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journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	2
page range	209-215
year	1950
URL	http://hdl.handle.net/10097/26317

On the Inhibitor for the Corrosion by Hydrochloric Acid on High-Chromium Steels*

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(Received January 24, 1950)

Synopsis

The action of potassium dichromate as the inhibitor for the corrosion by hydrochloric acid on high-chromium steels was investigated. High-chromium steels were made passive by addition of proper quantities of potassium dichromate in various concentration of hydrochloric acid. But the action of potassium dichromate is cathodic control and anodic inhibitor, therefore, it is a very dangerous inhibitor. The minimum quantity of potassium dichromate required for the complete passive state was proportional to square of specific concentration of chromium in alloys. Molybdenum added to high-chromium steels, so far as it existed in solid solution, was very effective to lower the minimum quantity of potassium dichromate and to prevent perfectly pit or cavity corrosion on high-chromium steels. For instance, the minimum numerical value of potassium dichromate was 100 g per litre for the steel containing 33 per cent chromium, but 0.01 g per litre for the steel containing 33 per cent chromium and 3 per cent molybdenum in 10 per cent of hydrochloric acid. When high-chromium-molybdenum steels were in heterogeneous structure, they became very difficult to get passive state. Tungsten was not so effective as molybdenum with respect to the corrosion resisting properties of high-chromium steels.

I. Introduction

In the previous paper⁽¹⁾, one of the writers reported on the passivity of high-chromium steels in sulphuric acid by the addition of salts having oxidizing power. The more the chromium content increases the heavier the high-chromium steel is corroded by hydrochloric acid; this acid is most obstructive to the passivity and chromium becomes readily passive, therefore, it is deemed very interesting to study the passivity of high-chromium steels by oxidizing reagents in hydrochloric acid.

In the present paper, the experimental results on the relations between the chromium content of alloys, the hydrochloric acid concentration and the quantity of potassium dichromate as an oxidizing reagent with respect to the corrosion reaction velocities of high-chromium steels are reported.

II. Experimental

Specimens. Flodin iron, metallic chromium, metallic molybdenum and metallic tungsten were used as the materials of alloys. The materials were melted with an electric induction furnace. The melt was then casted into an iron mould.

* The 559th report of the Research Institute for Iron, Steel and Other Metals.

(1) H. Endô and S. Morioka. Nippon Gakujutu Sinkôkai the Report of the Fifth Comitee. No. 15 (1939).

The cast was forged to a rod and all specimens were heated for 1 hour at 1,050°C in a vacuum electric resistance furnace, then they were quenched into water or slowly cooled in the furnace.

The specimen used for the corrosion test was in the form of a round rod, 7 mm in diameter and 5 cm in length. The surface of the test-piece was polished with No. 0.4 emery paper. Commercial potassium dichromate and hydrochloric acid were used.

The corrosion test was carried out by the immersion method; the test piece was kept calmly with a glass hook at the center of the solution (350 cc in volume) in a glass bottle for 30 days at room temperature. Potassium dichromate was dissolved readily in hydrochloric acid, but it was difficult to dissolve more than 150 g per litre at room temperature.

1. Effect of concentration

When high-chromium steels were in the water quenched condition, the alloys were made passive by the addition of an adequate quantity of potassium dichromate in accordance with hydrochloric-acid-concentration.

(i) When x was definite, C_o increased nearly in proportion to the square of C_a .

(ii) When C_a was definite, C_o decreased nearly in reciprocal proportion to the square of x .

(iii) When x and C_a were both definite, C_o was extremely decreased by the addition of molybdenum in the range of 3 to 7 per cent to high-chromium steels, where C_a is the hydrochloric-acid-concentration, C_o is the minimum quantity of potassium dichromate required for the perfect passive state and x is the chromium specific concentration in high-chromium steels. These results are summarized in Table 1.

