# THE ROLE OF CARBON IN THE SELF-PASSIVATION OF CHROME STEEL IN ACID SOLUTIONS AT ELEVATED TEMPERATURES

G. S. Raskin, G. M. Florianovich,
Ya. M. Kolotyrkin, É. A. Medvedev,
A. M. Zubko, and M. A. Vedeneeva

UDC 620.193.01:669.14

An effect of the self-passivation of steel Kh28, containing 0.15% carbon, in sulfuric acid at a temperature of 90°C has been observed. With a low carbon content in the steel (0.005%), self-passivation does not occur under these conditions. At ordinary temperature, both steels dissolve from an active state. It is shown that self-passivation is accompanied by the formation of a deposit on the surface of the steel, consisting of a mixed chromium and iron carbide. This leads to a lowering of the overvoltage of the cathode reaction and to inhibition of the anode process, as a result of which the stationary potential of the steel is shifted to a value which is more positive than the passivation potential. The accumulation of the carbide on the surface of the steel at 90°C is explained by the postulation of an anomalously high rate of dissolution of the steel at this temperature (in accordance with a chemical mechanism).

The change in the corrosion resistance of steels in nonoxidizing acids, with a change of their carbon content, is mainly connected with the effect of the carbon on the overvoltage of the cathode reaction of the evolution of hydrogen. Actually, for iron, for example, with a rise of the carbon content in the metal, the rate of anode dissolution varies only slightly [1].* With the introduction of carbon into the iron, the rate of the cathode process increases [3]. In the general case, this leads to an acceleration of the self-dissolution of steels which are in an active state (particularly if the carbon in them is present in the form of carbides) [4].

On the other hand, it is well known that cathode additives, which include also carbides [5-7], can promote self-passivation of steels [8-15]. And, although with an increase in the carbide content in the steel the stability of the passive state is lowered [16],† on the whole, the presence of carbides can lead to the inhibition of self-dissolution.

The present authors have studied the effect of carbon on the corrosion properties of steel Kh28 in sulfuric acid, in which the dissolution mechanism of chromium steels may be not only electrochemical, but also chemical [17].

The method of polarization measurements under potentiostatic conditions was used in the work. Under these circumstances, the rate of dissolution of the steels at different potentials was also evaluated analytically, using a photocolorimetric method for determining iron and chromium.

The experiments were carried out at 22 and 90°C in a 0.1 N solution of sulfuric acid, prepared from double distilled acid and water. Before the measurements the solution in the cell was deaerated using purified nitrogen. Polarization curves were recorded both under stationary and nonstationary conditions.

*A considerable effect on the anode behavior of iron in the system Fe–C is exerted by its phase composition [2].

† This is confirmed also by the results of the present authors.

L. Ya. Karpov Physicochemical Scientific-Research Institute. Translated from Zashchita Metallov, Vol. 8, No. 3, pp. 259-264, May-June, 1972. Original article submitted July 7, 1970.

TABLE 1

| Electrochemical characteristics | Steel 1 | Steel 2 |
|---|---|---|
| Stationary potential, V (n.h.e) | −0,300 | −0,280 |
| Density of critical passivation current, A/cm² | $2{,}1 \cdot 10^{-3}$ | $2{,}6 \cdot 10^{-3}$ |
| Passivation potential, V (n. h. e) | −0,250 | −0,250 |
| Rate of dissolution in passive state (at 0.4 V), A/cm² | $2 \cdot 10^{-7}$ | $2 \cdot 10^{-7}$ |
| Rate of cathode hydrogen evolution (at −0,6 V), A/cm² | $1{,}2 \cdot 10^{-2}$ | $2{,}1 \cdot 10^{-2}$ |
| Rate of dissolution $i_d$ (at −0.6 V), A/cm² | $7{,}6 \cdot 10^{-5}$ | $1{,}3 \cdot 10^{-4}$ |

The investigation was carried out using Kh28 steels with sufficiently high (0.15%) and low (0.005%) carbon contents, melted at the I. P. Bardin Central Scientific-Research Institute of Ferrous Metallurgy.

| Steel | C | Si | Mn | S | P | Cr | $O_2$ | $H_2$ | $N_2$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0,005 | 0,02 | 0,02 | 0,003 | 0,003 | 27,9 | 0,004 | 0,0003 | 0,016 |
| 2 | 0,15 | 0,38 | 0,42 | 0,005 | 0,022 | 27,75 | 0,075 | 0,0006 | 0,028 |

Melting of the steel with the low carbon content was carried out using carbonyl iron and electrolytic chromium, refined in hydrogen. The melting was done in an induction vacuum furnace. The ingots obtained were heated up to 1200°C, forged into billets, and rolled. After the hot rolling, strips with a thickness of 0.5-1.0 mm were quenched in water from a temperature of 780°C to convert the carbon into carbides. Melting of the steel with the high carbon content (0.15%) was done by the method of electroslag remelting.

