THE PASSIVATION CHARACTERISTICS OF IRON BASED ALLOYS

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The critical passivation current (i_{cr}) and the critical passivation potential (φ_p) of a metal can serve as measures of the metal's ability to pass into the passive state. The first of these parameters characterizes the minimum concentration of oxidizing agent (in chemical passivation), or the minimum external current (in anodic passivation), required for carrying the metal from the active state into the passive condition. It is clear that the metal is the more readily passivated the lower the characteristic i_{cr} value. The value of φ_p is of significance in selecting a chemical passivator. It has been shown earlier [1] that an oxidizing agent can exert a passivating action on a metal only if its oxidation–reduction potential is more positive than the oxidation–reduction potential of the metal itself. The value of φ_p varies from metal to metal, however, and it therefore follows that an oxidizing agent which is effective in passivating one metal may be completely ineffective in passivating another.

The critical potential and passivation current of an alloy are closely dependent on the alloy's composition and structure. The fact that many alloying additives are capable of reducing the corrosion of construction materials is undoubtedly due to the effect of these additives on the passivation characteristics.

The constructional materials most widely used at the present time are iron based alloys containing chromium and nickel as alloying additives. Despite this fact, the available data [2, 3] are inadequate for drawing definitive conclusions concerning a whole series of problems touching the role played by the various components in the passivation of Fe–Cr and Fe–Cr–Ni alloys.

The present work is a systematic study of the effect of chromium on the φ_p and i_{cr} values of two-component Fe–Cr alloys and of the effect of small quantities of nickel on the same characteristics of Fe–Cr–Ni alloys.

This study was carried out by using the galvanostatic and potentiostatic methods [4] for developing polarization curves. Use was made of pure two-component Fe–Cr alloys and steels of the types 12Kh6, 1Kh13, Kh17, Kh28, Kh22T, and Kh22N2T. All experiments were performed in sulfuric acid solutions (either additive-free or containing Na_2SO_4) which had been saturated with pure nitrogen.

The data on the Fe–Cr alloys are presented in Figs. 1 and 2. It is seen from these figures that an increase in the chromium content of the alloy displaced φ_p in the negative direction. This displacement was not uniform however. Increasing the chromium content from 12 to 13% brought about a change of almost 0.5 v in the value of φ_p; beyond this point there was a gradual alteration similar to that observed at low concentrations of the element (up to 12%). Raising the chromium content to 20% caused φ_p to become practically constant at a value approximately equal to that of pure chromium.

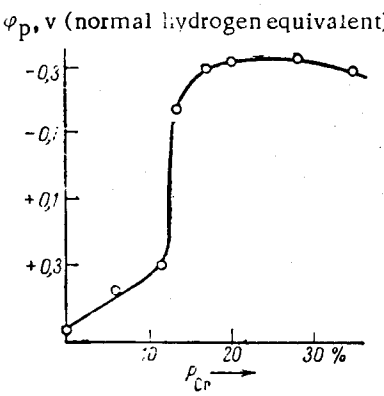

Fig. 1. The relation between the chromium content and the passivation potentials for Fe–Cr alloys in 0.1 N H_2SO_4.

Increasing the chromium content to 20-27% also gave rise to a rather considerable reduction in the critical passication current (Fig. 2A), the change being quite consistent with the alteration in φ_p described above. *

* The critical current, i_{cr}, for alloys containing less than 13 % chromium is diffusional in character; this accounts for the lack of any sharp change in i_{cr} in the p_{Cr} = 12 - 15% region (Fig. 2A).

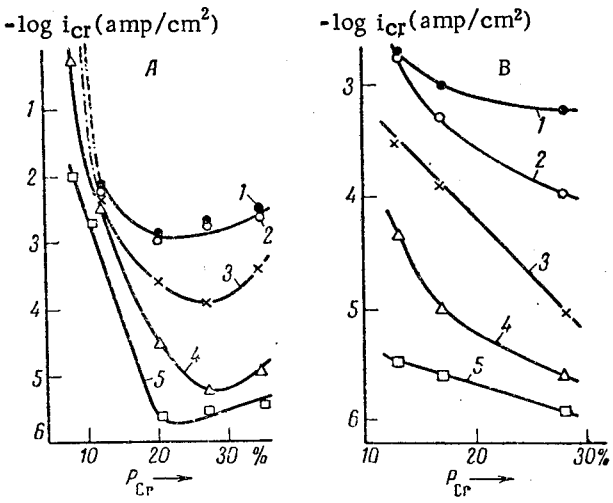

Fig. 2. The relation between the critical passivation current and the chromium content of Fe–Cr alloys in the following solutions: (A) 1) 0.1 N H_2SO_4; 2-5) H_2SO_4 + Na_2SO_4 (total concentration, 1 N) at pH; 2) 1.7; 3) 2.8; 4) 4.0; 5) 6.0; (B) the same, but for alloys containing 0.4% Ni.

Further increase of the chromium content to values > 20-27% markedly increased the value of i_{cr}, the situation being different from that met with φ_p. In order to explain this effect, study was made of the relation of the chromium content of the alloy and the kinetics of active alloy dissolution, it being clear that the critical passivation current is determined by the passivation potential and the dissolution overvoltage.* The overvoltage for anodic dissolution of the alloy in the active state showed a rather pronounced and uniform reduction with increasing content of chromium over the entire range of working concentrations (Fig. 3).

The results obtained here indicate that alloying chromium is capable of acting on the kinetics of active dissolution in such a way as to increase the critical passivation current at all concentrations. The fact that the reverse relation, namely, a diminution of i_{cr} with increasing content of chromium in the alloy, was observed at low chromium concentrations is readily explained in terms of the effect of alloying on the passivation potential (Fig. 1).

