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APPLIED ELECTROCHEMISTRY
AND CORROSION PROTECTION OF METALS

Contact Corrosion of Metals in Aqueous-Glycolic Solutions with High Content of Water

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Abstract—Corrosion behavior of aluminum, steel, and cast iron in aqueous-glycolic solutions containing 5 to 50 vol % was studied both in the absence of contact and in aluminum–steel, aluminum–cast iron, steel–cast iron, and aluminum–steel–cast iron contact systems.

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This study continues systematic analysis of the contact corrosion of aluminum, steel, and iron alloys in aqueous and aqueous-glycolic media in order to determine the influence exerted by the composition of an aqueous-organic solution on the corrosion process. Previously, a study of the corrosion of these metals in an aqueous medium and in solutions with content of ethylene glycol (EG) has been reported [1]. The present communication reports the results of a study of the corrosion behavior of separate metals and aluminum–steel, aluminum–cast iron, steel–cast iron, and aluminum–steel–cast iron contact systems in ethylene glycol solutions containing 5–50 vol % water. The metals and the composition of the aqueous–organic solution were chosen because these metals are the main construction materials in modern liquid-cooling systems and, in particular, internal combustion engines, as well as in various heat-exchange apparatus, and formulations based on solutions with high content of water in ethylene glycol are used as heat-carriers in regions with moderate and warm climate.

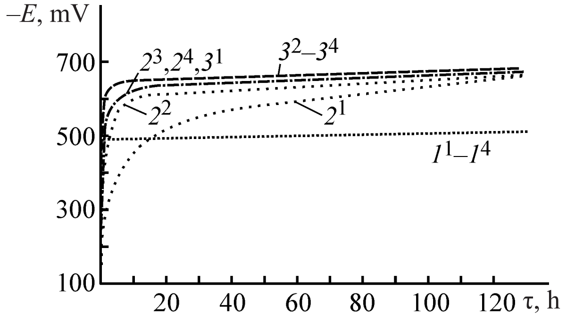

Fig. 1. Potentials E of the metals in the absence of contact vs. the testing time τ in aqueous solutions of ethylene glycol. Metal: (1^{1-4}) aluminum, (2^{1-4}) steel, and (3^{1-4}) cast iron. EG content (%) (1^1–3^1) 50, (1^2–3^2) 30, (1^3–3^3) 15, and (1^4–3^4) 5.

It should be noted that reports devoted to the behavior of electrochemically dissimilar metals in aqueous-organic media of various compositions are scarce [2–4], which makes the present study topical.

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].

In the absence of contact between the metallic samples in 5–50% aqueous-glycolic, the potential of aluminum remains nearly unchanged in the course of time (–0.48 to –0.51 V), whereas the potentials of steel and cast iron shift to more negative values (Fig. 1), which is apparently due to the gradual dissolution of these metals. In this case, the higher the water content of a solution, the faster the shift of the potentials. According to results of gravimetric measurements, the corrosion loss by steel and cast

Table 1. Steady-state corrosion rates V_{st} of aluminum, steel, and cast iron in purely aqueous and aqueous-glycolic solutions of various compositions

Metal	V_{st}, g m^{-2} h^{-1}, at indicated H_2O content, vol %				
	50	70	85	95	100
Aluminum, steel, and cast iron (without contact)					
Steel	0.020	0.032	0.045	0.063	0.068
Cast iron	0.033	0.041	0.051	0.064	0.074
Aluminum	0.0	0.0	0.0	0.0	0.0
Aluminum–steel–cast iron (in contact)					
Steel	0.032	0.044	0.056	0.064	0.082
Cast iron	0.040	0.050	0.064	0.078	0.112
Aluminum	0.0	0.0	0.0	0.0	0.013

iron in a 50% ethylene glycol solution linearly increases with the experiment duration, and in 5–30% solutions, the corrosion rates are the highest in the initial stage (as in aqueous solutions [1]), which also corresponds to the most pronounced change in the potentials of these metals (Figs. 1, 2), and then decrease to reach the limiting value (Table 1). However, in the case of aluminum, a slight increase in the sample mass is observed and traces of the pitting corrosion appear for all the solution compositions studied. It can be seen in Table 1 that, on passing from aqueous solutions to 50% aqueous EG, the corrosion rate steadily decreases by a factor of 2 for cast iron and by more than a factor of 3 for steel.

