

## **Anodic behavior of aluminum in $\alpha$ -alanine aqueous solutions at various pH values**

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### **Abstract**

The effect of  $\alpha$ -alanine on aluminum anodic behavior in its solutions with pH values from 4.2 to 8.5 has been studied. It has been found that, depending on the pH, the amino acid exhibits a dual effect. On the one hand,  $\alpha$ -alanine zwitter-ions (pH 4.2–5.6) behaving like an inhibitor slow down the anodic process, so aluminum is in a stable passive state at these pH values in the vicinity of the isoelectric point of the amino acid. The probable reason of the observed effect is that strong intermolecular hydrogen bridges that are formed between the amino and carboxy groups in the amino acid zwitter-ions predominate over interactions with the oxidized aluminum surface. On the other hand, it has been shown that the  $\alpha$ -alanine anions formed at pH = 8.5 stimulate pit formation on aluminum surface in these solutions. Based on literature and experimental data, a dissociative mechanism of pit formation on aluminum in the systems in question is suggested.

**Key words:** *pit formation, inhibition, aluminum,  $\alpha$ -alanine, pH.*

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### **Introduction**

Studies on the pitting corrosion of such passivating metals as aluminum are both of fundamental value and have a broad practical application in various electrochemical processes [1, 2].

In modern industry, structures that contact aqueous solutions containing organic compounds are often made of aluminum and its alloys. This fact requires an estimate of whether it is possible to apply the general concepts of the pit formation (PF) theory previously established for inorganic ions to the systems of interest and to reveal the specific processes that occur in such systems. Among numerous organic compounds, particular interest of researchers is drawn to amino acids (AA) that, because of their high complexing ability and adsorption properties, can act both as inhibitors and corrosion stimulators, depending on the nature of the physicochemical system and AA concentration [3, 4].

In spite of its significance, this problem requiring an accurate concept concerning the nature of the processes developing on metal/electrolyte interface has not found a proper solution for aluminum anodic dissolution in the presence of AAs. Therefore, this work

aimed at studying the effect of an organic additive, namely  $\alpha$ -alanine ( $\alpha$ -Ala), on the anodic behavior of aluminum in electrolytes with pH values ranging from 4.2 to 8.5.

## Experimental

The experiments were carried out using a stationary aluminum electrode (Al 99.9%) immersed in aqueous or weakly alkaline electrolytes containing  $\alpha$ -Ala at concentration varied from  $1.1 \cdot 10^{-4}$  to  $1.1 \cdot 10^{-1}$  M. All solutions were prepared from analytical reagent grade chemicals using distilled water. Their pH values were measured before and after each experiment with an N 5123 pH-meter (accuracy 0.1). The pH values for the first group of  $\alpha$ -Ala aqueous solutions changed from 4.2 to 5.6 with an increase in AA concentration. For the second group of weakly alkaline solutions, the solution pH was kept at a constant value of 8.5 (by adding 1 M NaOH to the system with simultaneous pH measurement).

A conventional electrolytic cell with three electrodes and divided cathodic and anodic spaces was used for electrochemical studies under naturally aerated conditions [5]. The system included three beakers from the heat-resistant glass connected by agar salt bridges with saturated  $\text{KNO}_3$  solution. A glass-carbon electrode served as a counter electrode. The electrode potentials of aluminum were measured with against a silver/silver chloride electrode ( $E = +0.20$  V) and then converted to the normal hydrogen scale (NHE).

The working surface of an aluminum electrode was mechanically polished (an electrode was ground on emery papers with decreasing grain radius, then polished on filter paper) and rinsed with distilled water and alcohol before each experiment.

To study aluminum anodic behavior in the solutions of interest containing  $\alpha$ -Ala, the experiments were carried out at a temperature of  $20 \pm 2^\circ\text{C}$  under potentiodynamic control on a IPC-Compact potentiostat with potential a scan rate ( $v$ ) of 0.2 V/min. The current passing through the system was measured with an M830V digital multimeter (accuracy 0.1  $\mu\text{A}$ ). After an electrode was immersed in the working electrolyte and exposed for 10 min, anodic polarization curves (APC) were recorded (from the free corrosion potential ( $E_{\text{corr}}$ ) in the positive direction up to  $E = +1.20$  V).

