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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Contact Corrosion of Metals in Concentrated Aqueous-Glycolic Solutions

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Abstract—Corrosion behavior of aluminum, steel, and cast iron was studied both in their individual state and in systems constituted of aluminum and steel, aluminum and cast iron, steel and cast iron, and aluminum, steel, and cast iron in ethylene glycol solutions containing 5 and 30 vol % of fresh water.

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This study continues the systematic analysis of the contact corrosion of aluminum alloys, steel, and cast iron in aqueous and aqueous-glycolic media in order to find out how the composition of an aqueous-organic solution affects the corrosion process. Previously, the corrosion of these metals has been studied in model fresh water [1]. The present communication reports examples of both the individual corrosion behavior of the metals under study and that in short-circuited systems constituted of aluminum and steel, aluminum and cast iron, steel and cast iron, and aluminum, steel, and cast iron in ethylene glycol solutions containing 5 and 30 vol % of fresh water. The composition of the water was described in [1].

The choice of the metals, organic solvent, and composition of the aqueous–organic solution was governed by the fact that modern liquid-cooling systems and, in particular, those of internal combustion engines and various heat-exchange apparatuses use the above metals as the main construction materials, and formulations based on ethylene glycol with low content of water serve as cooling agents at the Extreme North. In addition, fireproof hydraulic fluids of the HFC class (according to the classification by the International Standardization Organization, ISO) are widely used at present. These fluids contain, in addition to water (30–50%), a di- or triatomic alcohol (most frequently, ethylene glycol) [2, 3]. It should also be noted that ethylene glycol is frequently transported in winter as 95% aqueous solutions [4].

This study is also important theoretically, because the nonsystematic nature of previous analyses of the behavior of electrochemically diverse metals in aqueous-organic media hinders understanding of the fundamental aspects of the specific features of the contact corrosion of metals in aqueous-organic media [5].

EXPERIMENTAL

Planar 50×25×3 mm samples of steel 3 [GOST (State Standard) 380], GH 190 cast iron [VAZ (Volga Automotive Plant) industry standard 52205], and AK6M2 aluminum alloy (GOST 1583) were preliminarily polished and degreased. The electrical contact between metal plates was provided by an external low-resistance conductor. The electrode potentials were measured relative to a silver chloride reference electrode. Ethylene glycol (GOST 19710, extra quality) was used without preliminary purification. The procedures employed in the experiments were described in [1], including modeling of natural fresh water by introduction of typical concentrations of sodium sulfate, chloride, and hydrocarbonate into the distilled water.

In the absence of contact between the metallic samples, the potentials of aluminum, steel, and cast iron in ethylene glycol solutions containing 5 and 30 vol % of water shift to more negative values in the course of time (Fig. 1). However, a determination of the sample masses demonstrated that only cast iron

Steady-state corrosion rates V_{st} of aluminum, steel, and cast iron in aqueous and aqueous-glycolic solutions of various compositions

Metal	V_{st}, g m^{-2} h^{-1} at indicated content of H_2O, vol %			Metal	V_{st}, g m^{-2} h^{-1} at indicated content of H_2O, vol %		
	5	30	100		5	30	100
Aluminum, steel, and cast iron (without contact)				Aluminum + cast iron			
Steel	0.0	0.0	0.068	Steel	–	–	–
Cast iron	0.007	0.024	0.074	Cast iron	0.0	0.025	0.105
Aluminum	0.0	0.0	0.0	Aluminum	0.0	0.0	0.010
Aluminum + steel + cast iron 8) (in contact)				Steel + cast iron			
Steel	0.0	0.0	0.082	Steel	0.0	0.0	0.062
Cast iron	0.0	0.028	0.112	Cast iron	0.010	0.031	0.123
Aluminum	0.007	0.0	0.013	Aluminum	–		–
Aluminum + steel							
Steel	0.0	0.0	0.088				
Cast iron	–	–	–				
Aluminum	0.0	0.003	0.012				

dissolves and its corrosion loss linearly increases with the experiment duration (Fig. 2, straight lines *1* and *3*). The masses of most of the other samples remain unchanged, and that of aluminum samples slightly increases (by 0.5–1.5 mg). No indications of pitting were observed on aluminum in an ethylene glycol solution with 5% water; as, however, the content of water is raised to 30%, separate insignificant centers of pitting corrosion appear.