The corrosion behavior of the polymetallic contact system aluminum–steel–cast iron in the aqueous solutions of EG was found to be rather complex. It can be seen in Fig. 3 that the kinetic curves of corrosion loss by steel in 5 and 50% solutions (curves *1, 1'*) have three different portions, two of which are linear[a]. In the initial stage, the corrosion rates are substantially lower than those in the absence of contact (Figs.2a, 3). As the time of steel testing in aqueous-glycolic solutions becomes longer, the corrosion rates sharply increase and, having reached a maximum, remain constant afterwards.

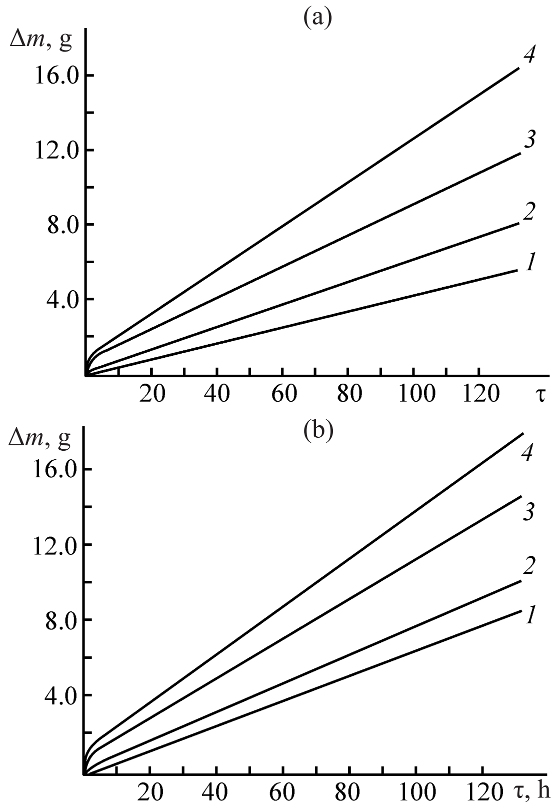

Fig. 2. Corrosion loss Δ*m* by (a) steel and (b) cast iron in the absence of contact vs. the testing time τ in aqueous solutions of ethylene glycol of various compositions. EG content: (*1*) 50, (*2*) 30, (*3*) 15, and (*4*) 5.

The kinetic curves of corrosion loss by cast iron (Fig. 3, curves *2* and *2*') differ from those for steel. In the initial portion, the corrosion rates of cast iron are the highest and exceed those in the absence of contact with other metals. Making longer the testing time of cast iron in aqueous-glycolic solutions leads to a decrease in the corrosion rates to their steady-state values. It is important to emphasize that an increase in mass was observed for aluminum in all the solution compositions with EG, whereas in water, aluminum dissolved and the corrosion loss by steel and aluminum was more pronounced. (Table 1).

To understand the contact corrosion in the polymetallic system aluminum–steel–cast iron in 5–50% aqueous solutions of EG, it was necessary to analyze the corrosion behavior of simpler systems: aluminum–steel, aluminum–cast iron, and steel–cast iron contact pairs.

In a study of the corrosion behavior of the aluminum–steel contact pair in a 50% solution of EG, anodic dissolution of aluminum occurred at a rate of

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[a] This and succeeding figures show kinetic curves of metal dissolution only in 5 and 50% solutions of EG in water, because the corresponding curves for 5, 15, and 30% solutions are similar and are arranged in the same order as that in the absence of contact between the metals studied (Fig. 2).