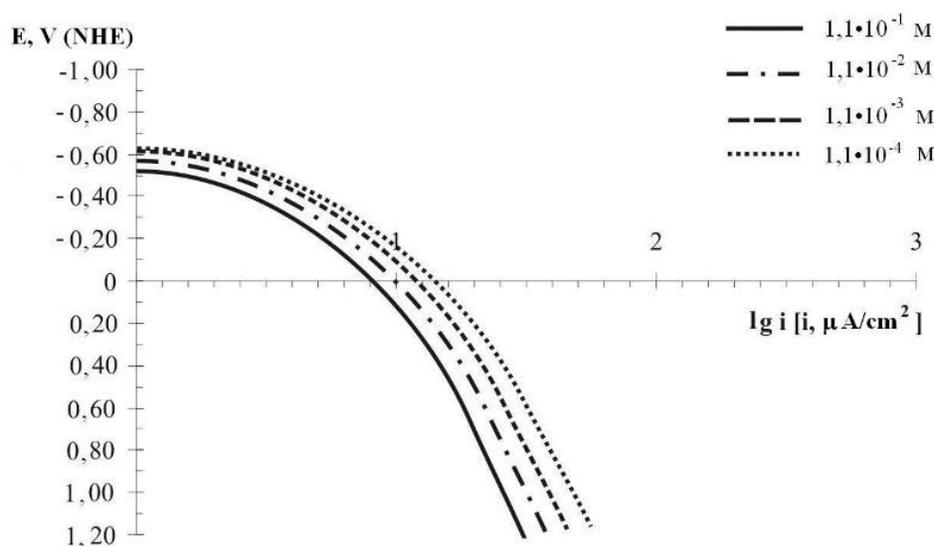
The electrochemical studies were supported by visual examination of the working surface of each electrode before and after the experiments (anodic polarization) under MBS-2 ( $\times 7$ ) and MIM-7 ( $\times 500$ ) optical microscopes. The degree of metal degradation in the solutions studied was determined by the surface topography. Furthermore, the working electrode surface was visually monitored by scanning electronic microscopy (SEM) using a JEOL 6380LV instrument equipped with INCA Energy-250 for qualitative and semi-quantitative chemical energy-dispersive X-ray analysis (EDXA) of the elements present on the metal surface.

## Results and discussion

The subject of the present study, according to its purpose, was to perform an experimental acquisition and systematization of data on the anodic behavior of aluminum in a series of

electrolytes with various pH = 4.2–8.5 containing  $\alpha$ -Ala in the concentration range from  $1.1 \cdot 10^{-4}$  to  $1.1 \cdot 10^{-1}$  M.

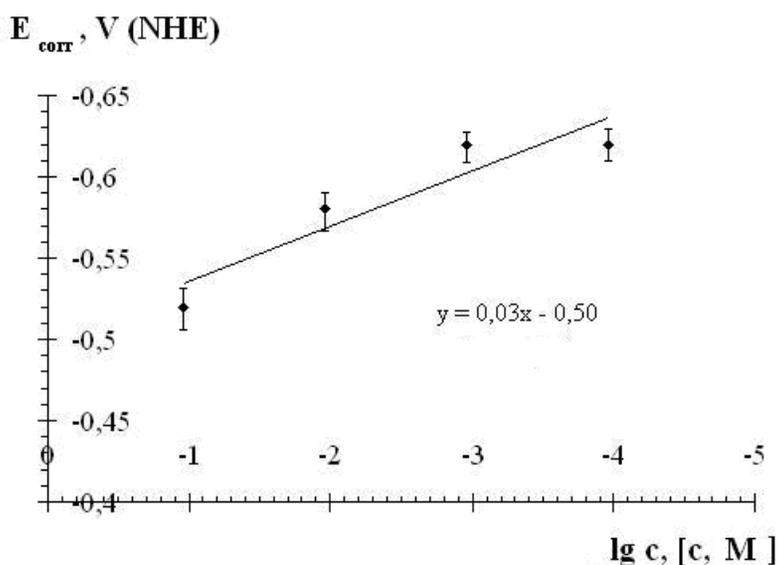
It is known from literature sources [1, 2] that in neutral aqueous solutions, aluminum exists in a passive state. Experimental results confirmed the validity of this conclusion for the systems studied. Moreover, the APC shape does not depend on the concentration of  $\alpha$ -Ala (Fig. 1), while the anodic currents decrease in parallel and the  $E_{\text{corr}}$  potentials of aluminum (Fig. 2) shift to more positive values with an increase in AA concentration in the system. The latter is probably due to an increase in the stability of the “aluminum /  $\alpha$ -Ala aqueous solution” system. The results of microscopic observations demonstrated the absence of any damage on the metal surface (Table 1).