2. State of corrosion

(i) The general type of the relation between the quantities of potassium dichromate and the corrosion reaction velocities are as shown in Fig. 2, 3 and 4. Striking pit or cavity corrosion was produced on high-chromium steels close to the passive state.

Table 1. The minimum quantities (gram per litre) of potassium dichromate required for the complete passive state of high-chromium steels and high-chromium-molybdenum steels in hydrochloric acid at room temperature.

Concentration of HCl(%)	2	5	10	20	30
Specimen					
14% Cr Steel	30 (30)	× (188)	× (750)	×	×
20% Cr Steel	20 (15)	100 (90)	× (367)	×	×
33% Cr Steel	<15 (6)	<15 (34)	100 (138)	× (548)	×
20% Cr-7% Mo Steel			2	×	×
33% Cr-3% Mo Steel			0.01	1	10

Remarks: All specimens were water quenched from 1,050°C. The mark × shows that a complete passive state could not be obtained even in the saturated solution of potassium dichromate.

The values in the round brackets are calculated by the formula; $C_o = 0.165Ca^2/x^2$

(ii) Pit or cavity corrosion on high-chromium steels was perfectly prevented by the addition of molybdenum in the range of 3 to 7 per cent and by the water quenching.

(iii) The addition of tungsten to high-chromium steels was not so effective as molybdenum to prevent the local corrosion and the passivity.

(iv) In the case of 33 per cent of chromium and 3 per cent of molybdenum steel, it became frequently passive in hydrochloric acid of 10 per cent, without potassium dichromate after it was considerably corroded and the surface became very rough.

3. Effect of heat treatment

To make high-chromium-molybdenum steels passive, it was always necessary that the alloys were water quenched to be in solid solution. If high-chromium

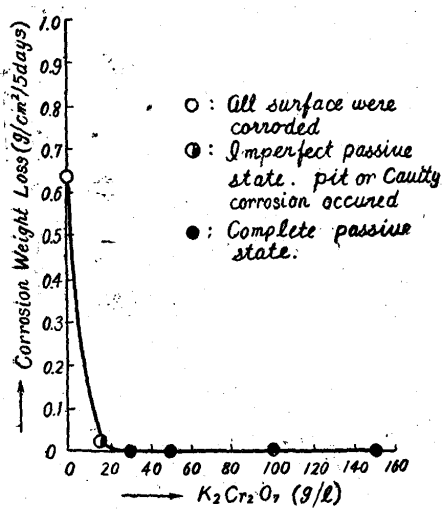


Fig. 1. 14% Cr Steel in 2% HCl solution.

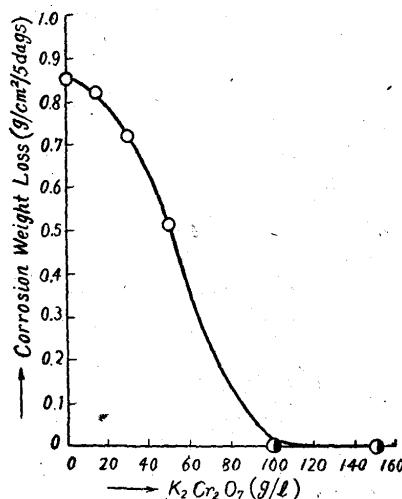


Fig. 2. 14% Cr Steel in 5% HCl solution.

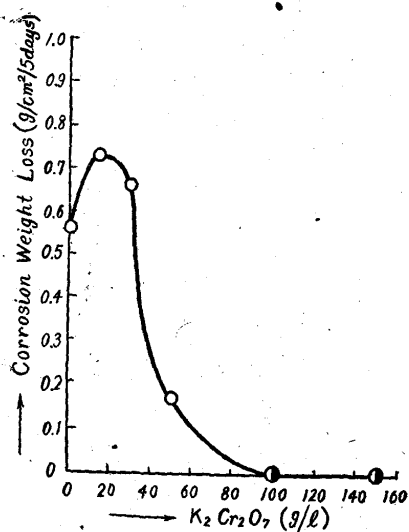


Fig. 3. 20% Cr Steel in 5% HCl solution.