The corrosion rates of the metals in the solutions under study and in water [1] are listed in the table. Compared with water, the rate of corrosion of cast iron decreases by a factor of 3 in an ethylene glycol

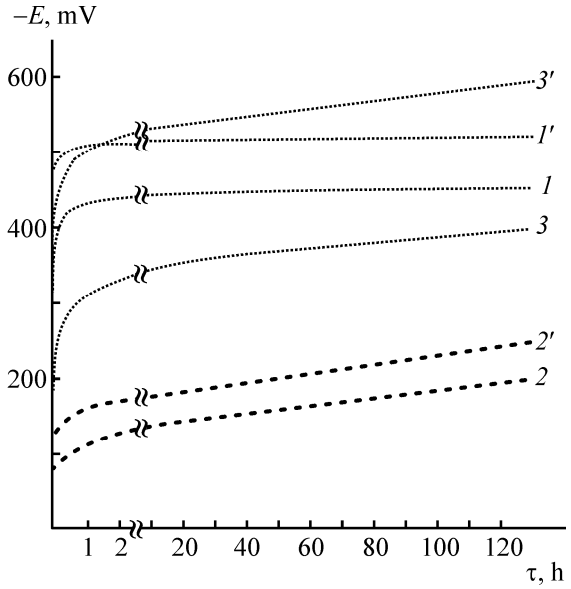

Fig. 1. Potentials E of (*1, 1′*) aluminum, (*2, 2′*) steel, and (*3, 3′*) cast iron vs. the test duration τ in ethylene glycol solutions containing (*1–3*) 5 and (*1′–3′*) 30% of water.

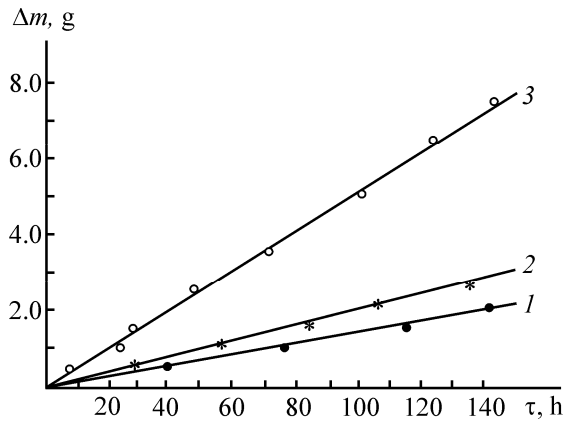

Fig. 2. Corrosion loss Δm of cast iron (*1, 3*) in the absence of contact and (*2*) in contact with steel vs. the test duration τ in ethylene glycol solutions containing (*1, 2*) 5 and (*3*) 30% of water.