**Fig. 1.** APC of aluminum in different  $\alpha$ -alanine aqueous solutions ( $v = 0.2$  V/min,  $t = 20^\circ\text{C}$ )

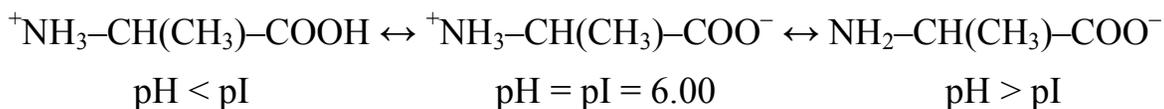
**Table 1.** Effect of  $\alpha$ -alanine concentration on pH,  $E_{\text{corr}}$  and aluminum surface appearance in aqueous solutions (MBS-2,  $\times 7$ )

Parameter	Concentration of $\alpha$ -Ala, M			
	$1.1 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$1.1 \cdot 10^{-1}$
pH	4.2	5.0	5.4	5.6
$E_{\text{corr}}$ , V (NHE)	-0.62	-0.62	-0.58	-0.52
Aluminum surface appearance				



**Fig. 2.** Effect of  $\alpha$ -alanine concentration on  $E_{\text{corr}}$  of aluminum in aqueous solutions at pH = 4.2–5.6.

The data obtained can be explained based on the  $\alpha$ -Ala properties that vary depending on pH. Since the isoelectric point of  $\alpha$ -Ala equals 6.00 [3],



more than 99% of the AA molecules exist as zwitter-ions at pH = 4.2–5.6 [6] and the concentration of the latter increases with the additive concentration.

As noted above, this results in stabilization of aluminum and decreases the rate of its dissolution from the passive state. Nitrogen was not found by SEM/EDXA methods in the surface film on the metal even in the most concentrated  $\alpha$ -Ala solutions (Fig. 3). It follows from this that  $\alpha$ -Ala zwitter-ions do not participate in the anodic process on aluminum, and the passive film on aluminum surface is formed upon metal–water interaction according to the following scheme [1,2,7] because of a high chemical affinity of aluminum to oxygen:

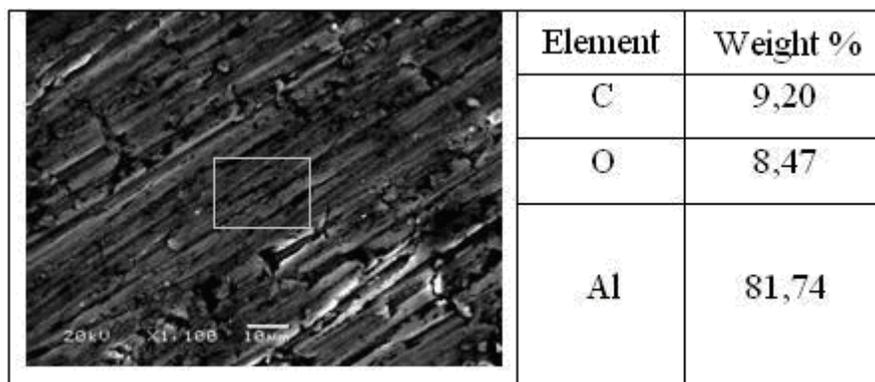


The probable reason of the observed effect is that strong intermolecular hydrogen bridges that are formed between the amino and carboxy groups ( $\text{NH}_3^+ \cdots ^-\text{OOC}$ ) of the AA zwitter-forms predominate over interactions with the oxidized aluminum surface.

At the same time, transition from weakly acidic solutions (at small  $\alpha$ -Ala concentrations) to neutral solutions (with increase in  $\alpha$ -Ala concentration) stabilizes the indicated passivating layer and interferes with metal damage.