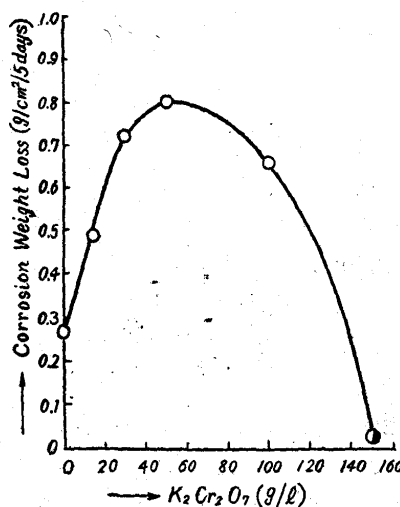


Fig. 4. 20% Cr Steel in 10% HCl solution

steels containing more than 7 per cent of molybdenum were slowly cooled in the furnace, the alloys became not only difficult to become passive but also the corrosion were stimulated by the addition of potassium dichromate in hydrochloric acid. The 20 per cent of chromium and 10 per cent of molybdenum steel could not be made passive even when the alloy was water quenched.

4. Effect of temperature

As a rule, the passive state of high-chromium steels by potassium dichromate in hydrochloric acid were broken in the range 30° to 40°C.

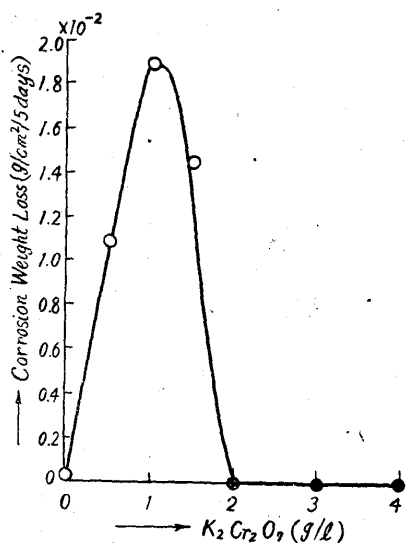


Fig. 5. 20% Cr-7% Mo Steel in 10% HCl solution.

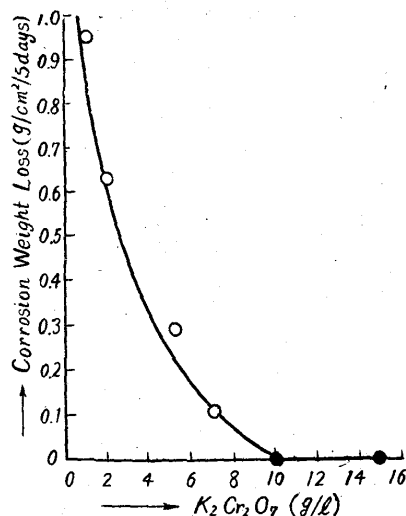


Fig. 6. 33% Cr-3% Mo Steel in 30% HCl solution.

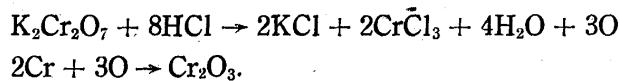
III. Discussion

The oxidizing action of potassium dichromate has two contrary influences on the corrosion of high-chromium steels in hydrochloric acid. Potassium dichromate suppresses the anodic reaction by the formation of metallic oxide film and, on the other hand, it accelerates the cathodic reaction by the action as the depolarizer. We also used hydrogen peroxide as the oxidizing reagent. The action of hydrogen peroxide was similar to that of potassium dichromate. When velocities of the two opposing reaction that the oxidizing reagent forms an oxide film and the acid destroys it are equal, alloys will be passive. Pure iron is not made passive in a dilute hydrochloric acid saturated by potassium dichromate, so the passivity of high-chromium steels will be chiefly due to chromium atoms. It is probable that chromium atoms are selectively oxidized, and then iron atoms near chromium atoms are made passive. We assume the elementary domain of passivity which consists of atoms having one or two chromium atoms as a center of passivity.