Table 2. Steady-state corrosion rates V_{st} of aluminum, steel, and cast iron in various contact systems in purely aqueous and aqueous-glycolic solutions

Metal	V_{st}, g m^{-2} h^{-1}, at indicated H_2O content, vol %				
	50	70	85	95	100
Aluminum–steel					
Steel	0.038	0.049	0.069	0.083	0.088
Cast iron	–	–	–	–	–
Aluminum	0.0	0.0	0.0	0.0	0.012
Aluminum–cast iron					
Steel	–	–	–	–	–
Cast iron	0.045	0.062	0.080	0.100	0.105
Aluminum	0.0	0.0	0.0	0.0	0.010
Steel–cast iron					
Steel	0.018	0.033	0.043	0.048	0.062
Cast iron	0.036	0.042	0.066	0.085	0.123
Aluminum					

0.002 g m^{-2} h^{-1} during 24 h and then became slower and was accompanied by a slight increase in mass. In 5–30% aqueous solutions of EG, only a slight increase in the mass of aluminum was observed during the whole experiment. In this pair, the kinetic curves of corrosion loss by steel are strongly different at different compositions of the aqueous-glycolic solution. In 50% EG, the dissolution of steel first decelerates and then becomes faster, whereas in 5–30% EG solutions, as well as in purely aqueous electrolytes, the opposite kinetic pattern is observed (Fig. 4a). In addition, the steady-state corrosion rate of steel in the aqueous electrolyte exceeds similar parameters for aqueous ethylene glycol. Comparison of the data obtained with the kinetics of variation of the electrode potentials of aluminum and steel (Fig. 1) suggests the following course of the corrosion process. In a 50% solution of EG, in the initial stage, while the potential of steel is more positive than that of aluminum (Fig. 1, curves *1* and *2*), aluminum behaves as the anode, and steel, as the cathode. This is confirmed by the zero corrosion of steel and by a decrease in the mass of aluminum. After 15–17 h of tests, the electrochemical potentials of

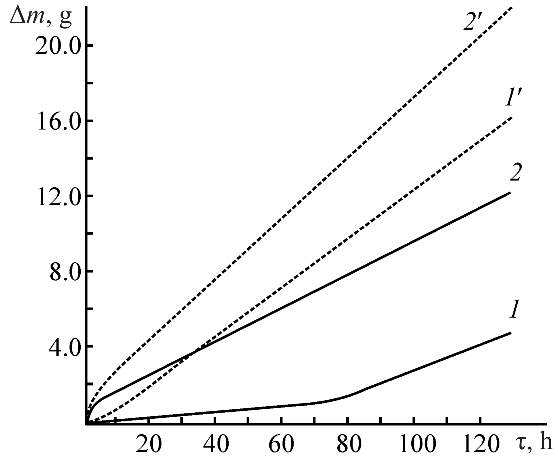

Fig. 3. Corrosion loss Δ*m* by (*1, 1*′) steel and (*2, 2*′) cast iron in the contact system aluminum–steel–cast iron vs. the testing time τ in (*1*′, *2*′) 5 and (*1, 2*) 50% aqueous solutions of ethylene glycol.

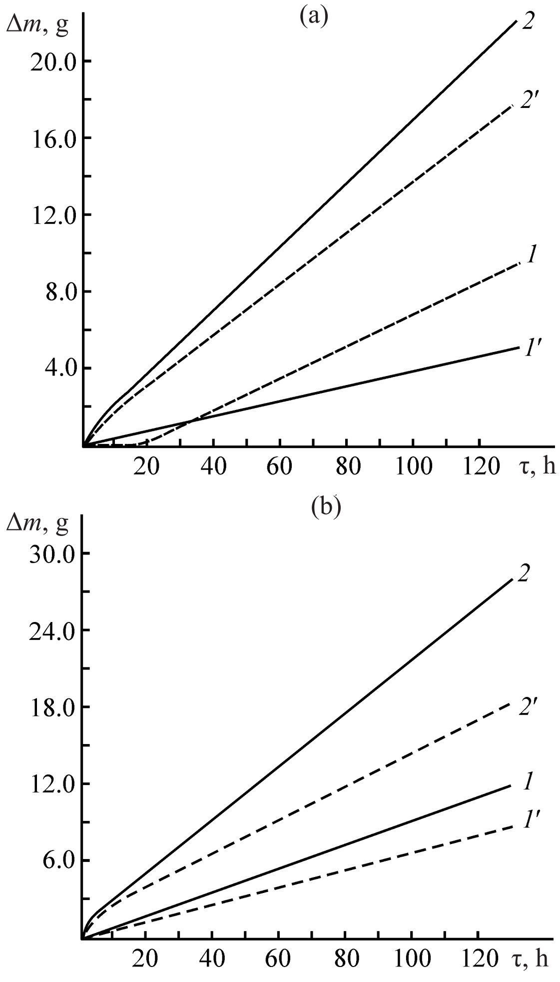

Fig. 4. Corrosion loss Δ*m* by (a) steel in the steel–aluminum contact pair and (b) cast iron in the cast iron–aluminum contact system vs. the testing time τ in (*1*) 50 and (*2*) 5% aqueous solutions of ethylene glycol.