In the context of available literature data about high complexing and adsorptive capacity of  $\alpha$ -Ala<sup>-</sup> [4], analysis of the anodic behavior of aluminum in systems where  $\alpha$ -

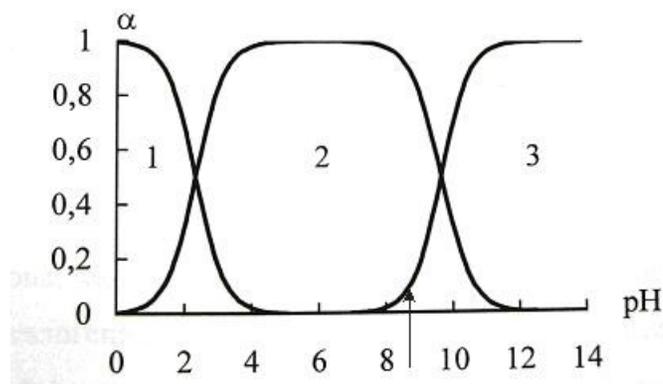
Ala exists in anionic form is of special interest. With this purpose, a cycle of experiments on the anodic behavior of aluminum similar to that described above was carried out in weakly alkaline  $\alpha$ -Ala solutions with fixed pH = 8.5.



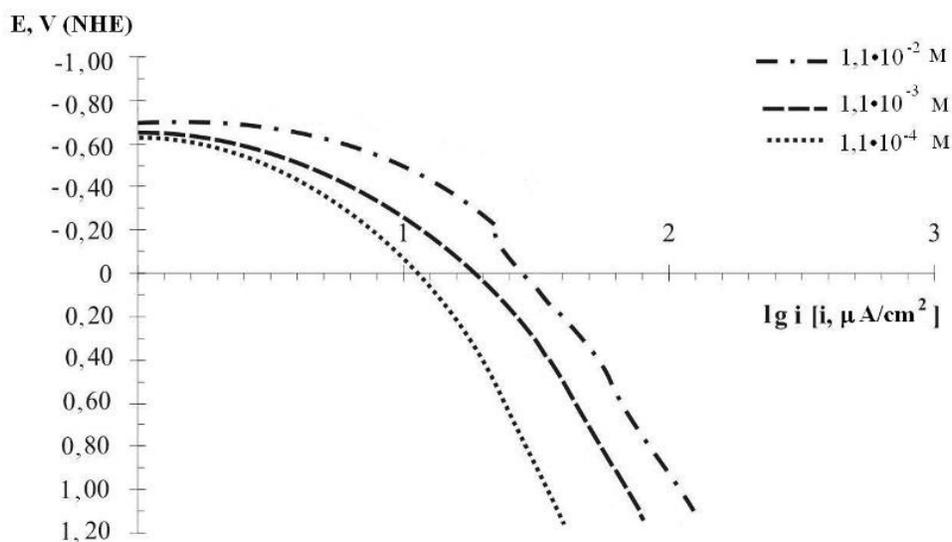
**Fig. 3.** SEM micrographs ( $\times 1100$ ) and EDXA of Al surface after voltammetric studies in  $1.1 \cdot 10^{-1}$  M  $\alpha$ -alanine aqueous solutions (pH 5.6) at  $20^\circ\text{C}$  (in the selected zone).

The choice of this pH value was caused by two reasons. At pH = 8.5, the system contains both inactive zwitter-ions along with  $\alpha\text{-Ala}^-$  anions (Fig. 4). On the other hand, solutions with higher pH might cause intense general corrosion of aluminum [2]. Analysis of the results obtained in weakly alkaline solutions containing  $\alpha$ -Ala has shown that they differ essentially from those presented above. In fact, as the concentration of  $\alpha$ -Ala in these systems is increased, a change in APC shape is observed (Figs. 5 and 6). In the concentration range from  $1.1 \cdot 10^{-4}$  to  $1.1 \cdot 10^{-2}$  M, the APCs are similar to those in the water/ $\alpha$ -Ala system. However, at  $C_{\text{Ala}} \geq 0.5 \cdot 10^{-1}$  M, their shape is typical of passive metals undergoing local damage. Results of microscopic studies also demonstrate local destruction of the metal at  $\alpha$ -Ala concentrations higher than  $0.5 \cdot 10^{-1}$  M (Table 2). The variation in  $E_{\text{corr}}$ , which becomes less noble with an increase in  $\alpha$ -Ala concentration but in all cases remains more negative than  $E_{\text{corr}}$  in the neutral medium (Fig. 7), also confirms the above conclusion on the breakdown of the passive state of aluminum, which according to voltammetric data takes place at PF potential ( $E_{\text{PF}} = +0.60$  V in the electrolyte with an  $\alpha$ -Ala concentration of  $1.1 \cdot 10^{-1}$  M. The results of SEM/EDXA measurements have shown the presence of nitrogen in the spectra of the passivating layer, which confirms that a nitrogen-containing compound with the probable composition  $[\text{Al}(\text{OH})_{y-k}]_{\text{ads}}^{z-y}$  [3, 6, 9] is present on the surface of aluminum (Fig. 8).

