EFFECT OF TEMPERATURE ON THE SUSCEPTIBILITY OF ALLOYS TO PASSIVATION

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The dissolution rate of metals in electrolytes generally increases with the temperature. In this respect the processes examined here do not differ from other chemical reactions.

However, there are cases where the corrosion rate passes through a maximum with increasing temperature [1]. This is usually explained by the change in the concentration of oxygen dissolved in the corrosive medium with temperature, since most of the experimental data refer to aerated solutions.

Our results show, however, that there is a similar effect in cases where the corrosion process occurs in deaerated solutions. This is shown by the results in Fig. 1 (curve 1) representing the rate of spontaneous dissolution of iron containing 35% Cr in a 0.1 N sulfuric acid solution with temperature. This result cannot be explained by the decrease of the concentration of the depolarizer, since the experiments were made in solutions saturated with nitrogen and under the condition of hydrogen depolarization.

To clarify the nature of this effect, we studied the temperature dependence of steady potentials φ_{st} of different iron alloys in deaerated sulfuric acid solutions. The experiments were made at temperatures of 20-90°C. The potential was considered to be steady after it had remained constant for a certain time. The corresponding results are given also in Fig. 1 (curve 2).* The figure shows that after a certain temperature is reached (we shall call this temperature the critical temperature, t_{cr}) not only the rate of dissolution decreases but the steady potential shifts toward more positive values.

Experiments made in solutions containing oxygen showed that in these cases the decrease of the dissolution rate of alloys with increasing temperature is accompanied by a shift of φ_{st} toward more positive values, as is the case in deaerated solutions. This result shows the fact that in aerated solutions as well, the decrease of the dissolution rate until t_{cr} is reached cannot be explained in the general case by the decrease of the concentration of the depolarizer, since the value of φ_{st} would be displaced toward more negative and not toward more positive values if this were so.

* The potentials are given with respect to a normal hydrogen electrode.

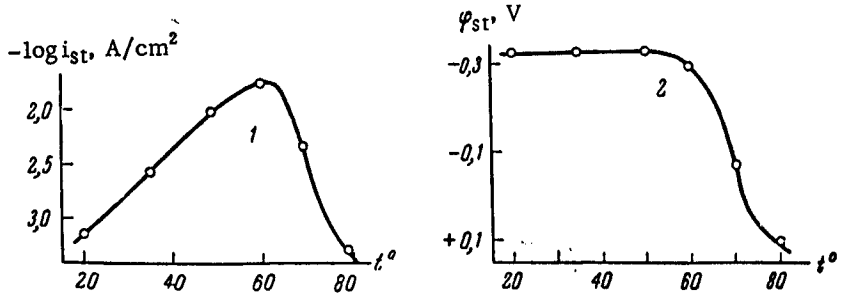

Fig. 1. Effect of temperature on the rate of spontaneous dissolution (1) and on the steady potential (2) of the alloy containing 35% Cr in a 0.1 N sulfuric acid solution.

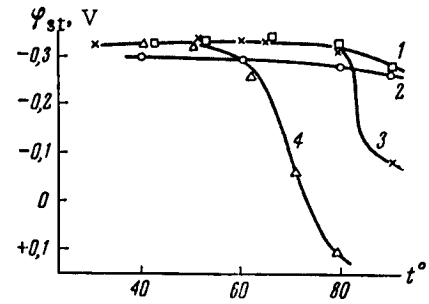

Fig. 2. Temperature dependence of the steady potentials of alloys of iron with 12% Cr (1), 20% Cr (2), 27% Cr (3), and 35% Cr (4) in sulfuric acid at pH = 1.

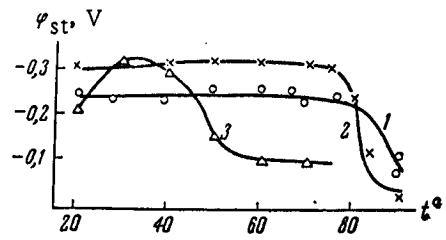

Fig. 3. Dependence of the steady potential of Kh17 steel on the temperature in sulfuric acid solutions with the following values of pH: 1) 0; 2) 1; 3) 2.

