. At the same time, the intermetallic particles presence in the aluminium alloys composition, makes these materials highly liable to localized corrosion, especially in marine environment [1–3].

For the industrial implementation of aluminium alloys, a reliable anticorrosion protection of these materials is required. Plasma electrolytic oxidation (PEO) method is very promising way to generate a protective and anticorrosion layer on the Al alloy surface [4–13].

The method of composite polymer-containing layer formation via superdispersed polytetrafluoroethylene (SPTFE) treatment of base PEO-coating was proposed for Mg alloys [14,15]. SPTFE treatment can be used to increase the anticorrosion protection of Al alloys. The use of SPTFE allows us to seal the PEO pores with the polymer and to make a reliable barrier that will sufficiently reduce ions penetration to the surface of the substrate, and upgrade the sample behavior in the corrosive environment [14,15].

In this work, the way of anticorrosion layer generation on the 1579 Al alloy surface is proposed. The polymer treated PEO-layer can be characterized by increased anticorrosion properties. The protective and electrochemical behavior of the formed coatings were studied.

In accordance with our works [4,16–19], the reliable methods to study the mechanism and kinetics of the corrosion include localized electrochemical techniques [11,20–26], such as Scanning Ion-Selective Electrode Technique (SIET) and Scanning Vibrating Electrode Technique (SVET).

The study of the corrosion on the welded joint area surface of the 1579 aluminium alloy by means of localized techniques is presented. The formation and study of composite coating on the sample surface, which increases protective properties of the working material, have been examined as well.
2. Experimental

2.1. Samples
In this work, the 1579 Al alloy with welded joint (6.701 wt. % Mg; 0.639 wt. % Zn; 0.138 wt. % Cu; 0.548 wt. % Mn; 0.150 wt. % Fe; 0.126 wt. % Zr; 0.107 wt. % Sc; 0.116 wt. % Cr; 0.095 wt. % Ni; 0.021 wt. % Ti; balance – Al) was a specimen for study.

To obtain the element distribution on the aluminium alloy surface and welded joint area the EDX-800HS (Shimadzu, Japan) was used.

The PEO-layer was obtained on the Al alloy surface at 0.5 A/cm². The contents of the electrolyte were: NaF, 0.3 g/l, C₄H₄O₆K₂∙0.5H₂O, 15 g/l. The time of PEO was about 160 s. The PEO-layer thickness was about 12 µm.

For polymer-containing layer formation, the subsequent treatment of the surface of PEO-coating using Forum® SPTFE was proposed to upgrade its anticorrosion behavior. The way of polymer-containing layer generation, suggested in this experiment, was presented in our previous works [14,15]. 10 wt. % SPTFE suspension in the ethanol was used to obtain the polymer layer. The immersion period of the sample in the suspension was 30 s. Then the material was dried at 25 °C for 0.5 hours. The time and temperature of treatment of the sample with polymer-containing layer after immersion were 20 minutes and 350 °C, correspondingly.

2.2. Electrochemical studies
To investigate the development of the corrosion process on the welded joint surface of the Al alloy and to study the anticorrosion properties increase after generation of the composite coating, the SVET – SIET equipment (Applicable Electronics, USA) was used.

The SVET probe was a Pt–Ir insulated wire. The tip of the probe was covered with a Pt black. This probe was located at 100 µm above the studied surface. The amplitude of probe vibration was equal to 15 µm. In this work, the SIET electrode was sensitive to the H⁺ ions. The composition of the SIET microelectrode membrane was described in [22]. 0.01 M KH₂PO₄ in 0.1 M KCl was the inner reference solution. The SIET microelectrode was located at 40 µm above the studied surface.

Specimens were investigated in 3% NaCl solution under open circuit potential conditions.

3. Results and discussion
To obtain the element distribution on the surface of the studied material the EDX analysis was used. The EDX data show the homogeneous element distribution in the surface and bulk layers of the Al alloy and welded joint zone of the specimen (figure 1). This result shows the probability of a homogeneous occurrence of the electrochemical processes on the sample surface, which will be investigated by localized techniques.

![Figure 1. SEM image of the Al alloy specimen with welded joint zone (a) and element distribution along the line AB, according to the EDX analysis (b).](image-url)
Figure 2 depicts the optical image of the studied welded joint zone before SVET/SIET measurements. This investigated zone is outlined by frame (figure 2). After 0.5 hours of the specimen exposure, the starting of the corrosion process happened. There is a generation of the anodic area on the welded joint zone.

![Optical Image of Welded Joint Zone](image)

Figure 2. The optical image of the welded joint zone of the Al alloy specimen before SVET/SIET measurements. The weld interface is marked by dashed line.

