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Abstract

Full Text

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ON THE PASSIVATION CHARACTERISTICS OF IRON-BASED ALLOYS

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The criterion for the ability of metals to pass into the passive state is given by the corresponding values of the critical passivation currents (i_{cr}) and potentials (φ_{p}). The first of these quantities characterizes the minimum concentration of oxidant (in chemical passivation) or the minimum external current (in anodic passivation) that is necessary in order to transfer a metal from the active to the passive state. Obviously, the smaller the value of i_{cr} characterizing a given metal, the easier it is to bring about its passivation. The quantity φ_{p} is of great importance in selecting a chemical passivator. As was shown earlier(1), only those oxidants whose oxidation-reduction potential lies more positive than the passivation potential of the metal can have a passivating effect with respect to a given metal. Since, on the other hand, the value of φ_{p} depends on the nature of the metal, oxidants that are effective passivators with respect to one metal may turn out to be completely ineffective with respect to another.

Fig. 1. Dependence of the passivation potentials of Fe—Cr alloys in 0.1 *N* H_2SO_4 on the chromium content in the alloy

In the case of alloys, the critical values of the passivation potential and current depend substantially on their composition and structure. The experimentally observed favorable effect of many alloying additions on the corrosion behavior of structural metallic materials is undoubtedly connected with the influence of these additions on the passivation characteristics of alloys.

Fig. 2

Figure 2: Fig. 2

The most widely used structural materials at present are iron-based alloys alloyed with chromium and nickel. Nevertheless, the data known from a number of works(2,3) on the influence of these elements on the passivation characteristics of Fe–Cr and Fe–Cr–Ni alloys are insufficient for unambiguous conclusions on a whole series of questions concerning the role of the components of iron-based alloys in the process of their passivation.

In the present work a systematic investigation was carried out of the influence of chromium content on φ_p and i_{cr} of binary Fe–Cr alloys, as well as of small amounts of nickel on the same characteristics of Fe–Cr–Ni alloys.

The investigation was carried out by means of galvanostatic and potentiostatic(4) methods for recording polarization curves. Pure binary Fe–Cr alloys were used, as well as steels of grades 12Kh6, 1Kh13, Kh17, Kh28, Kh22T, and Kh22N2T. All experiments were carried out in sulfuric acid solutions (without additives or in the presence of Na_2SO_4), saturated with pure nitrogen.

The data obtained for Fe–Cr alloys are given in Figs. 1 and 2. As can be seen from these data, with an increase in the chromium content in the alloy, φ_p shifts toward negative values. However, this shift occurs nonuniformly. An increase in the chromium content from 12 to 13% is accompanied by the sharpest change in the value of φ_p (almost by 0.5 V), after which a smooth change in φ_p begins, also characteristic of small concentrations of this element (up to 12%). When the chromium content is increased to 20%, the value of φ_p reaches a practically constant value close to the corresponding value for pure chromium.

Increasing the chromium content to 20–27% is also accompanied by a rather considerable decrease in the critical passivation current of the alloys (Fig. 2A), which is in qualitative agreement with, and is explained by, the change in φ_p^* noted above.

Fig. 2. Dependence of the critical passivation currents of Fe–Cr alloys on the chromium content in the alloy in 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 for alloys containing 0.4% Ni (B)

With a further increase in the chromium content in the alloy (> 20–27%), the value of i_{cr} (in contrast to φ_p) does not remain constant, but increases noticeably. To explain this effect, the influence of the chromium content in the alloy on the kinetics of its active dissolution was investigated in this work, since it is obvious that the value of the critical passivation current is determined by the values of the passivation potential and the overvoltage of active dissolution of the alloy**. In this case, over the entire range of chromium concentrations investigated, a rather noticeable and uniform decrease in the overvoltage of anodic dissolution

Fig. 3

Figure 3: Fig. 3

of alloys in the active state was established as their chromium content increased (Fig. 3).

The result obtained means that chromium, as an alloying element of the alloy, over the entire investigated range of concentrations affects the kinetics of active dissolution in a direction that promotes an increase in the critical passivation current. The fact that, in reality, in the region of relatively low chromium contents in the alloy, the opposite effect occurs—namely, a decrease in i_{cr} with increasing chromium content in the alloy—is easily explained by the influence of alloying on the passivation potential of the alloy (Fig. 1).

Obviously, in the region of low concentrations, with an increase in the chromium content in the alloy, φ_{p} changes more significantly than the overvoltage of active dissolution, which leads to a decrease in i_{cr}. At higher chromium contents in the alloy, φ_{p} is almost independent of the alloy composition, whereas the overvoltage of active dissolution continues to decrease, thus exerting a prevailing influence on i_{cr}, as a result of which the values of i_{cr} begin to increase (Fig. 2A).