It is clear that an increase in the chromium content in the region of low concentrations causes φ_p to alter more extensively than the overvoltage for active dissolution, and that this in turn leads to a reduction of i_{cr}. At the higher chromium contents, φ_p was almost independent of the alloy composition while the overvoltage for active dissolution continued to diminish, thus exercising a predominant influence on i_{cr} and causing the latter to increase (Fig. 2A).

It is to be noted that the data of Fig. 2A refer to pure two-component Fe–Cr alloys. A somewhat different passivation current–chromium content relation applies to Fe–Cr alloys containing up to 0.4% nickel (steels 12Kh6, 1Kh13, Kh17, Kh28) (Fig. 2B). In this case there was a regular diminution of i_{cr} with increasing chromium content over the entire working range of concentrations (up to 28% of the elements). At the same time, the introduction of nickel in such minute quantities did not lead to any appreciable alteration in the passivation potential (the data of Fig. 1 refer to all of the test Fe–Cr alloys). Thus the difference of the curves of Fig. 2 must have been due to the effect of nickel on the overvoltage for active alloy dissolution. In this connection, it is to be pointed out that the addition of up to 0.4% nickel to the alloy retarded the dissolution in the active state and repressed to a pronounced degree the above-mentioned activating effect of chromium (Figs. 3 and 4).

The increase in the overvoltage for anodic dissolution in the active state became more pronounced with further increase of the nickel content of the alloy. This led to a reduction in the value of i_{cr}. For example, our experiments showed that the introduction of 2% nickel into the alloy Kh22T reduced the value of i_{cr} so far that the metal could undergo spontaneous passivation in 0.1 N sulfuric acid, the stationary potential being displaced by 200 mv in the positive direction and the rate of dissolution markedly diminished while the hydrogen overvoltage remained practically unaltered.

On the basis of these data and the results of earlier experiments [6], the conclusion could be drawn that this spontaneous passivation of the alloy Kh22N2T resulted from the oxidizing action of the H^+ ions, the rate of discharge of the ions at the passivation potential being much greater than the critical current density.

Although such an effect is possible in principle, it must be kept in mind that spontaneous passivation from the oxidizing action of H^+ ions can occur only with alloys containing at least 13% chromium, the passivation potentials for alloys containing less than this amount of the element being more positive than the potential of the reversible hydrogen electrode in the same solution.

It must be noted that the data on the relation between the critical passivation current and the alloy composition is essentially of practical significance and that these data in themselves cannot be a basis for decisions concerning the passivation mechanism, even though they are frequently drawn on for this purpose [3].

* A similar approach has, in principle, been used by Uhlig [5] in deriving a relation between i_{cr} and the solution pH from the Tafel equation for the anodic reaction and data on the effect of pH on the Flade potential.

In fact, our measurements show that the minima of the curves of Fig. 2A (20-27% Cr) do not mark out characteristic alloy composition at which the dissolution law suddenly changes. There are cases in which no definite relation exists between i_{cr} and the content of the various components in the alloy [7]. Finally, judged from the behavior of the critical passivation current, the conclusion would be drawn that chromium and nickel would affect the passivation characteristics in the same way. The preceding data show, however, that the action of these two metals is markedly different, chromium exerting a strong effect on the passivation potential over a considerable range of concentrations while nickel principally effects the kinetics of the anodic reaction in the prepassivation region of potentials.

In order to understand this difference, account must be taken of the fact that passage of a metal into the passive state involves a chemico-adsorptional interaction between its surface atoms and the oxygen of the water with the formation at the solution–metal interface of barrier layers which impede the transfer of metal ions from the crystal lattice into solution. It follows from this that the passage of the alloy into the passive state must be favored by increasing the alloy's oxygen affinity. The critical passivation potential can serve as a quantitative characterization of this affinity since it is clear that passivation sets in earlier (i.e., at a more negative potential) the higher the affinity. The data presented here suggest that the favorable effect of the addition of chromium on the passivation of iron based alloys is principally due to an increase in the oxygen affinity. The introduction of nickel into two-component Fe–Cr alloys clearly does not bring about any marked alteration of the oxygen affinity.

Thus, a study of the effect of the alloy composition on the kinetics of active dissolution and the passivation potential is required for an understanding of passivation phenomena.

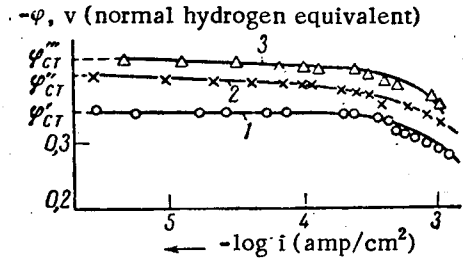

Fig. 3. Anodic polarization curves measured in 0.1 N H_2SO_4 + 0.9 N Na_2SO_4 for Fe–Cr alloys containing the following amounts of chromium: 1) 12%; 2) 27%; 3) 35%. φ_{st} values are stationary potentials.

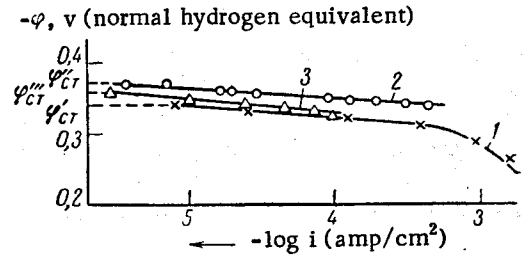

Fig. 4. Anodic polarization curves measured in 0.1 N H_2SO_4 + 0.9 N Na_2SO_4 for the alloys: 1) 1X13; 2) X17; 3) X28.

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