

INVESTIGATION OF THE Al-Mn ALLOY ELECTROCHEMICAL BEHAVIOUR IN THE CASPIAN SEA WATER UNDER DIFFERENT MOVEMENT SPEEDS AND HEAT TRANSFER CONDITIONS

A.F. ALIYEV

*Azerbaijan Power Research and Design Institute
Baku, G. Zardabi av., 94*

Key words: power engineering, electrophysics, electrochemical corrosion, aluminum alloys, sea water, heat transfer, cooling system, desalination of water.

Different speeds of movement and heat transfer parameters impact on electrochemical behaviour of aluminium alloy in the Caspian Sea water has been investigated including also methods used to prevent scaling by acidification of water and injection of anionic surfactants. It was found that increase in speed up to 2 m/s is the favourable stability factor against the pitting corrosion and the heat transfer through the surface under the temperature drop up to 90°C / 140°C at the metal-liquid system doesn't lead to dangerous contraction of passive area, i.e. is safe from the rise of the pointed-pitting corrosion standpoint.

Caspian Sea water is often used in the Fuel and Energy and Oil and Gas extractive industry Units' cooling systems due to deficiency of fresh water in the Caspian regions of Azerbaijan, Kazakhstan and Turkmenistan. Moreover, heat transfer surfaces, as a rule, are made of costly alloys on the base of copper (cupronickel, brass, bronze) and stainless steels.

Decrease in prime cost of Units and production is possible provided replacement traditionally used materials by some considerably cheaper and available aluminium alloys which are almost 3 times lighter and 5-6 times cheaper than the copper ones of the same size.

Corrosive and electrochemical characteristics as well as protective effect mechanism for number of aluminum alloys during thermal desalination of Caspian water have been studied under heat balance and intermixing of medium [1-6], i.e. when the metal-electrode and the solution-electrode temperatures are the same. However, the heat transfer surface (metal) temperature differs from the cooling (or warmed) liquid medium temperature in the heat transfer systems, i.e. the metal-liquid interaction process is on, under the heat transfer. Mixing up of the liquid may not also correspond to the actual speeds of movement observed in the heat exchangers.

According to the procedure [7] the anodic potentiostatic polarization curves have been read from the three-electrode cell made of pyrex-glass with electrode spaces for divided by taps, at the laboratory plant with rotating heat transfer disk electrode. Disk electrodes have been made of the Al-Mn alloy (1,0 – 1,4 % Mn; 0,2 – 0,5 % Mg, everything else is of – Al) – which is one of the most corrosion resistant alloys to sea water [1 – 6]. Natural Caspian sea water from the Absheron seacoast has been used as an electrolyte (total salt content is approx. 13g/l ; $\text{Cl}^- \approx 5,35$ g/l; $\text{SO}_4^{2-} \approx 3,1$ g/l; $(\text{Ca}^{2+} + \text{Mg}^{2+}) \approx 80,0$ mg-ekv/l; $(\text{HCO}_3^- + \text{CO}_3^{2-}) \approx 4,0$ mg-ekv/l; $(\text{Na}^+ + \text{K}^+) \approx 3,4$ g/l.

Model aluminum or it's alloy anodic potentiostatic polarization curve in the sea water is shown on the fig.1. As it is seen, there is no active dissolution area on this curve and metal is in passive state when corrosion potential is (φ_{cor}). As soon as definite pitting-formation potential (φ_{pf}) is achieved,

drastic rise in anode current is registered, caused by local breach of passivity and formation of pittings.

According to general theory of this process offered by Ya.M. Kolotirkin [8], migratory accumulation of activated anions takes place by the most active parts of the metal surface. When $\varphi = \varphi_{pf}$ the anions force out the passivated oxygen and take part in the local dissolution process (as catalyst) at this places. Passive area width is defined by the $\Delta\varphi_p = \varphi_{pf} - \varphi_{cor}$ difference during the anodic polarization. Potential at which the direct and back stroke anodic curves are intersected is defined as the pittings repassivation potential (φ_{rp}). Density of anodic current in passive area i_p corresponds to the metal corrosion speed in current units.

According to the published works [9,10] formation of pitting could not happen in the $\varphi < \varphi_{rp}$ area, arose pittings may develop and formation of pittings could happen during sufficient time delay in the $\varphi_{rp} \leq \varphi \leq \varphi_{pf}$ area and pittings arise practically at once in the $\varphi > \varphi_{pf}$ area. Development of pittings which are already arose will be stopped only in case if the potential becomes lower than φ_{rp} .

Thus, location of φ_{cor} potential regarding φ_{pf} and φ_{rp} potentials defines, in essence, the stability to the pitting corrosion. Movements speed impact on parameters of the Al-Mn alloy anodic polarization curves is studied in the sea water warmed up to 90° C under the disk electrodes rotation speeds of 1000, 2000, 3000, 4000 rpm that corresponds to the linear speeds of the liquid movement of 0,84; 1,19; 1,45 and 1,68 m/s inside the pipe.