It should be noted that the data in Fig. 2A refer to pure binary Fe—Cr alloys. The critical passivation currents of Fe—Cr alloys containing up to 0.4% nickel (steels 12Kh6, 1Kh13, Kh17, Kh28) are associated with a somewhat different dependence on the chromium concentration in the alloy (Fig. 2B). In this case a regular decrease in i_{cr} is observed with increasing chromium content over the entire investigated range of concentrations of this element (up to 28%). At the same time, the introduction of such small amounts of nickel into the alloy does not lead to any appreciable change in its passivation potential (the data in Fig. 1 refer to all the Fe—Cr alloys investigated). Consequently, the difference

Fig. 3. Anodic polarization curves measured in $0.1\,N$ $H_2SO_4 + 0.9\,N$ Na_2SO_4 on Fe—Cr alloys with chromium contents: 1—12%; 2—27%, 3—35%.
φ_{st}—stationary potentials

Fig. 4. Anodic polarization curves measured in $0.1\,N$ $H_2SO_4 + 0.9\,N$ Na_2SO_4 on alloys: 1—1Kh13; 2—Kh17, 3—Kh28

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* The values of i_{cr} for alloys with a chromium content below 13% have a diffusion nature; this is primarily responsible for the absence of a sharp change in i_{cr} in the region $p_{\mathrm{Cr}} = 12$—13% (Fig. 2A).

** Theoretically, a similar approach was also used by Uhlig (^{5}) in deriving the equation for the dependence of i_{cr} on the pH of the solution by means of the Tafel equation for the anodic process and data on the influence of pH on the value of the Flade potential.

Fig. 4

Figure 4: Fig. 4

between the curves in Fig. 2 must be connected with the influence of nickel on the overvoltage of active dissolution of the alloy. In agreement with this, experiment shows that nickel additions to the alloys (up to 0.4%) exert an inhibiting effect on their dissolution in the active state and appreciably suppress the above-noted activating influence of chromium on this process (Figs. 3 and 4).

The increase in the overvoltage of anodic dissolution of alloys in the active state becomes more significant with a further increase in their nickel content, which leads primarily to a marked decrease in the value of i_{cr}. Our experiments showed, for example, that when 2% nickel is introduced into alloy Kh22T, the value of i_{cr} becomes so small that such an alloy acquires the ability to passivate spontaneously in $0.1\,N$ sulfuric acid solution (the stationary potential shifts by 200 mV in the positive direction, and the rate of self-dissolution decreases appreciably). At the same time, the hydrogen overvoltage practically does not change.

On the basis of these data, as well as the results of earlier investigations ([6]), it may be concluded that the spontaneous passivation of alloy Kh22N2T is caused in this case by the oxidizing action of H^+ ions, the rate of discharge of which at the passivation potential of this alloy appreciably exceeds the critical passivation current density.

Taking into account the fundamental possibility of such an effect, it is necessary, however, to bear in mind that spontaneous passivation due to the oxidizing action of H^+ ions is possible only for alloys containing not less than 13% chromium, since the passivation potentials of alloys with a lower content of this element lie more positive than the potential of the reversible hydrogen electrode in the same solution.

It should be noted that the data on the dependence of the critical passivation currents of alloys on their composition, while of considerable practical importance, cannot, however, be of independent interest for judging about the mechanism of the passivity phenomenon, although such data are often used for this purpose [3].

In fact, from our data, for example, it follows that the minima on the curves in Fig. 2*A* (20–27% Cr) do not correspond to any characteristic alloy composition at which there is a sharp change in the regularities of its dissolution. Sometimes the values of i_{cr} are not found at all to have any definite dependence on the content of one of the components in the alloy [7]. Finally, if one judges by the behavior of the critical passivation current of the alloys studied, one might conclude that the influence of nickel additions on the passivation characteristics is analogous to the influence of chromium additions. However, from the data presented it is clear that the actions of these metals differ appreciably from one another: over a considerable range of its concentrations in the alloy, chromium exerts the strongest influence on the passivation potential, whereas nickel affects mainly the kinetics of the anodic process in the range of potentials preceding passivation.

In order to understand the reason for this difference, it must be borne in mind that the transition of metals to the passive state is the result of an adsorption-chemical interaction of the surface atoms of the metal with the oxygen of water, leading to the formation, at the metal-solution interface, of barrier layers that hinder the transfer of metal ions from the crystal lattice into the solution. It follows from this that an increase in its affinity for oxygen should favor the transition of an alloy to the passive state. A qualitative characteristic of the magnitude of this affinity may be the critical passivation potential, since it is obvious that the greater this affinity, the earlier (i.e., at the more negative potential) passivation should begin. On the basis of the data presented it may be concluded that the favorable influence of chromium additions to iron on the passivation characteristics of the alloys formed is associated chiefly with an increase in the affinity of these alloys for oxygen. The introduction of nickel into binary Fe—Cr alloys is apparently not accompanied by an appreciable change in the affinity of these alloys for oxygen.

Thus, in elucidating the nature of passivation phenomena in alloys of different composition, it is necessary to investigate the influence of alloy composition on the kinetics of its active dissolution and on the passivation potential.

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