Further measurements showed that the value of the critical temperature depends to a great extent on the composition of the alloy and on the pH of the solution. Figure 2 shows the dependence t_{cr} on the concentration of chromium in the alloy. It can be seen that an increase in the chromium concentration from 27 to 35% is accompanied by a decrease of t_{cr} from 80 to 60°C. The values of t_{cr} are apparently higher for alloys containing 12 and 20% Cr, and we did not reach these values in our experiments. The addition of nickel to the alloys leads to the decrease of t_{cr} and the effect increases with increasing nickel concentrations. A similar effect was observed in the case of the increase of the pH of the solution (Fig. 3).

Experiments showed that if one measures the potential not at constant temperature but during its increase, then on the curve representing the variation of φ_{st} with the temperature one can also detect a certain critical temperature at which the value of φ_{st} on the curve jumps. However, the value of this critical temperature $t_{cr'}$ coincides with the value of the steady t_{cr} only when the heating rate is very slow. The value of $t_{cr'}$ increases as the heating rate is increased. For example, the steady value of t_{cr} for 1Kh13 steel in a 0.1 N sulfuric acid solution is 110°C, while in the case of a high heating rate (1.4°/min) it is 150°C. For Kh22T steel in a 1 N H_2SO_4 solution the increase in the heating rate from 0.5 to 1.4°/min leads to an increase of $t_{cr'}$ from 70 to 82°C.

Comparison of the results in Fig. 1 with the curves representing the variation of the dissolution rate with the potential [2] and taking into account the effect of the temperature on the passivation potential [3-5] lead us to conclude that the initial value of the potential in Fig. 1 corresponds to the region of active dissolution of the alloys, while its final value corresponds to the passive state. Thus, these results mean that the observed deceleration of the corrosion process with increasing temperature is due to the transformation of the active alloy into a passive alloy at a certain temperature.

Self-passivation of the alloy beyond a certain temperature can be explained if one assumes that the rates of both conjugated reactions determining the spontaneous dissolution rate increase with increasing temperature and that the temperature coefficient of the rate of the depolarizing cathodic reaction is much higher than the temperature coefficient of the rate of the anodic process. In fact, under this condition an increase in the temperature necessarily leads to the displacement of the steady potential of the metal toward positive values. At some temperature the value of φ_{st} may reach the value of the passivation potential, and this is responsible for the transition to the passive state.

However, this assumption is not confirmed experimentally, as can be seen from the cathodic polarization curves and measurements of steady potentials of the alloy containing 27% Cr in a 0.01 N sulfuric acid solution at different temperatures. The displacement of the steady potential under these conditions (by 135 mV) with increasing temperatures between 40 and 50°C cannot be explained by the change in the overvoltage of the process determined experimentally. Another assumption concerning the deceleration of the anodic reaction with the increase in the temperature must be made to explain this phenomenon.

Making this assumption and keeping in mind that the dependence of t_{cr} on the rate of increase of the temperature of the system determined in our experiments, we may conclude that this effect is due to processes which proceed at a relatively low rate on the surface of the metal and that the rate increases with the temperature. Such processes may lead, in particular, to the covering of part of the metal's surface with layers having a high conductivity;

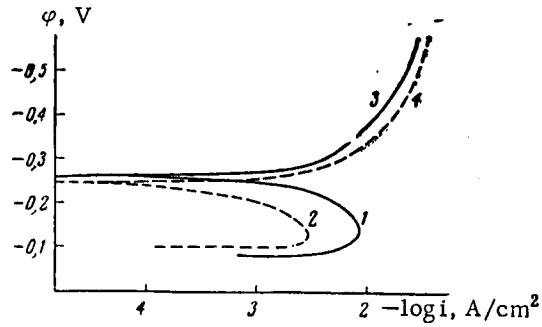

Fig. 4. Polarization curves for the alloy containing 27% Cr in 0.1 N H_2SO_4. 1) Anodic polarization at 50°C; 2) anodic polarization at 80°C; 3) cathodic polarization at 50°C; 4) cathodic polarization at 80°C.