steel and aluminum equalize (Fig. 1, intersection point of curves *1* and 2^{1}), after which an active dissolution of steel begins (the corrosion rate of steel is two times that in the absence of electrical contact, Table 2). In this case, no decrease in the mass of aluminum is observed, i.e., aluminum starts to behave as the cathode, and steel, as the anode. In 5–30% solutions of EG, the potentials of the metals under consideration are equalized in a substantially shorter interval of time, 0.5 to 4 h for 5% and 30% EG, respectively (Fig. 1, intersection points of curves *1* and 2^{2-4}). For this reason, steel almost immediately starts to experience anodic polarization by aluminum, which, in the end, leads to a change in the kinetics of its dissolution, compared with the 50% solution.

It was found in a study of the aluminum–cast iron contact pair (Fig. 4b) that the corrosion loss by cast iron in a 50% EG solution linearly depends on the testing time, whereas in 5–30% solutions, their corrosion rates, being the highest in the initial portion, decrease to steady-state values (Table 1). The reason for the more intense corrosion of cast iron is its anodic polarization appearing as a result of its contact with aluminum: it can be seen in Fig. 1 (curves 1 and 3^{1-4}) that the potential of cast iron rapidly (during 15 min after the beginning of an experiment) becomes more negative than the potential of aluminum. Comparison of the types of behavior of the aluminum–cast iron pair in the EG solutions studied and in water shows (Table 2) that the corrosion rate of cast iron decreases by a factor of 2.5 upon an increase in the EG content to 50%. It should also be noted that a slight increase in the mass of aluminum was observed in 5–50% aqueous-glycolic solutions, with no traces of its pitting corrosion revealed, similarly to the steel–aluminum pair.

A considerably more complex behavior was observed in a study of the steel–cast iron contact pair (Fig. 5). The kinetic curves of corrosion of metals in this pair clearly show three portions with different metal dissolution rates. In the initial portion, at a rather large potential difference between the metals (ΔE = 0.2–0.3 V) (Fig. 1, curves *2* and *3*), no steel dissolution is observed, whereas the corrosion rate of cast iron is the highest. Then, the corrosion rate of steel gradually starts to increase, and that of cast iron, to decrease, and finally, at a potential difference of 0.01–0.02 V between the metals, the corrosion rates of the metals reach their steady-state values (Table 2). It can be seen in Table 2 that, even in strongly diluted aqueous-glycolic solutions (5% EG), the corrosion rate of the metals in the steel–cast iron pair is 1.5 times lower than that in water.

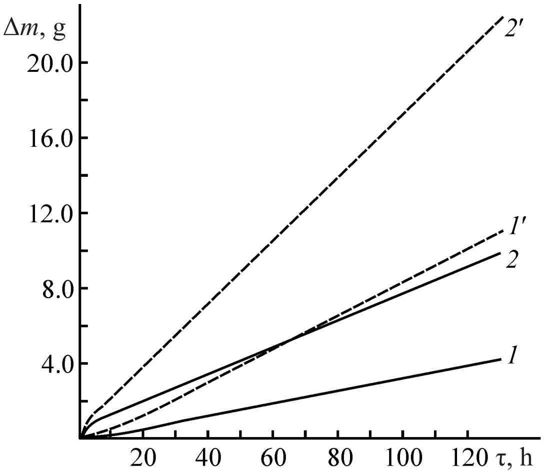

Fig. 5. Corrosion loss Δm by (*1, 1*′) steel and (*2, 2*′) cast iron in the steel–cast iron contact pair vs. the testing time τ in (*1*′, *2*′) 5 and (*1, 2*) 50% aqueous solutions of ethylene glycol.