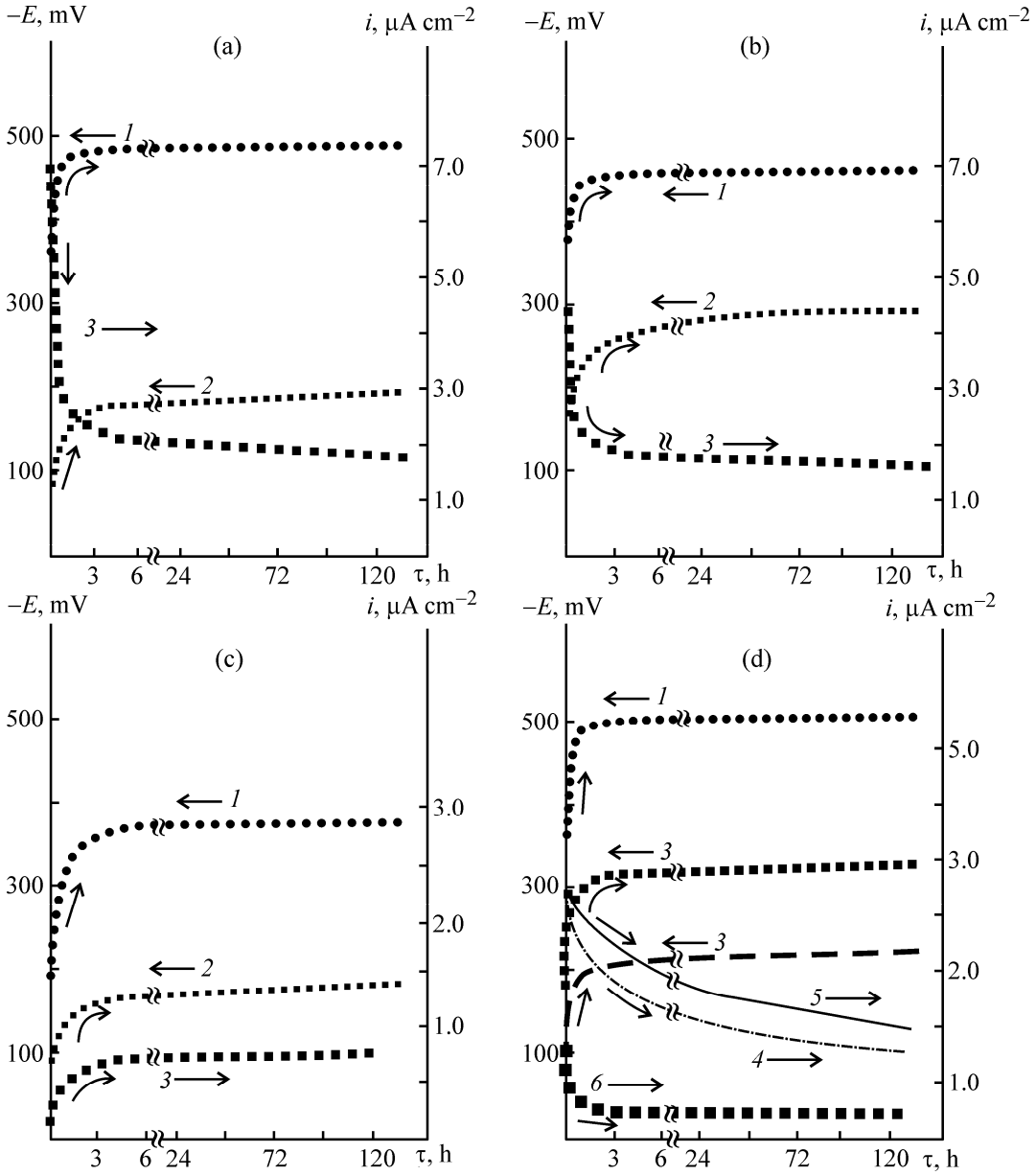

Fig. 3. Kinetic dependences of the electrode potentials E and current densities i for various systems in ethylene glycol containing 5% of water. (τ) Time. (a) (*1*) aluminum, (*2*) steel, and (*3*) current density in the aluminum + steel contact pair; (b) (*1*) aluminum, (*2*) cast iron, and (*3*) current density in the aluminum + cast iron contact pair; (c) (*1*) cast iron, (*2*) steel, and (*3*) current density in the steel + cast iron contact pair; (d) (*1*) aluminum, (*2*) steel, (*3*) cast iron, and (*4–6*) current density in the contact pairs constituted by (*4*) steel + cast iron, (*5*) aluminum + cast iron, and (*6*) aluminum + steel in the aluminum + steel + cast iron short-circuited system; the same for Fig. 4.

solution with 30% of water and by more than an order of magnitude in a solution containing 5% of water.

At a water content of 5 and 30% in ethylene glycol, the mass of steel in the steel + aluminum and steel + cast iron contact pairs and in the steel + aluminum + cast iron ternary system remains constant, i.e., steel is not subjected to uniform corrosion (see table). The kinetic curves describing the variation of the electrode potentials of the metals in the contact systems under consideration (Figs. 3, 4) account for the observed behavior of steel. It can be seen in Figs. 3 and 4 that steel is under a cathodic protection by aluminum or cast iron in the steel + aluminum and steel + cast iron pairs or by both the metals simultaneously in the steel + aluminum + cast iron system.

