ANODIC POLARIZABILITY IN NEUTRAL ELECTROLYTES OF Al ALLOYS WITH ALKALINE-EARTH ELEMENTS

`![Fig. 1](image)`

1957

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

A. L. SEIFER

ANODIC POLARIZABILITY IN NEUTRAL ELECTROLYTES OF Al ALLOYS WITH ALKALINE-EARTH ELEMENTS

(Presented by Academician I. I. Chernyaev on May 23, 1957)

It has been suggested ([1]) that the ennoblement of the electrode potentials of Al –Ca alloys in seawater is associated with destruction, by the corrosion products of the intermetallic compound Al_4Ca, of the oxide film on the alloy surface. At the same time, one must also take into account the fact that in seawater, which contains a certain amount of sulfate ions, there must also occur a process of formation, on the surface of aluminum-calcium alloys, of a film consisting of sparingly soluble Ca sulfates.

Fig. 1. Anodic polarizability of Al–Ca alloys.
1 –Al + 3.93% Ca in 0.5 N NaCl solution; 2 –Al + 12.26% Ca in 0.5 N NaCl solution; 3 –Al + 3.93% Ca in 0.5 N Na_2SO_4 solution; 4 –Al + 12.26% Ca in 0.5 N Na_2SO_4 solution; 5 –technically pure Al in 0.5 N NaCl solution; 6 –technically pure Al in 0.5 N Na_2SO_4 solution.

It therefore seemed of interest to study the anodic polarizability of Al alloys with Ca, Sr, and Ba not only in seawater, but also in its "limiting models" –solutions of sodium sulfate and chloride, since the character of anodic polarization in the indicated electrolytes could provide an indication of the character of the processes of formation or destruction of protective films on the electrode surface. It should be noted that Al alloys with Ca, Sr, and Ba possess an analogous structure with an intermetallic compound of the $Al_4\Theta$ type as a component of the eutectic ([2–4]).

By dissolving the corresponding pure metals in molten high-purity aluminum under a layer of carnallite flux, alloys of Al with Ca, Sr, and Ba were prepared. The composition of the alloys in weight percent is shown in Table 1. In the finished ingots the Fe content did not exceed 0.03%.

The anodic polarizability of these alloys was studied in Caspian seawater and in 0.5 N solutions of NaCl and Na_2SO_4 at polarizing current densities up to

20 mA/dm^2. The results are given in Table 1 and in Figs. 1–3.

As is evident from the graphs and the table, the character of the anodic polarizability of the alloys described is determined both by the nature of the electrolyte and by the nature of the added alkaline-earth element.

In 0.5 N NaCl solution the dominant process will be dissolution of the oxide film on the alloy surface. Moreover, the destructibility of the film, recorded as ennoblement of the electrode potential, increases

with the change in the nature of the added alkaline-earth element in the series Ca—Sr—Br and with an increase in the amount of metal of the Ca subgroup added to the alloy. With the change in the second dissociation constant of the hydroxides from 0.03 for $Ca(OH)_2$ to 0.23 for $Ba(OH)_2$ (5), and with an increase in the total amount of hydroxides formed (owing to the interaction of the intermetallic compounds Al_4E with water), proportional to the increase in the amount of alkaline-earth element added to the alloy, the amount of hydroxide ions in the near-electrode space of the anodically polarized alloy increases. The presence of hydroxide ions in the near-anode space is the principal factor in the dissolution of the oxide film on the alloy surface.

Table 1

Electrode potentials of Al alloys with Ca, Sr, and Ba in Caspian seawater at various densities of the anodic polarizing current (relative to the normal hydrogen electrode, in volts)

Alloy composition	Anode current density (mA/dm^2)	Anode current density (mA/dm^2)	Anode current density (mA/dm^2)
	0	10	20
Technically pure Al	−0.58	−0.45	−0.42
Al + 3.93% Ca	−0.59	−0.47	−0.44
Al + 6.85% Ca	−0.49	−0.45	−0.43
Al + 12.26% Ca	−0.62	−0.48	−0.45
Al + 1.06% Sr	−0.58	−0.45	−0.43
Al + 4.69% Sr	−0.65	−0.47	−0.45
Al + 7.25% Sr	−0.64	−0.55	−0.52
Al + 1.94% Ba	−0.67	−0.66	−0.66

Note. Electrolyte temperature 20°. The electrode surface was cleaned in air before immersion in the electrolyte.

In a 0.5 N solution of Na_2SO_4, in the absence of the activating action of the chloride ion on the protective film, a process occurs in which an additional protective film of sparingly soluble sulfates of elements of the Ca subgroup is formed on the alloy surface. Since the solubility of sulfates decreases in the series Ca—Sr—Ba, alloys with Ba are polarized more strongly than those with Sr and Ca. Increasing the amount of alkaline-earth element added to the alloy causes an increase in anodic polarizability owing to an increase in the total amount of sulfates formed. This is clearly seen in the graphs of Figs. 2 and 3.

Fig. 2

Fig. 3

Fig. 2. Anodic polarizability of Al—Sr and Al—Ba alloys in 0.5 N NaCl solution.
1 —Al + 1.06% Sr, 2 —Al + 4.69% Sr, 3 —Al + 7.25% Sr, 4 —Al + 94% Ba

Fig. 3. Anodic polarizability of Al—Sr and Al—Ba alloys in 0.5 N Na_2SO_4 solution.
1 —Al + 1.06% Sr, 2 —Al + 4.69% Sr, 3 —Al + 1.94% Ba

In Caspian seawater, the general course of the anodic polarization curves is similar to that of the curves in 0.5 N NaCl solution, but the electrode-potential values are considerably more positive owing to the formation on the electrode surface of a certain amount of sparingly soluble sulfates.

Thus, during anodic dissolution of aluminum alloys with elements of the Ca subgroup in seawater, two processes proceed in parallel: destruction of the oxide film under the action of hydroxide ions and formation of a new, sulfate film. It is clear, however, that the significantly smaller

the strength of the sulfate film as compared with the oxide film, and determines the analogy between the character of the polarizability of the alloys in seawater and the polarizability in a NaCl solution.

Received
12 XII 1956

References

1. I. N. Frantsevich, Z. P. Kamzolova, *Reports of the Academy of Sciences of the Ukrainian SSR*, No. 1, 82 (1955).

2. H. Nowotny, H. Wesenberg, *Zs. Metallkunde*, **31**, 363 (1939).

3. H. Nowotny, A. Mohrnheim, E. Wormnes, *Zs. Metallkunde*, **32**, 39 (1940).

4. E. Alberty, R. R. Andress, *Zs. Metallkunde*, **27**, 126 (1935).

5. B. V. Nekrasov, *Course of General Chemistry*, 9th ed., 1952, p. 642.

Note: Figure translations are in progress. See original paper for figures.