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Abstract

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G. M. FLORIANOVICH and Ya. M. KOLOTYRKIN

THE INFLUENCE OF CHROMIUM CONTENT ON THE ELECTROCHEMICAL AND CORROSION BEHAVIOR OF IRON-CHROMIUM ALLOYS

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In the literature there is a widely held opinion that increasing the chromium content in Fe-Cr alloys leads to an increase in their corrosion resistance. At the same time, reference is often made to the existence of a definite limiting value of the chromium concentration, equal to 13%, exceeding which leads to an especially sharp decrease in the corrosion rate of the alloy.

The existence of such a limiting concentration is usually associated with Tammann's rule, according to which, for alloys, there exists a boundary composition, called by Tammann the "resistance boundary," beginning from which dissolution of the alloy in a medium aggressive with respect to one of the components practically ceases. In this connection, however, it is often overlooked that the position of the "resistance boundary" is not a single-valued function of the composition of the alloy, but also depends on the composition of the medium, as is indicated in Tammann's own works (^1).

The corrosion resistance of an Fe-Cr alloy also depends substantially on the composition of the medium. Thus, for example, it may be noted that for certain concentrations of sulfuric acid, the transition to alloys in which the chromium content exceeds the above-mentioned "limiting" value leads to a sharp decrease in the corrosion rate (^2). A similar observation was also made for a 65% solution of HNO_3, in which the dissolution rate of Fe-Cr alloys containing at the same time some amount of nickel increases noticeably with an increase in chromium content from 9.8 to 19.9% (^2). In other cases, however, the curve of the dependence of the alloy dissolution rate on the chromium content in it passes through a minimum, as, for example, occurs for Fe-Cr-Ni alloys in a mixture of sulfuric and nitric acids, where an increase in the chromium content of the alloy from 5 to 19% leads to a decrease, and from 23 to 27% to an increase in the corrosion rate (^3).

The question of the dependence of the position of the "resistance boundary" on the degree of aggressiveness of the medium was considered in the works of

Figure 1

Figure 1: Figure 1

a number of authors ([4,5]). However, to the present time there has been no satisfactory explanation of the experimental regularities indicated above.

In works carried out in our laboratory ([6]), it has been shown repeatedly that the most objective characterization of the corrosion and electrochemical behavior of metals and alloys can be obtained by means of the potentiostatic method of investigation. This method, especially when combined with one of the methods for direct determination of the dissolution rate, makes it possible to evaluate the corrosion characteristics of metals or alloys at different potentials and, consequently, in different states of the metallic surface—active, passive, or transpassive. Since the magnitude of the electrode potential and, consequently, the state of the metallic surface of an alloy depend substantially on its composition and on the composition and concentration of the solution, such a method makes it possible to characterize most fully the corrosion behavior of a metal as a function of these parameters of the system.

In the present work, the potentiostatic method, in combination with a colorimetric method for determining the concentration of corrosion products in solution, was used by us to evaluate the effect of chromium content on the corrosion behavior of iron–chromium alloys. Measurements were carried out in a 0.1 N solution of sulfuric acid in a nitrogen atmosphere. The specified potential values were maintained by means of an electronic potentiostat. Curves of the dependence of the steady dissolution rate on potential were obtained for pure iron of the Armco and Hilger grades, as well as for binary Fe–Cr alloys (prepared from Armco iron and 99.9% chromium) with Cr contents from 0.1 to 35%, and for Fe–Cr alloys of grades 12Kh6, 1Kh13, Kh17, and Kh28, containing, in addition to chromium, up to 0.4% Ni.

Fig. 1. Dependence of the steady dissolution rate of Fe–Cr alloys with different chromium contents on potential: 1 –0.1%; 2 –4%; 3 –8%; 4 –12%; 5 –20%; 6 –27%; 7 –35%; 8 –cathodic curves

The curves obtained are shown in Figs. 1 and 2. For some potential values, the dissolution rates of the alloys corresponding to different sections of these curves were also determined directly, i.e., by analyzing the solutions for dissolution products. In the range of potentials lying more positive than the steady-state potential and more negative than +1.5 V vs. the hydrogen electrode, the data obtained in this way coincided with the measured current values.

As in our earlier investigations with other metals and alloys, the curves obtained in the present work for the dependence of the steady dissolution rate of alloys on potential are generally characterized by the presence of several regions (Fig. 1): active dissolution (AB), the first limiting current (BC), passivation (CD), the passive state (DE), transpassivation (EF), and the second limiting current

Figure 2

Figure 2: Figure 2

(FG). The section of the curve GH following the FG region corresponds to an increase in the dissolution rate as the positive potential increases, i.e., it is a region of activation of the alloy. This is shown using alloy Kh17 as an example, for which dissolution rates over the entire potential range were determined by the analytical method (Fig. 2, 5).

