THE ANTI-CORROSION PERFORMANCES OF THE ECO-FRIENDLY PIGMENTS BASED ON NATURAL MONTMORILLONITE LOADED WITH ZINC CATIONS AND/OR PHOSPHATE ANIONS

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Inhibitory properties of eco-friendly anticorrosion pigments based on natural montmorillonite loaded with zinc cations and/or phosphate anions by the liquid phase ion exchange method for increasing the corrosion resistance of AA2024 aluminium alloy in an acid rain environment were investigated by electrochemical impedance spectroscopy method. It was established that the inhibitory efficiency of zinc and phosphate loaded montmorillonite was the highest due to the simultaneous deposition of anti-corrosion components on the anodic and cathodic areas of the aluminium alloy.

Keywords: aluminium alloy, inhibitory, pigments, montmorillonite, corrosion

Introduction. One of the most common and effective methods of protecting these materials is the use of paint coatings [1]. the long-term effectiveness of these coatings can be enhanced by the presence in them of active substances capable of lixiviation. These substances are designed to limit the processes of electrochemical corrosion that can occur under the coating due to their damage or the deterioration of the polymer properties during operation [2].

Strontium chromate and zinc chromate are the most commonly used as ingredients in pigments for anti-corrosion coatings. The high toxicity and carcinogenicity of chromates requires the development and introduction of new, eco-friendly alternatives [3]. One of the most advanced technologies for the production of anti-corrosion pigments is the use of ion-exchange materials [4].

The natural ion-exchange materials for anti-corrosion pigments can be clay minerals with a labile structure, especially montmorillonite, a clay mineral constituent of the rock bentonite [5, 6]. Montmorillonite is used as micro- or nano-containers, which are loaded with an active inhibitor in their pores and/or shell. In our previous studies, the inhibitory efficiency of zinc loaded montmorillonite for corrosion protection of an aluminium alloy in acid rain environment was evaluated. It was shown that the inhibitory capacity of Zn-montmorillonite increases with increasing concentration of the solution from which it was modified, and reaches a maximum at 0.5 M $Zn(NO_3)_2$ solution [7].

Therefore, the aim of the work is to obtain eco-friendly anticorrosion pigments based on natural montmorillonite, loaded with zinc cations and/or phosphate anions by the liquid phase ion exchange method, and to evaluate their inhibitory properties on AA2024 aluminium alloy in an acid rain environment.

Materials and experimental methods. To obtain anticorrosion pigments based on montmorillonite, natural bentonite from the Ilnytsky deposit in the Zakarpattia region (Ukraine) was used. Montmorillonite was obtained from bentonite by sedimentation of the coarse dispersed phase [8]. The loaded montmorillonite with zinc cations and/or phosphate anions was modified by liquid phase ion exchange [9].

The corrosion resistance of the AA2024 aluminium alloy in the frequency range of 10000...0.1 Hz with applied signal amplitude of 10 mV was investigated by electrochemical impedance spectroscopy (EIS) method using a Versa STAT 3 frequency response potentiostat analyzer. For EIS tests, a three-electrode cell was used, which consisted of a silver chloride reference electrode, a platinum auxiliary electrode and a working sample. The working area of the aluminium alloy sample was 1 cm^2.

The obtained results correspond to the equivalent circuit, which included R_s, R_f, R_{ct}, CPE_f, and CPE_{dl} – solution resistance, protective film resistance, charge transfer resistance, constant phase element of the protective film and the double layer, respectively.

The efficiency of corrosion inhibition (IE, %) was determined by the formula:

$$Z = \frac{1/R_{ct} - 1/R_{ct}^{inh}}{1/R_{ct}} \cdot 100, \quad (1)$$

where R_{ct} and R_{ct}^{inh} – resistance of the charge transfer in environment without and with loaded montmorillonite, respectively, Ohms.

Results and discussion. In fig. 1 and 2 is shown EIS plots for the aluminium alloy after 3 h immersion in an acid rain environment without and with loaded montmorillonite at room temperature. The impedance modulus of aluminium alloy enhances with addition loaded montmorillonite. The efficiency of corrosion inhibition of zinc and phosphate loaded montmorillonite was higher compared to zinc loaded montmorillonite or phosphate loaded montmorillonite, due to the simultaneous deposition of anti-corrosion components on the anodic and cathodic areas of the aluminium alloy (see table).