Table 1 compares the main electrochemical characteristics of steels 1 and 2 at a temperature of 22°C, obtained on the basis of measurement of the stationary anode and cathode polarization curves. The table also gives the results of an analytical determination of the rates of dissolution of the steels, $i_d$, in the region of sufficiently negative potentials (with cathode polarization), at which, in accordance with [17], the rate of dissolution does not depend on the potential.

As can be seen from Table 1, a change in the composition of the steel is not accompanied by any appreciable change of its electrochemical characteristics. There is noted only a certain increase, with a rise in the content of impurities in the steel, of its rate of dissolution, $i_d$, and of the rate of the cathode evolution of hydrogen.

The stationary potentials of steels 1 and 2 in 0.1 N sulfuric acid at 22°C correspond to active dissolution (as follows from the results of polarization measurements) and do not vary with time (Fig. 1, curves 1 and 2). A different picture is observed at 90°C. As is evident from curves 3 and 4 in Fig. 2, at 90°C the stationary potential does not vary with time only for steel 1 (low carbon content). For steel 2, there is a shift of the stationary potential with time toward the side of positive values. In view of this, it is impossible to obtain stationary anode polarization curves for a steel with a high carbon content in the region of sufficiently negative potentials. In this region, the electrochemical characteristics can be evaluated using curves recorded rapidly from the potential which establishes itself immediately after immersion of the electrode into the solution.

Taking account of the data from the stationary and nonstationary measurements (Fig. 2), as well as of the results of Fig. 1, the conclusion may be drawn that, at 90°C, the stable value of the stationary potential of steel 2 corresponds to its passive state. This means that a steel with a high carbon content, with the conditions under consideration, goes over spontaneously into a passive state.*

In contrast to this, the self-dissolution of a steel with a low carbon content proceeds in the active state (Fig. 3).

An analysis of the polarization curves and of specially constructed experiments permits drawing a conclusion with respect to the reasons for the self-passivation of steel 2 at high temperature. A comparison between cathode polarization curves for steel 2, recorded immediately after its immersion in the solution and after holding of the samples for a period of 30 min at a potential of −0.6 V, showed that preliminary

*An analogous result was obtained in our laboratory by S. R. Vlodarchik and V. M. Knyazheva, who established that, in contrast to pure iron and steel 3, gray iron is self-passivated in 95% sulfuric acid at 200°C.

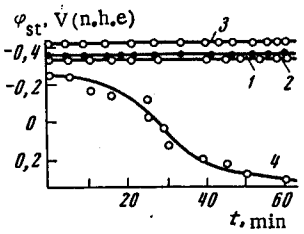


Fig. 1

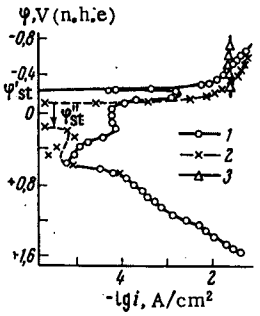


Fig. 2

Fig. 1. Change with time of the stationary potentials of steel 1 (1 and 3) and steel 2 (2 and 4) in 0.1 N sulfuric acid at a temperature of 22°C (1 and 2) and 90°C (3 and 4).

Fig. 2. Polarization curves for steel 2 in 0.1 N $H_2SO_4$ at 90°C: 1) nonstationary (rate of recording 1.2 V/h); 2) close to stationary; 3) dependence of dissolution rate on the potential.

cathode polarization always brings about an accelerated evolution of hydrogen. On the other hand, from the results of nonstationary polarization measurements it follows that acceleration of the cathode process is observed also with a transition from steel 1 to steel 2 (Fig. 4). The facilitation of the cathode depolarization process is thus one of the reasons for the self-passivation of a steel with a high carbon content. As follows from the anode polarization curves, another reason for the self-passivation of steel 2 is the inhibition, over the course of time, of the anode reaction of active dissolution. With what are connected the observed changes with time of the electrochemical properties of a steel with a high carbon content?