Fig. 2. Cathodic (1) and anodic (2-6) potentiostatic curves, measured for Fe (2) and alloys of grades: 3 –12Kh6, 4 for 1Kh13; 5 –Kh17; 6 –Kh28

As can be seen from Fig. 2, anodic passivation of iron causes its dissolution rate to decrease, in comparison with the rate in the region of the first limiting current, by only one order of magnitude. Alloys with a low chromium content (up to 4%) undergo anodic passivation with still greater difficulty. At

curves for these alloys contain no passivation regions (Fig. 1, *1, 2). A further increase in the chromium content in the alloy has different effects on the character of the potentiostatic curves. Alloys containing less than 13% Cr, within the investigated range of potentials, are characterized by the absence of regions of transpassivation and of the second limiting current. In the curves for alloys with a chromium content of 13% and higher, the region of the first limiting current is absent. The principal difference consists in a sharp decrease (almost by three orders of magnitude) in the dissolution rate of the alloys in the passive state on going from alloys with a Cr content below 13% to alloys with 13% Cr and higher.

At the same time, the data obtained lead to the conclusion that there also exist such potential regions in which increasing the Cr content in the alloy leads not to a decrease, but to an increase in its dissolution rate.

This applies to the region of the second limiting currents (see Figs. 1 and 2), and also to the region of active dissolution, as is seen from Table 1, which gives the values of the stationary potentials and the corresponding self-dissolution rates of iron and Fe–Cr alloys.

Table 1

Cr content in Fe–Cr alloy, %	$-\varphi_{\text{stat}}$, mV (N.C.E.)	i_0, A/cm^2
0	560	$9 \cdot 10^{-5}$
0.1	560	$9 \cdot 10^{-5}$
4	570	$3 \cdot 10^{-4}$
8	580	$4 \cdot 10^{-4}$
12	600	$4 \cdot 10^{-4}$
20	620	$8 \cdot 10^{-4}$

Cr content in Fe–Cr alloy, %	$-\varphi_{stat}$, mV (N.C.E.)	i_0, A/cm^2
27	630	$7 \cdot 10^{-4}$
35	630	$7 \cdot 10^{-4}$

Thus, for Fe–Cr alloys, increasing the chromium content leads to an increase in the dissolution rate in sulfuric acid at potentials close to the stationary potential and more positive by 1 V with respect to the normal calomel electrode, and to its decrease at intermediate potential values–especially sharply on going from alloys with 12% Cr to alloys with 13% Cr.

It should be noted that the data we obtained for Fe and some of its alloys with Cr differ quantitatively from the data of Frank ([7]) for Fe and of Olivier ([8]) for Fe–Cr*, according to which the dissolution rates of Fe in 1 N H_2SO_4 and of its alloys with 2.8–18% Cr in 10% H_2SO_4 in the passive state, decreasing monotonically with increasing chromium concentration, have values below 10^{-5} A/cm^2.

The possible reasons for this discrepancy were indicated by us earlier ([9]). Here it is only necessary to emphasize that, in contrast to the conclusions we have drawn, Olivier' s data do not imply the existence of a limiting composition of Fe –Cr alloys that characterizes a sharp change in their corrosion resistance in any region of potentials. At the same time, the existence of such a composition for a number of media (expressed by the value 13% Cr) may be considered a firmly established fact. From the results we obtained it follows that the composition of an alloy cannot serve as an unambiguous characteristic of its dissolution rate. In order to judge the influence of a regular change in alloy composition on its corrosion behavior, it is necessary to use potentiostatic curves, from which one can determine the character of the change in the alloy dissolution rate as a function of its composition for each value of the potential.

The conclusions we have drawn are confirmed by the data of Sukhotin and Antonovskaya ([10]) and Pražák ([11]).

If it is assumed that the dissolution rates of alloys of a given composition are a single-valued function of the potential, then, in accordance with the results of ([6]), the potentiostatic curves measured in a given medium can be used to determine the self-dissolution rates of alloys in the same medium with any additives. For this it is sufficient to measure the stationary potentials in the corresponding solutions with additives. In this case,

* See also ([4]) and ([7]).

Of course, it should be borne in mind that some additives may affect the overvoltage of the anodic reaction or alter the limiting currents. In such cases, in the corresponding potential regions it is necessary additionally to carry out potentiostatic measurements in solutions with these additives.

For Fe–Cr alloys this applies, above all, to the region of the second limiting currents, for whose values at a given potential, both according to the data of (10) and according to the data obtained by us (which will be published separately), the composition of the solution is of very great importance.

It follows from this work that an explanation of Tammann' s rule is impossible without taking into account the values of the potentials of the alloy and its potentiostatic curve.

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