Electrochemical measurements have been made in the thermostatic three-electrode cells made of pyrex glass with electrode spaces divided by taps. Investigated heat transmitting disk electrode has been placed in the middle part of the cell and connected to the reference electrode by Luggin capillary. Platinum has been used as an auxiliary electrode (AE) and silver chloride in the saturated solution of KCl – as a reference electrode.

The cells had plane bottom enabling mixing up of solution by MM – 3 type magnetic mixer when necessary. Working volume of the cell (investigated electrode's section) is $50 \div 100$ sm^3 , quantity of solution in it is $20 \div 50$ sm^3 .

Polyethylene hose connected the cell to the vessel for preparation of solution, equipped by casing for thermostating purpose like the cell itself. U-1, U-10, LP-201, TC-16

thermostats have been used for thermostating. The thermostat's liquid is distilled water (up to 90°C) or glycerol (over 90°C).

Investigated disk electrodes have been made of aluminum alloy reds pressed into the teflon. To avoid gap effects, close fitting to the insulating material's metal had been carefully checked.

Before experiment the disk electrodes have been cleaned out by fine files of different numbers with consecutively decreasing size of the abrasive grains, degreased by ethyl alcohol, washed by distilled water and working solution.

Polarization curves have been taken based on steady-state corrosion potential (φ_{cor}) after 1-2 hours following immersion of the electrode. The potential have been changed by 10 – 30 mV steps with 2 – 3 min time delay per step. The delay have been extended up to 10 – 20 min nearly the pitting formation potential φ_{pf} (when potentials were approx. 100 mV lower than φ_{pf}). To take cathode curves the polarization have been stopped at potentials 0.5 – 0,6V lower φ_{cor} . Each polarization curve have been taken 3–6 times. Findings have been averaged.

Taking into consideration the recommendations [5, 6], stability to pitting have been estimated according to conventional width of passive area $\Delta\varphi_p = \varphi_{rp} - \varphi_{cor}$, i.e. according to potentials interval higher φ_{cor} , where metal is passive as well as according to difference between repassivation potential and corrosion potential ($\varphi_{rp} - \varphi_{cor}$) i.e. according width of the area where pittings could not happen; to measure the pittings repassivation potential (φ_{rp}) after the current density achieves approx. 10^{-3} A/sm² during the anodic activation process, polarization have been changed in the opposite direction and back stroke anodic polarization curve have been taken with the same speed until intersection with the part of the direct stroke curve corresponding to the passive area.

Time delay per each potential have been extended up to 5–7 minutes nearly φ_{rp} . Results of the φ_{rp} measurement by potentiostatic method (potential shifting speed is 20mV/min) are the same.

Findings (fig.2) show that along with increase in the disk rotational speed the corrosion and repassivation potentials are changing a little like the corrosion current in the passive area, passive area $\varphi_{rp} - \varphi_{cor}$ width exceeds 200 mV all over the investigated liquid speeds' range (the potential values are shown reduced to the n.h.e. – normal hydrogen electrode). Along with increase in rotation speed up to 2000 rpm, the φ_{pf} potential is shifting into the passive side (that is in conformity with data [11] for aluminum in the (NaCl) solution at 110 mV); further increase in the electrode rotation speed shifts the φ_{pf} into the more negative values' side, however this potential is more positive than in the static conditions ever when $n = 4000$ rpm.

Experiments with disk electrodes have been made under heat transfer conditions with $n = 1000$ rpm (0,84 m/s). Presented in the table are the parameters of received anodic polarization curves competitive to the relevant characteristics under the heat balance.

As it seen from the table, if there are no descalers in the water, the corrosion speed and pittings repassivation potential are unchangeable under heat transfer through the disk, φ_{cor} potential is shifted first 30 mV into the negative side under the temperature drop of 120° C/90° C and then 90 mV – into

the positive side under the temperature drop of 140° C/90° C. φ_{pf} Potential is shifted into the negative side maximum 100mV under the temperature drop of 140° C/90° C, however $\Delta\varphi_p$ (0,28V) and $\varphi_{rp} - \varphi_{cor}$ (0,21V) values are quite sufficient to avoid pitting corrosion in this case.

Under the temperature drop of 140° C/90° C and the electrode rotation speed of 1000 rpm the anodic polarization curves have been also taken in the modes of scale prevention by acidification of water by sulfuric acid ($5,7 \leq \text{pH} \leq 6,3$) and injection of 100 mg/kg of anionic surfactant – sulphonic carbonate acid dysodium salt.