Visual observation shows that, as a result of self-dissolution, as well as with dissolution in the region of cathode polarization, a slime appears on the surface of steel 2. X-ray-structural and photocolorimetric* analysis have shown that it consists of a mixed carbide of chromium and iron with the composition $(Cr, Fe)_{23}C_6$.†

A conclusion with respect to the reasons for the appearance of this slime on the surface of the electrode can be drawn from the results of a direct determination of the rates of dissolution of steels at high temperature. It has been found that, at potentials of −0.3 to −0.7 V, the rate of dissolution of steel 2 does not depend on the potential (Fig. 2). The rate of dissolution of steel 1 does not depend on the potential only in the interval −0.5 to −0.7 V, while at more positive potentials it rises (Fig. 3). The results obtained do not depend on time or on the agitation conditions. In the region of independence of the potential the rate of dissolution of steel 2 is higher than that of steel 1. It is significant that, in this region of potentials, the rate of dissolution of steel 2 appreciably exceeds the corresponding anode currents. This is in accordance with the postulation of the dissolution of steel by a chemical mechanism, and shows that, in the absence of an external current, the dissolution reaction proceeds at an anomalously high rate. A comparison of the anode polarization curves for steel 2 at 90 and 22°C has shown that, at these temperatures, the rates of its dissolution due to an electrochemical mechanism are commensurate. However, the accumulation of carbide on the surface of the steel is observed only at a high temperature, at which there is accelerated dissolution of the steel due to a chemical mechanism. It is obvious that it is precisely such an accelerated anomalous dissolution which leads to the accumulation of chromium and iron carbides on the surface of steel 2. The conclusion drawn is confirmed also by the fact that the accumulation of carbide on the surface of steel 2 is observed not only with a stationary potential, but also with a considerable degree of cathode polarization,‡ with which the rate of electrochemical dissolution becomes extremely small.

*After dissolution in boiling sulfuric acid in air.

†The accumulation of carbides on the surface of iron containing carbon under similar conditions has been demonstrated in a number of investigations [7, 18, 19].

‡It should be noted that this result permits drawing a conclusion with respect to the possibility of using the phenomenon of the chemical dissolution of steels for the development of a method for phase analysis with cathode polarization.

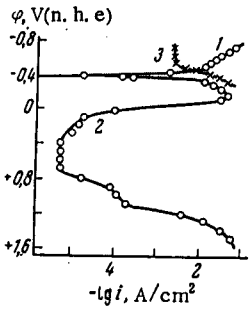


Fig. 3

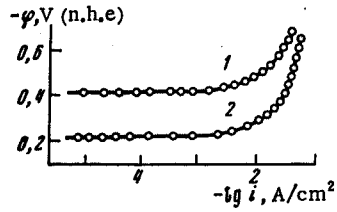


Fig. 4

Fig. 3. Stationary cathode (1) and anode (2) polarization curves for steel 1 in a 0.1 N solution of $H_2SO_4$ at 90°C; 3) analytically determined dissolution rates.

Fig. 4. Cathode polarization curves, measured at a rate of 0.6 V/h, in steel 1 (1) and steel 2 (2) in 0.1 N $H_2SO_4$ at 90°C.

It has been postulated earlier [20] that the reason for the self-passivation of an alloy at high temperature could be a change in the composition of its surface as the result of dissolution, leading to inhibition of the anode process. In complete accordance with this postulation, it may be assumed that the carbides accumulating on the surface of steel 2 during its dissolution are the reason for the inhibition of the anode reaction. It is obvious that they also bring about a lowering of the overvoltage of the cathode process, acting as cathode additives [8-15]. This result is in agreement with known literature data [21-25] on the rather high stability of iron and chromium carbides at potentials more negative than the passivation potential (1.1-1.3 V). According to the data of [22], for example, the rate of dissolution of $(Cr, Fe)_{23}C_6$ in 3.7% HCl at potentials from −0.6 to +1.3 V does not exceed $10^{-5}$ A/cm$^2$.

To verify the above postulation with respect to the reasons for the self-passivation, a special investigation was made, aimed at clarifying the importance of the carbon content in a steel for its self-passivation. For this, it was necessary to transform the carbon in steel 2 from a carbide into a solid solution. For a chrome steel, this problem involves great difficulties, since the diffusional mobility of carbon is several orders of magnitude greater than that of chromium. Therefore, it is practically impossible to completely transform the carbon in steel 2 into a solid solution. The authors selected and put into effect conditions for the heat treatment of steel (heating to 1150°C and rapid cooling), at which there is a maximal conversion of the carbon into a solid solution. The degree of this transition was evaluated by the method of phase analysis [26]: the amounts of carbide separated out from steel 2 before and after its high-temperature heat treatment were compared. It was shown that in the latter case, a considerable part of the carbon actually went over into a solid solution. An electrochemical investigation showed that, after an additional heat treatment, although a shift of the potential of the steel is observed at 90°C, it is, however, not as marked as for the steel before heat treatment (0.0 V instead of 0.4-0.5 V). There is a correspondingly marked difference also in their rates of self-dissolution: $4 \cdot 10^{-2}$ A/cm$^2$ (at 0.0 V) for the steel after high-temperature treatment, and $8 \cdot 10^{-6}$ A/cm$^2$ (at 0.5 V) after low-temperature treatment. The results are in agreement with data of polarization measurements for steel 2, containing a reduced amount of carbide. On the anode nonstationary curve for this steel, an activation center was observed at potentials near 0.0 V; this obviously also ensures a "lag" of the potential.