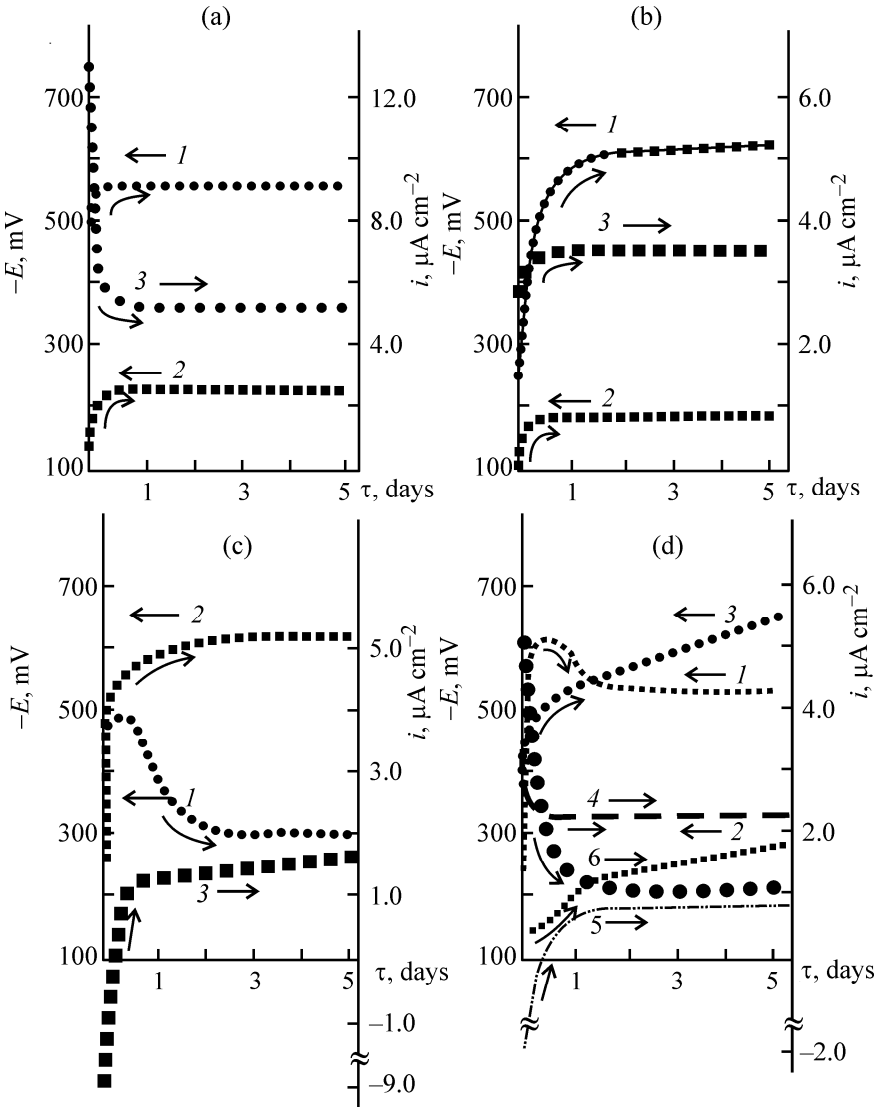

Fig. 4. Kinetic dependences of the electrode potentials E and current densities i for various systems in ethylene glycol containing 30% of water. (τ) Time.

In contrast to steel, aluminum shows different types of behavior in 5 and 30% aqueous–glycolic solutions: in the 5% solution, a change in its mass was only observed in the ternary steel + aluminum + cast iron system, whereas an increase in the content of water to 30% led to dissolution of aluminum in the steel + aluminum pair at a rate of 0.003 g m^{-2} h^{-1}.