The data on aluminum anodic behavior in  $\alpha$ -Ala solutions (pH = 8.5) were analyzed on the basis of the nucleophilic substitution theory [9–11], according to which PF observed on aluminum involves nucleophilic substitution of ligands of adsorbed surface complexes by corrosive solution components with subsequent hydrolysis of a compound formed.



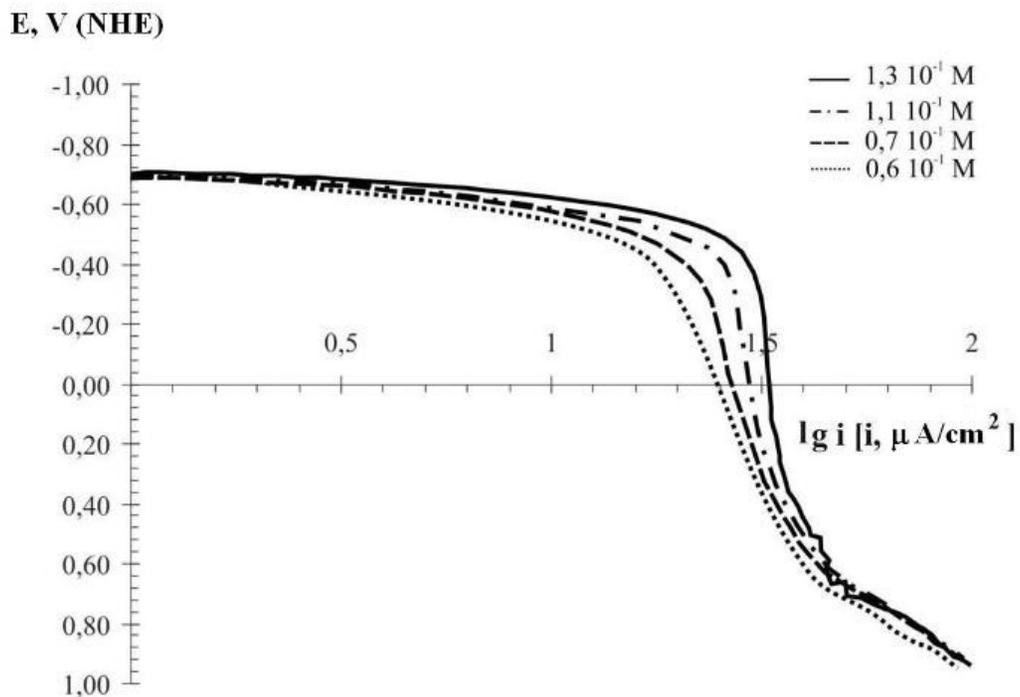
**Fig. 4.** Distribution of various ionic forms of  $\alpha$ -alanine in solution at different pH: 1 –  $\alpha$ -Ala<sup>+</sup>; 2 –  $\alpha$ -Ala<sup>0</sup>; 3 –  $\alpha$ -Ala<sup>-</sup> [8].