It follows from the results obtained that even a partial transition of the carbide carbon into a solid solution is accompanied by a loss of the ability of the steel for self-passivation. It is important to note here that the rate of dissolution in accordance with a chemical mechanism (at sufficiently negative potentials) does not depend on the state in which the carbon exists. This means that although the rate of dissolution of steel in accordance with a chemical mechanism also plays a role in the process of self-passivation, its possibility, however, is determined above all by the carbon content in the steel.

## CONCLUSIONS

In sulfuric acid at high temperature, steel Kh28 with a sufficiently high carbon content goes over spontaneously into a passive state. Under these conditions, steel with a low carbon content is not subject to self-dissolution.

The reason for self-passivation of the steel is the accumulation on its surface of a chromium–iron carbide, leading to acceleration of the cathode reaction and to inhibition of the anode reaction. The accumulation of the carbides is the result of dissolution of the steel in accordance with a chemical mechanism, taking place at a high rate with a sufficiently high carbon content in the steel and at high temperature. The ability of the steel for self-passivation appears only with the condition that the carbon exists in the steel in the form of the carbide, and not in a solid solution.

## LITERATURE CITED


1. K. F. Bonhoeffer, Z. Elektrochem., 55, 151 (1951).
2. A. R. Tourky, A. A. Azim, and S. H. Sanad, Corros. Sci., 8, 857 (1968).
3. Z. A. Foroulis and H. H. Uhlig, J. Electrochem. Soc., 111, 522 (1964).
4. N. D. Tomashov, The Theory of Corrosion and Protection of Metals [in Russian], Izd. Akad. Nauk SSSR (1960), p. 437.
5. T. P. Hoar and D. Havenhand, J. Iron Steel Inst., 239, 133 (1936).
6. V. A. Obolonchik and A. A. Semenov-Kobzar', Poroshkovaya Met., No. 9, 57 (1968).
7. H. J. Cleary and N. D. Green, Corros. Sci., 9, 3 (1969).
8. W. D. Richardson, Trans. Electrochem. Soc., 38, 265 (1920).
9. G. V. Akimov, Theory and Methods of Investigating the Corrosion of Metals [in Russian], Izd. Akad. Nauk SSSR (1945), p. 199.
10. N. D. Tomashov, G. P. Sinel'shchikova, and M. A. Vedeneeva, Dokl. Akad. Nauk SSSR, 62, 105 (1948).
11. G. M. Florianovich, Ya. M. Kolotyrkin, and N. K. Smirnova, Dokl. Akad. Nauk SSSR, 120, 845 (1958).
12. N. D. Tomashov, The Theory of Corrosion and Protection of Metals [in Russian], Izd. Akad. Nauk SSSR (1960), p. 320.
13. T. G. Owe Berg, Metalloberfläche, 19, 47 (1965).
14. V. M. Novakovskii, E. F. Lapshina, and M. Sh. Blokh, Z. Phys. Chem., 230, 313 (1965).
15. N. D. Tomashov, Proceedings of IIIrd Congress on Corrosion of Metals [in Russian], Vol. 1, Moscow (1968), p. 39.
16. A. P. Tourky, A. A. Abdub Azim, and M. M. Anwar, Corros. Sci., 5, 301 (1965).
17. Ya. M. Kolotyrkin and G. M. Florianovich, Zashchita Metal., 1, 7 (1965).
18. K. F. Bonhoeffer, V. Haase, and G. Z. Langhammer, Z. Elektrochem., 52, 29, 60 (1948).
19. K. J. Vetter and N. J. Boss, Z. Elektrochem., 56, 16 (1952).
20. G. M. Florianovich, Zashchita Metal., 1, 157 (1965).
21. T. Ya. Kosolapova and G. V. Samsonov, Ukrainsk. Khim. Zh., 28, 931 (1962).
22. A. Boimel', Chernaya Metallurgiya, No. 13, 34 (1964).
23. K. Osozawa, K. Bohnenkamp, and N. Engell, Corros. Sci., 6, 421 (1966).
24. A. A. Semenov-Kobzar' and V. A. Obolonchik, Poroshkovaya Met., No. 5, 75 (1969).
25. M. Kh. Freid, "Investigation of the electrochemical and corrosion behavior of secondary phases and their role in the intercrystalline corrosion of chrome–nickel steels," Author's Abstract of Candidate's Dissertation [in Russian], Ivanovo (1970), p. 15.
26. N. M. Popova, Carbide Analysis [in Russian], Oborongiz (1957).