The maximum phase angle in the impedance spectra of the aluminium alloy in the in an acid rain environment without and with initial montmorillonite, occurs in the low-frequency region, indicating the presence of electrochemical corrosion reactions. The appearance of a high-frequency peak in the phase angle dependence after the 3 h immersion when using loaded montmorillonite suggests the formation of a protective film on the metal surface.

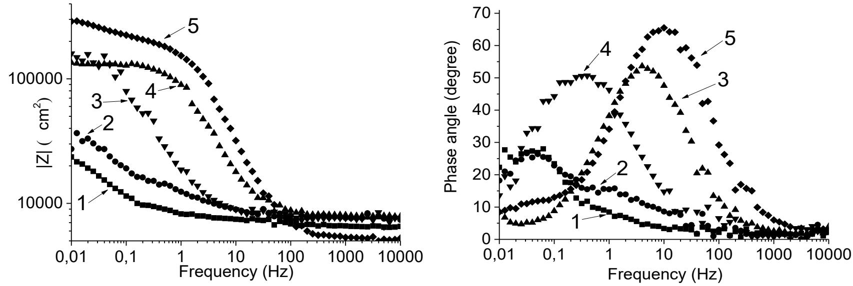

Fig. 1. Bode plots of the aluminium alloy after 3 h immersion in an acid rain environment: 1 – without montmorillonite; with: 2 – initial montmorillonite; 3 – zinc loaded montmorillonite; 4 – phosphate loaded montmorillonite; 5 – zinc and phosphate loaded montmorillonite.

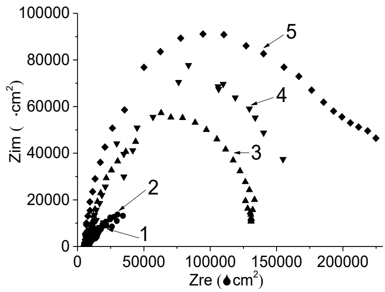

Fig. 1. Nyquist plots of the aluminium alloy after 3 h immersion in an acid rain environment: 1 – without montmorillonite; with: 2 – initial montmorillonite; 3 – zinc loaded montmorillonite; 4 – phosphate loaded montmorillonite; 5 – zinc and phosphate loaded montmorillonite.

Table. EIS characteristics for the aluminium alloy after immersion in an acid rain environment.

environment	R_s, Ohms	R_f, Ohms·cm^2	CPE_f, s^n/Ohms·cm^2	R_{ct}, Ohms·cm^2	CPE_{dl}, s^n/Ohms·cm^2	*IE*, %
without montmorillonite	6379	2170	$5.58\cdot10^{-5}$	32806	$1.83\cdot10^{-4}$	–
initial montmorillonite	7676	11657	$3.82\cdot10^{-5}$	32104	$1.47\cdot10^{-4}$	–
zinc loaded montmorillonite	5189	3004	$3.23\cdot10^{-7}$	132680	$1.60\cdot10^{-6}$	75.27
phosphate loaded montmorillonite	7457	2719	$7.84\cdot10^{-7}$	169350	$6.88\cdot10^{-6}$	80.63
zinc and phosphate loaded montmorillonite	5237	2483	$2.44\cdot10^{-7}$	223950	$6.63\cdot10^{-7}$	85.35

The anticorrosion action of the loaded montmorillonite consists in the release of Zn^{2+} cations from the montmorillonite framework, followed by interaction with the OH^- anions, leading to the formation of insoluble $Zn(OH)_2$ hydroxides on the aluminium alloy surface and the formation of aluminium phosphates with stabilization of the protective film.

Conclusions. Natural montmorillonite was loaded with zinc cations and/or phosphate anions using liquid phase ion exchange. The anticorrosion properties of the loaded montmorillonites increase in the following order: zinc loaded montmorillonite < phosphate loaded montmorillonite < zinc and phosphate loaded montmorillonite. The efficiency of corrosion inhibition of zinc and phosphate loaded montmorillonite against corrosion of the aluminium alloy in acid rain after 3 h immersion was approximately 85%. Natural montmorillonite loaded with zinc cations and phosphate anions, can be a promising eco-friendly anti-corrosion pigment for paint coatings to protect metal structures in atmospheric conditions.

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