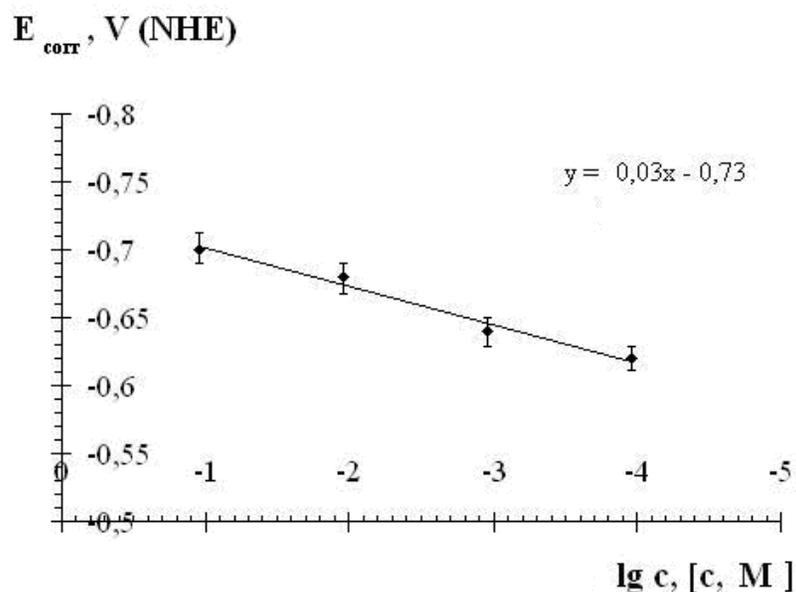
**Fig. 5.** APC of aluminum in  $\alpha$ -alanine solutions at pH = 8.5 ( $v = 0.2$  V/min,  $t = 20^\circ\text{C}$ ).

**Table 2.** Effect of  $\alpha$ -alanine concentration on  $E_{\text{corr}}$  and aluminum surface appearance in weakly alkaline solutions at pH 8.5 (MBS-2,  $\times 7$ ).

Parameter	Concentration of $\alpha$ -Ala, M				
	$1.1 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	$1.1 \cdot 10^{-2}$	$0.5 \cdot 10^{-1}$	$1.1 \cdot 10^{-1}$
$E_{\text{corr}}$ , V (NHE)	-0.62	-0.64	-0.68	-0.70	-0.70
Aluminum surface appearance					



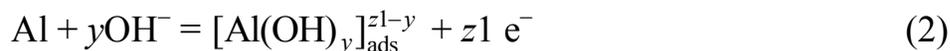
**Fig. 6.** APC of aluminum in  $\alpha$ -alanine solutions at pH= 8.5 ( $v = 0.2$  V/min,  $t = 20^\circ\text{C}$ ).



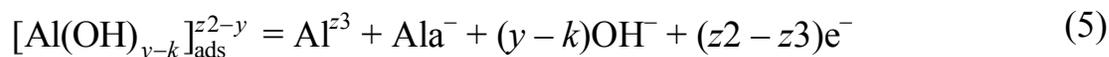
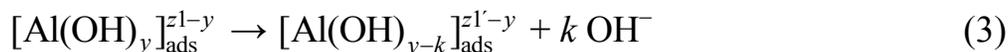
**Fig. 7.** Effect of  $\alpha$ -alanine concentration on  $E_{\text{corr}}$  of aluminum in aqueous solutions at pH 8.5.

Generalization of experimental data and literature data allowed us to suggest the following multistage mechanism of the PF process.

– Film formation on the metal surface:



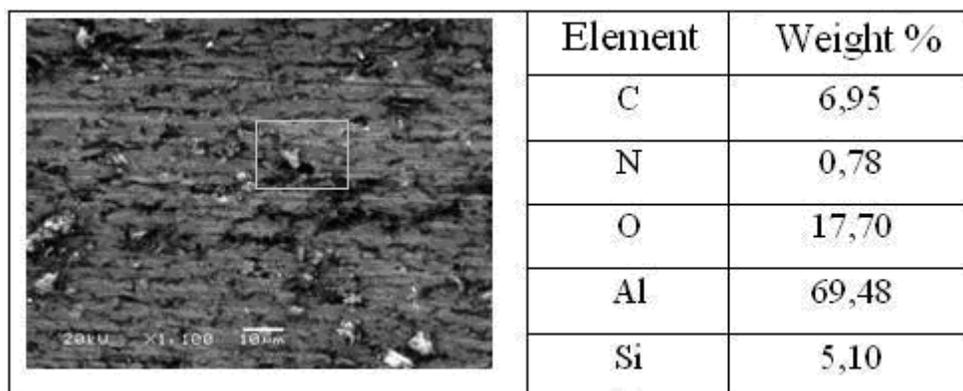
– PF process:



