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V. P. Batrakov

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Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

Abstract

Full Text

Physical Chemistry

V. P. Batrakov

Electrochemical Principles of the Protection of Metals in Strong Oxidizers

(Presented by Academician S. I. Volfkovich, 11 V 1957)

At present it has been established that the high corrosion rate of many metals and alloys in strong oxidizers is associated with transpassivation, i.e., with the destruction of protective films or the weakening of their protective properties because of the high oxidation-reduction potential, owing to the formation of ions or soluble compounds of metals of higher valence ([1–6]).

The fundamental polarization diagram of metals under conditions of transpassivation is shown in Fig. 1. At a high metal potential

Fig. 1. Polarization diagram explaining the mechanism of corrosion of metals under transpassivation.

Fig. 2. Polarization diagram explaining the mechanism of protection of metals under transpassivation by decreasing the oxidation-reduction potential of the medium.

its anodic polarizability sharply decreases, and the anodic polarization curve **1** assumes a flatter form, as a result of which the rate of self-dissolution of the metal (I_{per}) increases ([4]). Methods of protecting metals under these conditions reduce either to lowering the potential to the value of the potential at which stable passivity arises (the potential must lie between the first and second critical potentials) ([5,6]), or to strengthening the surface film, which hinders anodic processes at high potential, i.e., to increasing its protective properties ([4]). In accordance with the foregoing, the following should be included among the principal methods for protecting metals under transpassivation.

Fig. 3 and Fig. 4 polarization diagrams

Figure 3: Fig. 3 and Fig. 4 polarization diagrams

1. Lowering the oxidation-reduction potential of the medium.

When the oxidation-reduction potential of the medium is decreased from E_k to E_k', the cathodic polarization curve $2'$, in contrast to curve $1'$, intersects the anodic polarization curve 1 in the region characterizing passivation of the metal. The magnitude of the stationary potential and the strength of the local current are thereby reduced from E_{per} to E_{pass} and from I_{per} to I_{pass} (Fig. 2). The metal passes from the state of transpassivation into a state of stable passivity. A lowering of the oxidation-reduction potential of the medium can be achieved by reducing the concentration of the oxidizer or by adding a reducing agent $(2, 5, 7)$.

This method of protection cannot always be used, since it entails a decrease in the oxidizing properties of the medium and a change in its composition.

Fig. 3. Polarization diagram explaining the mechanism of protection of metals during transpassivation by increasing the overvoltage of the anodic process

Fig. 4. Polarization diagram explaining the mechanism of protection of metals during transpassivation by increasing the overvoltage of the cathodic process (cathodic passivity)

2. Increasing the overvoltage of the anodic process.

An increase in the overvoltage of the anodic reaction can be achieved by strengthening the surface film, as a result of which the anodic polarization curve will be characterized by a steeper course. In this case, the effect of transpassivation appears only at a considerably higher potential (Fig. 3, 2), owing to an increase in the overvoltage of formation of ions or compounds of metals of higher valence. The oxidizing properties of the solution are thereby preserved without change. The cathodic polarization curve $1'$ will intersect the anodic polarization curve 2, unlike anodic curve 1, in the region characterizing the passive state of the metal. As a result, the strength of the corrosion current decreases from I_{per} to I_{pass} (Fig. 3) (4). The stationary potential of the metal thereby increases somewhat and reaches the value E_{pass}. An increase in the protective properties of the film can be achieved in one of the following ways: a) by appropriate alloying of alloys with elements that increase the overvoltage of the anodic reaction; b) by introducing into the solution surface-active substances—anodic corrosion inhibitors; c) by relieving internal stresses in the metal and in the film by appropriate heat treatment.

In all cases, anodic polarization increases sharply, and the metal remains in a stable passive state at a high potential. Surface-active substances either adsorb or form sparingly soluble surface compounds that strengthen the protective film on the metal.

3. **Increasing the overvoltage of the cathodic process.** This method of protection differs in principle from the methods considered above. In this case the lowering of the metal potential is achieved not by reducing the oxidizing properties of the solution (Fig. 2), but by increasing the overvoltage of the cathodic reaction. The stationary potential of the metal is thereby lowered to a value at which a stable passive state is attained (cathodic passivity) ([5,6]). The corrosion current decreases from I_{per} to I_{pas} (Fig. 4). Strong cathodic polarization can be achieved:

a) by appropriate alloying of alloys with elements that increase the overvoltage of the cathodic reaction;

b) by introducing into the solution surface-active substances (cathodic corrosion retarders);

c) by sacrificial and cathodic protection in the case of formation of a protective film under cathodic polarization (cathodic passivity).

Along with the protection methods considered, combined methods may be very effective. Sacrificial and cathodic protection under conditions of repassivation may also be considered in the usual conception of electrochemical protection, i.e., without taking into account the formation of protective films on the metal.

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Note: Figure translations are in progress. See original paper for figures.