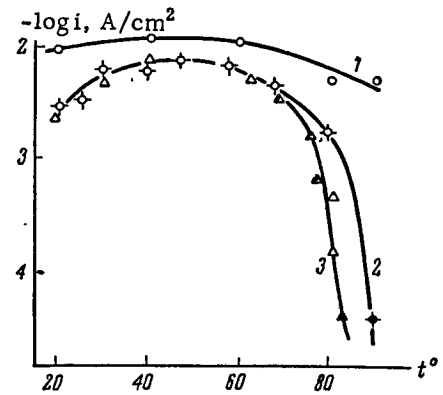

Fig. 5. Effect of the temperature on the critical passivation currents of alloys of iron with chromium in a 0.1 N sulfuric acid solution. The concentration of chromium in the alloys was: 1) 12%; 2) 20%; 3) 27%. The dots indicate that under these conditions the steady potentials are in the passive region.

these layers have very little effect on the rate of the cathodic reaction but significantly decrease the total rate of the anodic reaction* (calculated with respect to the total visible surface).

On the basis of the results given, one can conclude that the formation of thin layers is favored by increasing concentrations of chromium and nickel in the alloy and also by an increase in the pH of the solution.

If we accept the hypothesis given above it is easy to see that the effect of surface films on the electrochemical and corrosion characteristics of the system is equivalent to a decrease of the density of the anodic current at constant potentials, including the critical passivation current calculated with respect to the total visible surface of the electrode.

This conclusion is confirmed by the anodic polarization curves and the measurements of the densities of the critical passivation currents i_{cr} at different temperatures. Figure 4 shows that within a certain temperature range (50-80°C) one observes a decrease of the density of anodic current with increasing temperature with a rather wide range of potentials.† The effect of the temperature on the anodic current density is shown in Fig. 5, which shows the dependence of i_{cr} on the temperature. It follows from these results that under the conditions of the experiment the values of i_{cr} generally increase (in agreement with published data in [4, 7, 8]) and then decrease. The decrease of i_{cr} occurs at temperatures close to t_{cr} determined from the curves of the variation of the steady potential with temperature. In cases where t_{cr} is not reached at temperatures up to 100°C the value of i_{cr} does not decrease. This occurs, for example, in the case of dissolution of 1Kh13 steel in 0.1 N H_2SO_4.

In accordance with our hypothesis, the value of t_{cr} (other conditions being equal— the composition of the alloy and pH of the solution) should also depend on the rate of the cathodic reaction and the increase of this reaction rate should lead to a certain decrease of the value of t_{cr}. The correctness of this conclusion is confirmed, for example, by comparing the results of measurements of t_{cr} in deaerated acid solutions and in solutions saturated with oxygen. These results show that 1Kh13 steel is active in a deaerated solution of sulfuric acid at pH = 2 up to 100°C, while it becomes passive in the same solution saturated with oxygen at 60°C.‡ The higher the pH of the solution, the greater the effect of oxygen. Thus, 1Kh13 steel does not undergo spontaneous passivation in a solution with pH = 1 up to 100°C either in a nitrogen or an oxygen atmosphere. But when the pH of the solution is 2 then t_{cr} for the same alloy in the solution saturated with oxygen is about 55°C; at pH = 3 the steel is passive in the solution containing oxygen even at room temperature.

Thus, the hypothesis concerning the nature of self-passivation at high temperature is indirectly confirmed by experimental data and therefore can be considered to be one of the possible explanations of this phenomenon. It should be noted that although the hypothesis given here is based on electrochemical concepts it is valid also in the case of the dissolution of alloys by a chemical mechanism, since it was shown in [9] that electrochemical passivation is accompanied by a simultaneous deceleration of the dissolution process by a chemical mechanism.

* The legitimacy of this assumption follows from the results obtained in [6].

† Let us recall that, in accordance with different hypotheses, only the apparent values of i calculated with respect to the visible surface of the electrode decrease. It is assumed that the real values of i increase with increasing temperatures.

‡ According to our preliminary data, this phenomenon may be due not only to the effect of oxygen as a depolarizer but also to its effect on the overvoltage of the anodic reaction.

CONCLUSIONS

We investigated the kinetics of dissolution of iron alloys with chromium and nickel in sulfuric acid at different temperatures. It was shown that for these alloys there is a certain critical temperature beyond which the alloys pass from the active to the passive state under conditions of spontaneous dissolution (self-passivation).

This critical temperature decreases with increasing concentrations of chromium and nickel in the alloys, with increasing pH of the solution, and also when oxygen is added to the solution. We have proposed a hypothesis to explain self-passivation of alloys at a certain temperature.

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