The nature of the limiting stage is determined from kinetic analysis data. The main equation is as follows:

$$i = k \cdot C_{\text{Ala}^-}^n,$$

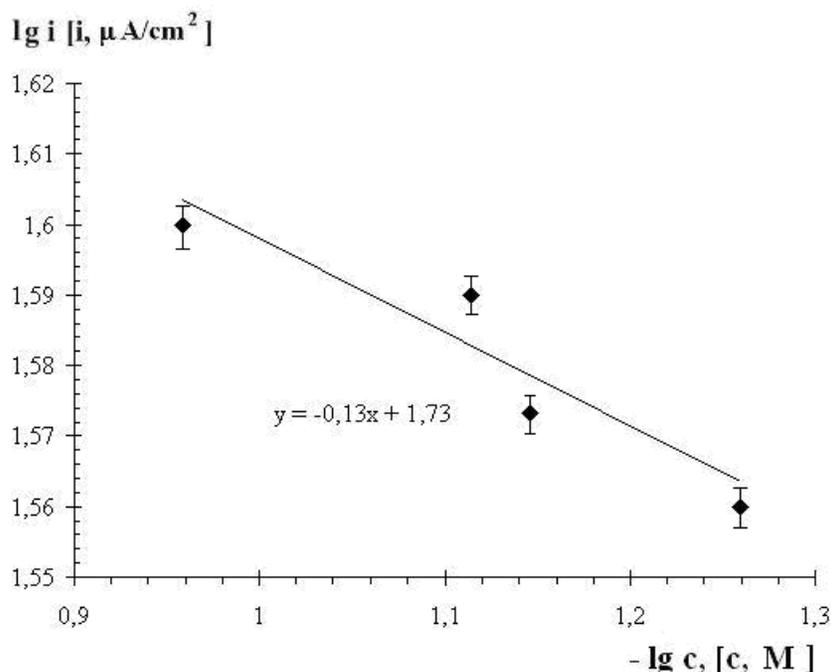
where  $i$  is a value proportional to the mean PF rate;  $C_{\text{Ala}^-}$  is the concentration of the activator ion; and  $n$  is the reaction order with respect to the corrosive ion [12].



**Fig. 8.** SEM micrographs ( $\times 1100$ ) and EDXA of Al surface after voltammetric study in  $1.1 \cdot 10^{-1}$  M weakly alkaline (pH 8.5)  $\alpha$ -alanine solutions at  $20^\circ\text{C}$  (in the selected zone).

According to literature data, if  $n_{\text{Ala}^-} \rightarrow 0$ , the limiting stage of the process is dissociation of the initial complex (Scheme 3) with subsequent addition of the attacking nucleophile. At  $n_{\text{Ala}^-} \rightarrow 1$ , the limiting stage of the process is association of the complex with  $\alpha$ -Ala anions (Scheme 4).

According to the data obtained in the present study,  $n_{\text{Ala}^-} \rightarrow 0$  at  $E = 0.00$  V (Fig. 9) and the limiting stage of the process studied is stage (3), *i.e.*, dissociation of the initial  $[\text{Al}(\text{OH})_y]_{\text{ads}}^{z1-y}$  complex.



**Fig. 9.** Effect of  $\alpha$ -alanine concentration on the rate of aluminum anodic process at  $E = 0.60$  V (NHE)

## Conclusions

1. The anodic behavior of aluminum in a series of aqueous solutions containing  $\alpha$ -Ala ( $1.1 \cdot 10^{-4}$  to  $1.1 \cdot 10^{-1}$  M) at pH = 4.2–8.5 has been studied using a complex of physicochemical methods.
2. It has been shown that  $\alpha$ -Ala zwitter-ions (pH = 4.2–5.6) only slightly inhibit the anodic process, and aluminum exists in a stable passive state at pH close to the isoelectric point of the amino acid.
3. On the other hand, the concentration of the amino acid at pH = 8.5, where  $\alpha$ -Ala<sup>-</sup> anions are present in the system, change the anodic behavior of aluminum essentially. At  $\alpha$ -Ala<sup>-</sup> concentrations  $C_{\alpha\text{-Ala}} \geq 0.5 \cdot 10^{-1}$  M,  $\alpha$ -Ala<sup>-</sup> anions cause local damage of aluminum.
4. Based on the modern theories of competitive adsorption and nucleophilic substitution, a PF mechanism on aluminum was suggested and confirmed by independent electrochemical and SEM/EDXA methods. It has been found that the PF process on passive aluminum in the presence of  $\alpha$ -Ala anions occurs as dissociative nucleophilic substitution.

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