In anodic polarization of aluminum, its dissolution is accompanied by oxidation under the action of water present in the solution. In a solution with 30% of water, the dissolution rate somewhat exceeds the rate of oxidation. At a lower content of water in the solution (5%), the rates of both the processes are comparable, probably because of the high content of ethylene glycol, and the sensitivity of the balance is insufficient for detecting their difference. The dissolution of aluminum in the contact system steel + aluminum + cast iron in an EG solution containing 5% of water may be due to a pronounced anodic polarization of aluminum by both steel and cast iron (Fig. 3d). However, no indications of pitting corrosion of aluminum were observed in any of the contact systems considered.

Cast iron was found to be the most corrosion-unstable under the conditions used in the study (see table). It was not subjected to corrosion only in ethylene glycol containing 5% of water in the cast iron + aluminum pair and steel + aluminum + cast iron

system. In the rest of the cases, cast iron was corroded. The reason for this difference becomes clear upon analysis of Figs. 3b, 3d. It can be seen that, similarly to steel, cast iron is cathodically protected by aluminum.

The type of variation of the electrode potentials and current densities in the steel + cast iron pair (Figs. 3c, 4c) shows that the main reason why cast iron corrodes when in contact with steel is its considerable anodic polarization by steel. In this case, the corrosion loss by cast iron linearly increases with time (Fig. 2, straight line *2*; Fig. 5, curve *3*), its corrosion rate grows with the content of water in ethylene glycol (see table).

In ethylene glycol containing 30% water, cast iron dissolves in the aluminum + cast iron contact pair (Fig. 5, curve *2*), with the mass of the aluminum electrode slightly increasing. The very fact of corrosion of cast iron and the increase in the corrosion rate are due to a change in the sign of cast iron polarization by aluminum, which is indicated by the change of the direction of the corrosion current (Fig. 4b).

In the steel + aluminum + cast iron contact system placed in ethylene glycol containing 30% of water (Fig. 4d), the cast iron is cathodically protected by aluminum during the first 24 h of experiment, despite the anodic polarization resulting from the contact with steel, which decelerates the corrosion of cast iron (Fig. 5, curve *4*). Then, aluminum becomes an increasingly noticeable cathode for cast iron (Fig. 4d) and accelerates its dissolution to the point of steady-state values. The considerable difference in corrosion behavior between cast iron and steel is probably due to the specific "graphitizing" selective corrosion of the former, in which graphite inclusions uncovered in ferrite dissolution form an increasingly developed system of microcathodes and, accordingly, accelerate the dissolution of the ferrite phase to an increasing extent.

Comparison of the results of this study with the corrosion behavior of the metals under study in an aqueous solution [1] can reveal the effect of the composition of the solutions studied on the corrosion processes.

It follows from the data in the table that passing from aqueous electrolytes to ethylene glycol electrolytes containing 5 and 30% of water results in a complete termination of the uniform corrosion of steel in all the contact systems studied. As regards the corrosion behavior of cast iron and aluminum, it was found that such a transition results in the absence of corrosion in some cases, or its substantial deceleration

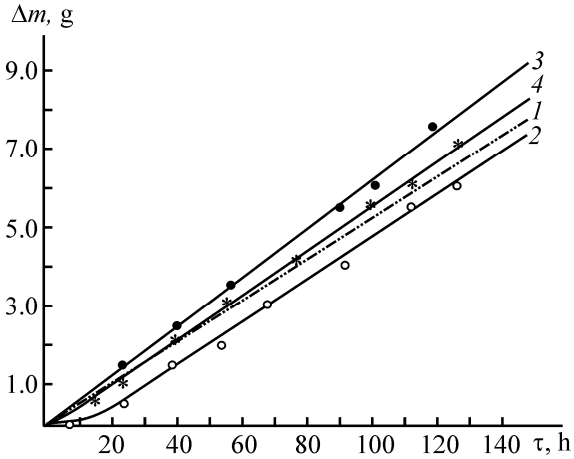

Fig. 5. Corrosion loss Δm by cast iron in various contact systems vs. the test duration τ in ethylene glycol solutions containing 30% of water. (*1*) Without contact, (*2*) cast iron + aluminum, (*3*) cast iron + steel, and (*4*) aluminum + steel + cast iron short-circuited system.

in others. Owing to the presence of an oxide film on its surface, aluminum submerged in water is a cathode with respect to both the ferrous metals, which leads to loss of continuity by the oxide film and to subsequent dissolution of aluminum via chemical interaction of the metal with water. Such a behavior of aluminum in water fundamentally differs from that in concentrated aqueous solutions of ethylene glycol, in which aluminum undergoes anodic dissolution.