The results obtained enable interpretation of the kinetic curves of metal dissolution in the polymetallic contact system steel–cast iron–aluminum (Fig. 3). At the beginning of a run, steel is under cathodic protection by aluminum and cast iron and dissolves at the minimum rate. At that same time, cast iron behaves as anode with respect to both steel and aluminum, which predetermines the maximum rate of its corrosion. Further the dissolution rate of steel starts to gradually increase, because steel experiencing anodic polarization by aluminum still remains under cathodic protection by cast iron. And finally, when the potentials of steel and cast iron become nearly equal, the dissolution rates of both metals experiencing anodic polarization by aluminum become closer (Fig. 3).

These results demonstrate that contact with aluminum makes the corrosion rates of steel and cast iron higher both in the polymetallic system and in the aluminum–steel and aluminum–cast iron contact pairs, with aluminum not subject to pitting corrosion. The considerable difference of the corrosion behavior of cast iron from that of steel can probably be attributed to appearance in cast iron of contact pairs between iron and carbon-containing compounds of iron, and also between iron and graphite formed in graphitization of cast iron.

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

Passing from purely aqueous electrolytes to aqueous-glycolic solutions with an EG content of 5 to 50% results in a slower corrosion in all the contact systems studied. It can be seen in Table 1 that, as the content of EG in an aqueous-glycolic solution increases, the corrosion rates of the metals steadily decrease. In this case, aluminum in water behaves as a cathode with respect to both ferrous metals, which leads to reduction of its protective oxide film and subsequent dissolution via chemical interaction of aluminum with water. Such a behavior of aluminum in water differs from that in the aqueous solutions of ethylene glycol, in which, also behaving as a cathode with respect to steel and cast iron, it is not dissolved. Somewhat different is the behavior of aluminum in the pair with steel in a 50% EG, where aluminum undergoes anodic dissolution during a short time.

An increase in the mass of aluminum was observed in 15–50% solutions of EG for all the systems studied. Probably, this can be attributed to formation of surface films of hydrated aluminum oxide $Al_2O_3 \cdot nH_2O$ ($n \geq 0$) [1, 5] and metallic iron that passes from solution to the surface via cathodic reduction of Fe^{2+} cations by aluminum.

The substantial decrease in the corrosion rate of steel and cast iron and also the absence of indications of a uniform corrosion of aluminum in all the electrochemical systems under consideration in aqueous solutions of ethylene glycol (compared with water) are probably due to a change in the structure of the electrical double layer upon adsorption of ethylene glycol. Owing to their planar arrangement on the electrode surface, ethylene glycol molecules can form a dense shielding film [6], which presumably can hinder the corrosion process [7, 8].

The increase in the corrosion rate of the metals on making higher the content of water in the aqueous-glycolic solutions considered can be attributed to the fact that, instead of dense outer iron oxide layers formed via incorporation of EG molecules [9], the surface of these metals starts to be predominantly covered by three-layer surface phases of aqua-oxide-metallic nature [1, 10, 11]. This disturbs the passive state of the metals. In addition, the influence of free water molecules which are yet unbound into dense multilayer structures and, therefore, act as corrosive agents starts to be important in dilute EG solutions (5–30%) in early stages of corrosion of steel and cast iron. It is the interaction of monomeric water molecules with the surface of iron that predetermines the higher initial corrosion rates of the metals, compared with those in the steady state in these solutions (Fig. 2, curves *2–4*) and in water [1].

CONCLUSIONS

(1) In all the aqueous-glycolic solutions studied, aluminum behaves as a cathode with respect to steel and cast iron and is not corroded. The observed behavior of aluminum is due to the appearance of a surface film largely composed of hydrated aluminum oxide. The most corrosion-hazardous systems are the aluminum–steel and aluminum–cast iron contact pairs, in which the corrosion rates of steel and cast iron in the solutions studied are the highest, compared with other systems, but are lower than those in water.

(2) The difference between the corrosion behavior of the metals tested in purely aqueous solutions and that in 5–50% aqueous-glycolic solutions can be attributed both to specificity of the surface state of iron in water and to a change in the structure of 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.

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