Lower pH in the anodic area for the Al alloy can be described by the following reaction, which makes the pit medium more acid, and, therefore, the corrosion is realized:

\[
\text{Al} + \text{nH}_2\text{O} \rightarrow \text{Al(OH)}_{3-n} + \text{nH}^+ + 3\text{e}^-, \quad n = 1 - 3. \tag{1}
\]

Analysis of the SVET and SIET data indicated the development of corrosion process from the edge of the investigated zone to the bulk layers of the weld interface during the specimen immersion from 1.5 to 9 hours (figure 3(a)). The weld interface underwent the intensive corrosion destruction in accordance with the SVET/SIET results. Microdefects in the morphological structure are the reason of high electrochemical activity of the welded joint. In the welded joint zone, there are areas with different potential, which result in the occurrence of the corrosion process.

![Maps of Current Density and pH Distribution](image)

Figure 3. Maps of the current density (a) and pH distribution (b) on the surface of the Al alloy specimen with welded joint zone after 9 hours of the immersion in 3% NaCl.

It was ascertained that weld interface under the influence of chloride environment, accelerated the corrosion degradation of the investigated sample. Thereby, the anticorrosion protection of Al alloy is necessary.
SVET and SIET detected the high corrosion in the bulk layers of the welded joint area after 9 hours of the sample immersion in chloride-containing medium (figures 3(a) and 3(b)). In the anodic zone, the current density reached 170 μA/cm$^2$. The pH in the anodic zone reduced down to 5.6 (figure 3(b)), in accordance with the reaction (1). Therefore, it was established that welded joint zone of 1579 Al alloy was the area of the corrosion process passing, according to SVET/SIET maps (9 hours).

Figure 4 shows the optical image of the studied surface after PEO and SPTFE treatment. The studied area is limited by a frame (figure 4). Since the electrochemical activity of the polymer treated specimen practically did not change during all experimental time SVET and SIET maps presented after 500 hours of specimen exposure to 3% NaCl. The SVET/SIET methods registered a small corrosion activity changes on the surface of the studied specimen (figure 5). After polymer-containing layer generation on the sample surface, the welded joint area became a cathodic one (figure 5).

![Figure 4](image)

**Figure 4.** The optical image of the studied welded joint area of the Al alloy specimen with composite coating after 500 hours of specimen exposure. The weld interface of sample is marked by dashed line.

![Figure 5](image)

**Figure 5.** Maps of the current density (a) and pH distribution (b) on the weld interface of the Al alloy specimen with composite layer after 500 hours of the immersion.

In contrast to the homogeneous distribution of elements in the material investigated by the EDX analysis, the SVET/SIET data show the passing of different electrochemical processes on the sample surface. Corrosion activity of the welded joint area is connected with the microdefects in this zone, which were registered by SVET and SIET methods. After generation of the composite coating, these defects were covered, and the weld interface became a cathodic area (figure 5). The other part of the specimen is the anodic area with low corrosion activity; anodic current density is 3 μA/cm$^2$ (figure 5(a)).
Unopened pores of PEO-layers, which is one of the features of such type of coatings [14–16,27–30], is the reason of low anodic current density on the surface of the studied material. The current density gradient values for the bare Al specimen after 9 hours of the sample immersion in 3% NaCl solution (figure 3(a)) was about 180 μA/cm². This parameter for the specimen with composite layer was 11 μA/cm² (figure 5(a)). Cathodic zone at the welded joint area was also detected by SIET (figure 5(b)). Higher pH in the cathodic zone is connected with the oxygen reduction reaction [26]. The pH in cathodic and anodic areas for the specimen with the composite layer is 8.2 and 8.1, correspondingly (figure 5(b)) and 6.3 and 5.6 for the bare specimen (figure 3(b)). This is the result of corrosion process inhibition by means of polymer treatment of the specimen, thus indicating the high anticorrosion properties of the sample with composite layer.

Figure 6 shows the kinetic development of the Al alloy corrosion for the bare sample and for the sample with composite coating. The results confirm the anticorrosion behavior increase due to the coating generation. The total current, calculated from the SVET data, significantly reduced for the polymer treated sample.

![Image](image.png)

Figure 6. The total current changing with time for 1579 aluminium alloy samples with welded joint.

This result revealed a sufficient protection of the Al alloy specimen against the corrosive environment via the PEO process and polymer treatment. Such layers reduce the corrosion activity on the investigated sample surface. The weld interface became a cathodic area, and the corrosion stability of the studied sample was increased.

4. Conclusion
Features of the corrosion of 1579 Al alloy with welded joint zone have been studied. Corrosion process passing along the weld interface was investigated by SVET/SIET methods. The high electrochemical activity of the welded joint area is connected with microdefects in its morphological structure.

The composite coating reduces the corrosion intensity of the investigated specimen. The current density gradient values between anodic and cathodic area on the specimen surface decreased from 180 μA/cm² down to 11 μA/cm² as a result of PEO and SPTFE treatment. These methods enable us to sufficiently improve anticorrosion properties of the 1579 Al alloy with welded joint area in accordance with the SVET/SIET data.

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