If the oxide film is in the form of Cr_2O_3 or Fe_2O_3 , alloys will become readily passive at the sites where pairs of chromium exist.

When chromium and iron atoms exist perfectly at random in alloys, the probability of finding the pairs of chromium atoms at the optional point of space

lattice is x^2 , where x is the specific concentration of chromium. The oxidizing action of potassium dichromate will be as follows.



The formation of oxide film will occur readily when the molecule of potassium dichromate collides with the pairs of chromium atoms, consequently the reaction velocities of oxide film formation v_0 will be as follows.

$$v_0 = K_0 x^2 C \quad (1)$$

where K_0 is a velocity constant, x is the specific concentration of chromium, and C is concentration of potassium dichromate. The activation reaction of oxide film by acid will be as follows. $\text{Cr}_2\text{O}_3 + 6\text{H}^+ + 6\ominus \rightarrow 2\text{Cr} + 3\text{H}_2\text{O}$.

The reaction velocities of activation v_a will be as follows by assuming that the reaction is of the second order with respect to hydrogen ions.

$$v_a = K_a C_a^2 \quad (2)$$

where K_a is a velocity constant, C_a is the concentration of hydrochloric acid.

When v_0 is equal to v_a , alloys will be passive, so we can derive the following relation from the formulas (1) and (2).

$$C_0 = \frac{K_a}{K_0} \frac{C_a^2}{x^2} \quad (3)$$

where C_0 is the minimum quantity of potassium dichromate required for the perfect passive state of high-chromium steels. The numerical value of K_a/K_0 calculated from the measured value on the steel containing 14 per cent of chromium in hydrochloric acid of 2 per cent is 0,165. Then we can get the following equation

$$C_0 = 0,165 \frac{C_a^2}{x^2} \quad (4)$$

The numerical value of C_0 calculated by the equation (4) [are put in the round brackets of Table 1.

We assume that the rate-determining step of the corrosion reaction is the process of the depolarization which is controlled by the diffusion of the oxidizing reagent and the anodic reaction is controlled by the surface area of bare metal. Accordingly, we put the following equation with respect to the corrosion reaction velocity V ,

$$V = K(K' + C)S \quad (5)$$

where K is a velocity constant, K' is a constant which is determined by the alloy constituents and hydrochloric acid concentration, and S is the surface area of bare metal.

There may exist many fissures on the metal surface, so the diffusion of the solute will be different at sites. The composition and the structure of alloys, of course, are not strictly uniform. We take an elementary domain of passivity as an unit of site. The diffusion velocity of hydrochloric acid is larger than that of potassium dichromate and hydrochloric acid attacks readily both iron and chromium, so we will consider only the nonuniformity due to potassium

dichromate in the reaction of passivity.

The value of S can be calculated by assuming that the distribution of the elementary passive domains can be represented as the arithmetical stochastic process⁽²⁾ with the concentration of potassium dichromate. Metals will become passive when v_0 is equal to v_a , so the probability for the existence of the passivified elementary domains may be shown as $\exp(-mc) \cdot (mc)^n / n!$, where c is the potassium dichromate concentration, m is the number of metal atoms which can be made passive at a site when c is unity on the average, and $n = mc_0$.