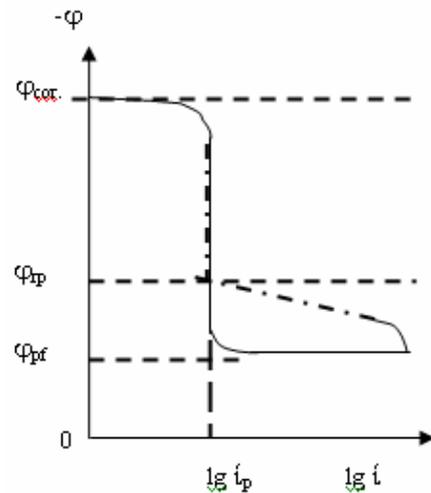


Fig.1. Schematic anodic potentiostatic polarization curve of direct (—) and back (---) stroke for aluminium and its alloys in the Caspian sea water.

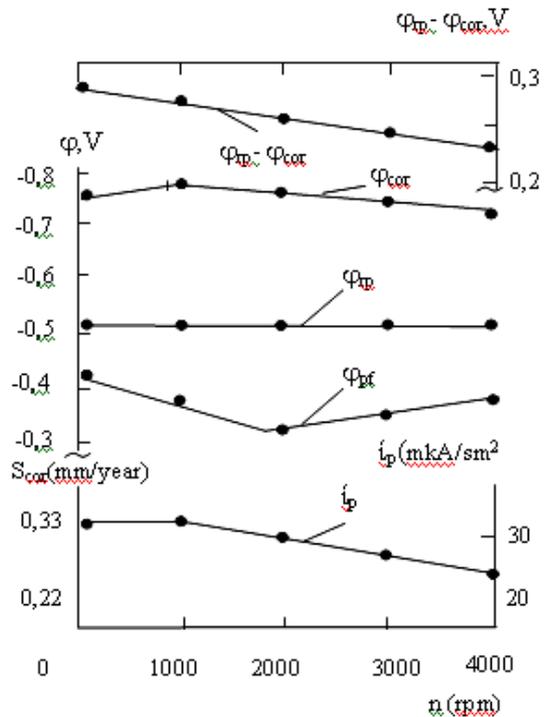


Fig.2. $\varphi_{rp} - \varphi_{cor}$, φ_{cor} , φ_{rp} , φ_{pf} and dependences of the Al-Mn alloy in sea water under 90°C on disk electrode rotation speed.

Acidification itself shifts φ_{cor} to 40 mV into the negative side and φ_{pf} to 30 mV into the positive side under some increase

of corrosion current in the passive area (from 28 up to 50 mA/cm²). Injection of surfactant shifts φ_{cor} , to 80 mV into the negative side and φ_{pf} to 100mV into the positive side increasing significantly the passive area width $\Delta\varphi_{pf}$. Thus, the alloy corrosion speed decreases 17,5 times (from 28 to 1,6 mA/cm²).

Pittings repassivation potential is unchangeable in the scale prevention modes mentioned, however $\varphi_{pf} - \varphi_{cor}$ and $\varphi_{pf} - \varphi_{rp}$ values are increased 70 and 30 mV accordingly in case of acidification and 180 and 100 mV accordingly – in

case of descaler injection (anionic surfactant) due to change of φ_{cor} and φ_{pf} . So, from the stability to pitting corrosion standpoint, movements of the sea water is a favorable (factor) facilitating removal of the metal dissolution products out of metal surface. As a result, the, φ_{pf} potential is more positive in dynamic conditions than in static conditions. Heat transfer through the surface doesn't lead as well to the dangerous contraction of passive area especially when descaler (anionic surfactant exists).

Table
Corrosion potential and parameters of anodic polarization curves for the Al - Mg alloy in the sea water under the heat balance and the heat transfer conditions (n = 1000 rpm)

Measurement conditions	φ_{cor}, V	φ_{pf}, V	φ_{rp}, V	$i_p \cdot 10^5, A/sm^2$	$\Delta\varphi_p, V$	$\varphi_{rp} - \varphi_{cor}, V$	$\varphi_{pf} - \varphi_{rp}, V$
Heat balance, 90° C	-0,79	-0,35	-0,52	3,0	0,44	0,27	0,17
Heat transfer, 120° C/90° C	-0,82	-0,43	-0,52	3,2	0,30	0,30	0,09
Heat transfer, 140° C/90° C	-0,73	-0,45	-0,52	2,8	0,28	0,21	0,07
The same in acidified sea water (5,7 ≤ pH ≤ 6,3)	-0,77	-0,42	-0,52	5,0	0,35	0,25	0,10
The same in the sea water with 100 mg/kg of anionic surfactant additive	-0,81	-0,35	-0,52	0,16	0,46	0,29	0,17

