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## Abstract

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# On Thermogalvanic Corrosion of Metals

*(Presented by Academician A. N. Frumkin on November 4, 1961)*

A temperature difference, as is known, may serve as one of the causes of differentiation of a metal surface into anodic and cathodic regions and of the thermogalvanic corrosion associated with this ([1,2]). In this case, according to the accepted point of view, the heated regions of the surface are considered anodic, while the cold regions perform the function of cathodes of the thermogalvanic cell. In accordance with such a distribution of polarity, corrosion damage should be concentrated in the zone of elevated temperature. There are definite grounds in favor of this view, confirmed by a number of examples from the practice of operating metallic structures in the presence of a temperature gradient. An increase in temperature is accompanied, as a rule, by an overall increase in the rate of corrosion, provided that such side phenomena do not occur as a decrease in the solubility of oxygen or a change in the structure and protective properties of the oxide film ([1,3]). At the same time, a shift of the potential of the corroding metal toward negative values is observed, which indicates a relatively greater depolarization of the anodic process in comparison with the cathodic one.

Model experiments carried out by us on a number of pure metals and certain alloys, reproducing the operation of a thermogalvanic cell, show that under certain conditions a distribution of polarity directly opposite to that indicated arises. Consequently, the proposition that the more heated region of the metal must undergo corrosion damage cannot be regarded as obligatory. The essence of the experiments performed was as follows. The metal or alloy specimens under study, after preliminary preparation, were fastened in plastic stoppers at the ends of a quartz tube at a distance of 140 mm from one another. The upper part of the tube was placed in a tubular electric furnace, while the lower part was immersed in a bath with ice. In this way a temperature gradient of about 75° was produced between the upper and lower electrodes. To maintain a constant temperature and to regulate it, a small resistance thermometer was placed in the upper part of the quartz tube, connected into the circuit of an electronic regulator associated with the electric furnace. The proposed construction of the thermogalvanic-cell vessel, in addition to its simplicity, also has the advantage that it is distinguished by a small internal resistance in comparison with H-shaped vessels. At the same time, convective mixing of the liquid in it was insignificant, since the hot solution was placed above and the cold one below. The same cell model was also used for recording polarization curves on the electrodes

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

of the thermogalvanic cell, which was successively closed through increasing external resistance after a stationary value of the current in the external circuit had been established.

Figure 1 presents curves of the time dependence of the current in a thermogalvanic cell with iron-Armco electrodes in acidic, neutral, and alkaline solutions with one and the same anionic composition. The right-hand part of Fig. 1 gives an idea of the arrangement of the polarization

curves of the anode and cathode of such a cell. In acid and neutral solutions the hot electrode serves as the anode; consequently, the usual polarity of the corrosion couple is established, but in alkaline solution the situation changes and the cold electrode becomes the anode.

As the polarization diagrams show, the transition from acid solutions to alkaline ones in this case was accompanied by a substantial increase in the degree of anodic control, owing to the increasing inhibition of the anodic process.

**Fig. 1.** Change in the current strength of thermogalvanic cells on Armco iron with time and the corresponding polarization diagrams:
1 –0.1 $N$ $H_2SO_4 + 0.9$ $N$ $K_2SO_4$; 2 –1 $N$ $K_2SO_4$; 3 –0.1 $N$ KOH + 1 $N$ $K_2SO_4$; 4 –1 $N$ KOH + 1 $N$ $K_2SO_4$. Solid lines –hot electrode, dashed lines –cold electrode.

**Fig. 2.** Change in the current strength of thermogalvanic cells on Kh13 steel with time and the corresponding polarization diagrams:
1 –0.1 $N$ $H_2SO_4 + 0.9$ $N$ $K_2SO_4$; 2 –1 $N$ $K_2SO_4$; 3 –0.1 $N$ KOH + 1 $N$ $K_2SO_4$. Solid lines –hot electrode, dashed lines –cold electrode.

This circumstance suggested that the appearance of "anomalous" polarity in a thermogalvanic cell may be connected with the presence in the solution of passivating agents, whose action is manifested to a greater degree with respect to the hot electrode.

Table 1 gives the values of the current strength in a thermogalvanic cell on Armco iron and nickel in solutions, some of which contained an addition of passivating agents—potassium dichromate and caustic potash. These data confirm the observations made on pure iron. If the nature of the metal is such that it has a greater tendency to passivation than pure iron, then thermogalvanic cells with "anomalous" polarity, as experiment shows, can arise in

Table 1

Current strength and polarity of thermogalvanic elements in various media

| Metal | Corrosive medium | Anode | $i$, $\mu$A/cm$^2$ |
|---|---|---|---|
| Iron-armco | $1N$ $K_2SO_4$ +<br>$0.04N$ $K_2Cr_2O_7$ | Cold | 2.2 |
| Steel type 18/8 | $1N$ $K_2SO_4$ | » | 0.3 |
| Steel type 18/8 | $0.1N$ $H_2SO_4$ +<br>$0.9N$ $K_2SO_4$ | » | 0.4 |
| Steel type 18/8 | $1N$ $H_2SO_4$ | Hot | 11.5 |
| Steel type 18/8 | $5N$ $H_2SO_4$ | Cold | 50.0 |
| Steel type 18/8 | $10N$ $H_2SO_4$ | » | 360.0 |
| Nickel | $0.1N$ $H_2SO_4$ +<br>$0.9N$ $K_2SO_4$ | Hot | 7.2 |
| Nickel | $1N$ $K_2SO_4$ | » | 4.0 |
| Nickel | $0.1N$ KOH +<br>$1N$ $K_2SO_4$ | Cold | 0.6 |
| Zirconium | $0.1N$ $H_2SO_4$ +<br>$0.9N$ $K_2SO_4$ | » | 0.1 |
| Zirconium | $1N$ $H_2SO_4$ | » | 0.15 |
| Zirconium | $5N$ $H_2SO_4$ | » | 0.4 |
| Zirconium | $10N$ $H_2SO_4$ | » | 0.6 |

solutions without any additions of passivators. An example is chromium steel Kh13, the data for which are given in Fig. 2. In an acid solution the hot electrode is the anode, but already in neutral and alkaline solutions steel Kh13 forms a thermogalvanic pair with "anomalous" polarity. Nickel, steel of the 18-8 type, and zirconium behave in a similar manner. The curves of the dependence of current strength on time show (Fig. 2) that such a distribution of poles is not established immediately after the electrodes are immersed in the solution. A certain time is required for reversal of polarity to occur.

The distribution of poles in a thermogalvanic element in such a way that the hot metal is the cathode in a pair with the cold one can be explained by the fact that the facilitation of the cathodic process with increasing temperature will be stronger than a similar influence on the anodic process. Therefore the stationary potential of the corroding metal on heating will shift in the positive direction, which also determines the appearance of a thermogalvanic element with "anomalous" polarity. In other words, in this case, with increasing temperature, a transition of the metal to a more deeply passive state is observed. The possibility of such a transition was shown for stainless steels by Ya. M. Kolotyrkin and co-workers (4). In Fig. 3 the passivation effect at elevated temperature is shown using the example of iron-armco in an alkaline solution.

Fig. 3. Change in the potentials of hot (1) and cold (2) iron-armco electrodes in a solution of $1N$ KOH + $1N$ $K_2SO_4$

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