The above mentioned probability between c and $c + dc$ will be $\exp(-mc) \cdot (mc)^{n-1} / (n-1)! \cdot m dc$, accordingly, the probability for the existence of the elementary domains which are not yet made passive at c is as follows.

$$P = \frac{\int_c^\infty e^{-mc} \frac{(mc)^{n-1}}{(n-1)!} m dc}{\int_0^\infty e^{-mc} \frac{(mc)^{n-1}}{(n-1)!} m dc} = \frac{1}{\Gamma(n)} \int_c^\infty e^{-c} c^{n-1} dc \quad (6)$$

P represents the bare metal surface area per unit area of high-chromium steels at c , so we can deduce the following equation from (5) and (6).

$$V = \frac{K(K'+C)}{\Gamma(n)} \int_c^\infty e^{-c} c^{n-1} dc \quad (7)$$

The assumption that alloys become passive only at s is zero, will not be strictly correct, because there may be, in fact, numerous minute holes on the passive surface of the oxide film.⁽³⁾

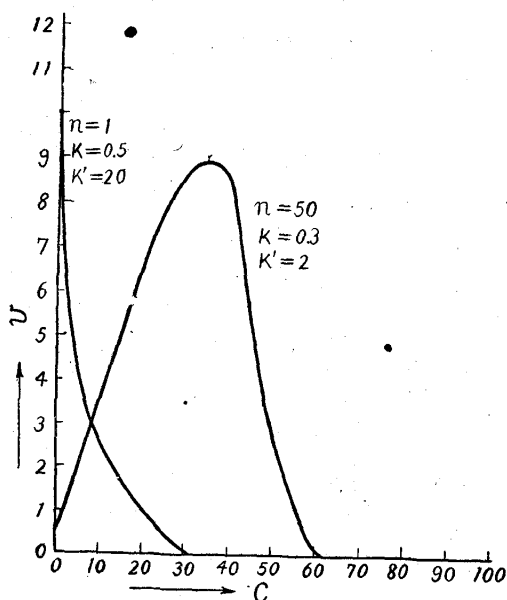


Fig. 7. The model of C-V curve represented by the equation,

$$V = \frac{K(K'+C)}{\Gamma(n)} \int_c^\infty e^{-c} c^{n-1} dc$$

A single elementary passive domain itself will be unstable and disappear in no time and it may be necessary for the stability of elementary passive domains to grow up to a certain magnitude. In the case of concentrated hydrochloric acid and of small amounts of oxidizing reagents, the corrosion of hydrogen gas evolution type will occur at the same time. In the equation (7) these facts were not taken into consideration.

It is difficult to determine the numerical value of n . But, roughly, it is known by measuring the time required for the destruction of oxide film formed in air on high-chromium steels. Supposing, number of atoms which exist in a sectional area of elementary passive

(2) K. Fusimi, *The Probability and the Statistics* (1943).

(3) W. T. Miller, *Electro Chem. Soc.* 76 (1939) Paper. No. 28,

domain is n' , the oxide film has n'' atoms in thickness and the time required to destroy the oxide film is t , it may be shown as $n = n'n''/t$. So far as n is small, qualitatively, the equation (7) agrees with the observed results. The C-V curves by the equation (7) are shown in Fig. 7.

The fluctuation σ of the above mentioned Γ distribution is given by $\sigma = \sqrt{n}/m = K'' C_a/x^2$, where K'' is a proportional constant. According to the fluctuation, the critical range of local corrosion will be proportional to the hydrochloric acid concentration and inversely proportional to the square of specific concentration of chromium. These agree roughly with the observed results.

Summary

Potassium dichromate as an inhibitor for the corrosion by hydrochloric acid on high-chromium steels has two contrary actions, i. e., anodic inhibitor and cathodic accelerator, so it is a very dangerous inhibitor.

The minimum quantities of potassium dichromate required for the complete passive state of high-chromium steels are proportional to the square of hydrochloric acid concentration and inversely proportional to the square of specific concentration of chromium in alloys.

The relation between the potassium dichromate concentration and the corrosion reaction velocity on high chromium steels for a definite concentration of hydrochloric acid, can be qualitatively represented by a simple equation by assuming that the cathodic reaction is controlled by the diffusion of potassium dichromate, anodic reaction is controlled by the surface area of the anode and the formation of oxide film by potassium dichromate is a statistical process.

The pit or cavity corrosion on high-chromium steels can be completely prevented by the addition of a certain amount of molybdenum so far as it exists in solid solution.