- [1] A.F. Aliyev. Investigation of influence of temperature and Caspian Sea water compositions on corrosion and electrochemical behavior of some alloys. Transaction of the A – URI “Vodgeo”. Moscow, 1974, 45 edition, p.103-115.
- [2] A.A. Abdulla-zade, A.F. Aliyev. Some ways of Efficiency Increasing of Sea Water Desalination by Distillation, Reprinted from Proceedings of the Second World Congress. Intern. Water Resources Association, New Delhi, December, 1975, vol.3. p. 73-75.
- [3] A.F. Aliyev. Corrosion and electrochemical behavior of aluminum alloys in Caspian sea water thermal desalination in accordance to the methods of scaling prevention. Transaction of the A – URI “Vodgeo”. Moscow, 1975, 53 edition, p. 63-73.
- [4] A.F. Aliyev, L.I. Freynman. Investigation of electrochemical behavior of aluminum alloys in Caspian Sea thermal desalination plants working condition. “Metal protection” Moscow, 1976, №4, p. 387-392.
- [5] A.F. Aliyev, L.I. Freynman. Investigation of impact of water rewime parameters of Caspian Sea distillation plants on electrochemical behavior of aluminum alloys. The II All – Union scientific and technical conference Reports on “Utilization of sea and saltish waters on TES and problems of scientific investigation”. Baku, 1976, p.230-233.
- [6] A.F. Aliyev, L.I. Freynman, A.A. Abdulla-zade., Investigation of anionic surfactants impact on corrosion and electro-chemical behavior of aluminum alloys in thermal desalination of Caspian Sea. The II All – Union conference reports on Utilization of Sea and saltish waters on TES and problems of scientific investigation. Baku, 1976, p. 233-235.
- [7] L.I. Freynman, V.A. Makarov, I.E. Briksin. Potentiostatic methods in the corrosion investigations and electrochemical protection. House “Chimiya”, Leningrad, 1972.
- [8] Ya.M. Kolotirkin. The pitting corrosion of metals “Chemicheskaya promishlennost”, Moscow, 1963, №9, p. 678.
- [9] R.A. Bonewits. «Corrosion» (USA), 1973, 29, №6, 215.
- [10] R.A. Bonewits. The Intern. Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials. March 19-23, 1973, Anaheim, Calif, Paper №66.
- [11] F. Frans, P. Novak. Sponsored by the National Association of Corrosion Engineers (Dec. 6-10, 1971), Williamsburg, Virginia, USA, 576.
- [12] L.I. Freiman, Lap Le Min. Z.phys. Chem. (Leipzig), 1973, 252, № 12,65.
- [13] I.L. Rozenfeld. Corrosion and metal protection. (Local corrosion processes) House “Metallurgiya”, Moscow, 1970, p. 292.

A.F. Əliyev

DİNAMİK İSTİLİK ÖTÜRMƏ ŞƏRAİTİNDƏ XƏZƏR DƏNİZİ SUYUNDA ALÜMİNİUM ƏRİNTİSİNİN ELEKTROKİMYƏVİ CƏHƏTDƏN ÖZÜNÜ APARMASI

Xəzər dənizi suyunda müxtəlif hərəkət sürətlərinin və istilik ötürmə parametrlərinin alüminium ərintisinin elektro-kimyəvi təsiri, o cümlədən suyun turşusunu artırmaqla və anionlu səthi-aktiv maddələrin daxil edilməsi üsullardan istifadə olunması tədqiq edilib.

Müəyyən olunmuşdur ki, 2 m/s – dək sürətin artması, pitting-korroziyasının dayanıqlığı üçün əlverişli amildir, amma səthdən istilik ötürmə maye-metal sistemində temperaturun 90 °C / 140 °C – dək dəyişilməsi passiv sahənin təhlükəli daralmasına gətirmir, yəni nöqtəli-yaralı korroziyanın əmələ gəlməsinə təhlükə yaratmır.

А.Ф. Алиев

ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ АЛЮМИНИЕВОГО СПЛАВА В КАСПИЙСКОЙ ВОДЕ ПРИ ДИНАМИЧЕСКИХ УСЛОВИЯХ ТЕПЛОПЕРЕДАЧИ

Исследовано влияние различных скоростей движения и параметров теплопередачи на электрохимическое поведение алюминиевого сплава в каспийской морской воде в том числе при использовании методов предотвращения накипи подкислением воды и введением анионных поверхностно-активных веществ. Установлено, что увеличение скорости до 2 м/с является благоприятным фактором устойчивости к питтинговой коррозии, а теплопередача через поверхность при перепаде температур в системе жидкость-металл до 90° С / 140° С не приводит к опасному сужению пассивной области, т.е. не представляет опасности с точки зрения возникновения точечно-язвенной коррозии.

Received: 14.09.04