The increase in the mass of aluminum, almost the same in an aqueous electrolyte and aqueous solutions of ethylene glycol, can be probably attributed to the low content of water, which is only sufficient for a discontinuous film of hydrated aluminum oxide $Al_2O_3 \cdot nH_2O$ ($n \geq 0$) to be formed [1, 6]. No changes in the mass of aluminum were observed under similar conditions in nonaqueous ethylene glycol.

The high corrosion resistance of steel in the electrochemical systems under consideration, as well as the absence of any signs of corrosion of aluminum and cast iron in some systems and a substantial decrease in the corrosion rate in others (compared with water), are possible due to a change of the structure of the electrical double layer upon adsorption of ethylene glycol. Owing to the planar arrangement on the electrode surface, its molecules can form a dense screening film [7], which can presumably hinder the corrosion process [8, 9]. The outer layer of iron and aluminum oxides can become thicker via incorporation of ethylene glycol molecules. As a result, a denser layer is formed, which, together with the planarly

oriented adsorbed layers of ethylene glycol, effectively prevents disruption of the passive state of the metal [10].

CONCLUSIONS

(1) At a water content of 5 vol % in ethylene glycol, aluminum behaves in all the aqueous-glycolic solutions studied as an anode with respect to steel and cast iron, but is subjected to anodic dissolution only in the steel + aluminum + cast iron contact system. The pair steel + cast iron is the most corrosion-hazardous in such a solution. For this pair, the corrosion rate of cast iron is higher than that in other systems in this solution, but is an order of magnitude lower than that in an aqueous electrolyte.

(2) In ethylene glycol solutions containing 30 vol % of water, cast iron behaves in all the systems studied as an anode with respect to both steel and aluminum, which enhances its corrosion, whereas neither steel, nor aluminum corrode when in contact with cast iron. Cast iron undergoes the strongest corrosion disintegration in contact with steel. Aluminum also anodically dissolves when in contact with steel.

(3) The aqueous ethylene glycol solutions studied are inert toward steel, and this markedly differs from its corrosion behavior in water. Aluminum dissolves under an external anodic current in ethylene glycol solutions and under a cathodic current in an aqueous electrolyte. Cast iron is the least corrosion resistant in a diluted ethylene glycol, although its dissolution rate in water is substantially higher.

(4) The difference in the types of behavior of the metals tested in aqueous and aqueous-glycolic solutions can be attributed both to the specific state of the iron surface in water and to structural changes in the electrical double layer upon adsorption of ethylene glycol, whose molecules can form a dense protective film owing to their planar arrangement on the electrode surface.

REFERENCES

1. Esenin, V.N. and Denisovich, L.I., *Zashch. Met*., 2007, vol. 43, no. 4, p. 1.
2. Sukhotin, A.M., Kazankina, A.F., and Zaretskaya, L.V., *Khim., Tekhnol. Topl. Masel*, 1977, no. 7, p. 55.
3. RF Patent 2083646.
4. GOST (State Standard) 28084–89, *Low-Freezing Cooling Fluids: General Technical Specifications*, Moscow: Izd. Standartov, 1989.
5. RF Patent 2241784.
6. Korshunov, V.N. and Sviridova, L.P., *Elektrokhimiya*, 1991, vol. 27, p. 1226.
7. Dzhaparidze, Dzh.I., *Elektrokhimiya*, 1977, vol. 13, no. 5, p. 668.
8. Kuznetsov, Yu.I., Oleinik, S.V., and Rozenfel'd, I.L., *Elektrokhimiya*, 1981, vol. 17, p. 942.
9. Veselyi, S.S. and Kuznetsov, Yu.I., *Zashch. Met*., 1994, vol. 30, p. 479.
10. Kuznetsov, Yu.I., Veselyi, S.S., and Oleinik, S.V., *Zashch. Met*., 1992, vol. 28, no. 1, p. 88.