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ANODIC PROTECTION OF TITANIUM IN SULFURIC ACID

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Titanium in sulfuric acid at concentrations above 10% does not possess sufficient corrosion resistance ($^{1-3}$). Anodic protection is not among the widely used methods for protecting metals from corrosion, since for most metals under anodic polarization, along with suppression of the operation of microelements on the metal surface (positive differential effect), the metal continues to dissolve anodically in accordance with the applied current. But for metals with a pronounced tendency toward passivity (stainless steel, iron), under conditions where a stable passive state can be attained at a small anodic current density, anodic polarization by an external current can produce an overall protective effect. The possibility of using anodic polarization for corrosion protection of stainless steels and iron in sulfuric acid has been shown in a number of works ($^{4-6}$). Titanium, in comparison with stainless steels and iron, has a considerably greater tendency toward passivity. Thus, for example, the onset of the passive state of steel 1Kh18N9 under anodic polarization in a 30% solution of H_2SO_4 is observed at a current density of about 1.5 ma/cm^2 (^{4}), whereas for titanium in a 45% solution of H_2SO_4 anodic passivity occurs at a current density of 0.32 ma/cm^2, i.e., approximately five times lower. Taking this into account, it may be assumed that the use of anodic polarization for protecting titanium in sulfuric acid should be still more effective than for stainless steels and iron. In this connection, the present investigation was devoted to studying the processes of formation of oxide films during the self-passivation of titanium in sulfuric-acid solutions and the processes occurring on the metal surface during anodic polarization. The work was carried out on titanium of grade VT-1D (O 0.23-0.26%, H 0.022-0.023%, N 0.017%, Fe 0.12%, Si 0.05%) in sulfuric-acid solutions at room temperature.

The investigation with abrasion of the metal surface under the solution was carried out in an apparatus specially designed by us (^{7,8}). After establishment of the steady potential of the metal, the abrasion of the surface was stopped, and the change in the metal potential with time was recorded.

Figure 1 presents the results of studying the behavior of titanium when its surface was abraded under sulfuric-acid solutions. As can be seen from the figure, titanium restores the passive state after abrasion of the surface under a 5% H_2SO_4 solution, as follows from the fact that the potential of titanium returns to values of about +0.3 V, corresponding to the passive state of titanium in sulfuric acid. The potentials in the present article are everywhere given on the hydrogen scale. Stirring of the 5% H_2SO_4 solution further facilitates the restoration of passivity. In 10% H_2SO_4, after abrasion, titanium remains in the active state. The potential of the active state of titanium in sulfuric acid was approximately −0.3 V.

In maintaining the stability of the passive state of titanium in dilute ···

solutions of sulfuric acid, as follows from Fig. 1, the principal role is played by the oxygen of the air dissolved in the electrolyte, since in an atmosphere of hydrogen, i.e., in the absence of oxygen in the electrolyte, after stripping the surface in 5% H_2SO_4 titanium remains in the active state. But if the atmosphere of hydrogen is replaced by an atmosphere of air (point A in Fig. 1), titanium rapidly passes into the passive state, as is evident from the sharp shift of its potential in the positive direction.

Fig. 1. Change in the potential of Ti with time after stripping the surface under H_2SO_4 solutions. 1 −5% H_2SO_4 (air atmosphere), 2 −the same, but with stirring of the solution, 3 −5% H_2SO_4 (hydrogen atmosphere), 4 −10% H_2SO_4 (air atmosphere), 5 −10% H_2SO_4 (oxygen atmosphere), 6 −5% H_2SO_4 + 2% NaF (air atmosphere). Line MN denotes the moment at which stripping is switched off. Point A −the moment at which the hydrogen atmosphere is replaced by an air atmosphere.

In addition, if stripping of the titanium surface is carried out in a 10% H_2SO_4 solution in an atmosphere of oxygen, then after the stripping is stopped titanium also passes into the passive state. Restoration of the passive state of titanium in a 10% H_2SO_4 solution can likewise be achieved in an air atmosphere, but on the condition that, after the stripping is stopped, the electrolyte is stirred. It should be noted that the difference between the potential of titanium during surface stripping and the potential of titanium in the passive state is about 0.85 V. This indicates that on the surface of titanium in the passive state there exists a stable, protective oxide film that ensures the passive state. As follows from Fig. 1, the potential of titanium in the active state in a 10% H_2SO_4 solution also differs considerably (by 0.3 V) from the potential of titanium during surface stripping in the same solution. Consequently, the surface of titanium, even in its active state, is partially covered with an oxide film. It also follows from Fig. 1 that, in the formation of an oxide film on the surface of titanium, in addition to the oxygen dissolved in the electrolyte, water also takes part, since even in an atmosphere of hydrogen in 5% H_2SO_4 solution the potential of titanium in the active state is 0.3 V more positive than the potential during surface stripping. The interaction of titanium with water may proceed, for example, according to reaction ([10]):

Fig. 2. Anodic polarization of Ti in H_2SO_4. 1–27% H_2SO_4. 2–40% H_2SO_4, 3 –50% H_2SO_4, 4–64% H_2SO_4

Figure 1: Fig. 2. Anodic polarization of Ti in H_2SO_4. 1–27% H_2SO_4. 2–40% H_2SO_4, 3–50% H_2SO_4, 4–64% H_2SO_4

$$\mathrm{Ti} + 2\mathrm{H_2O} = \mathrm{TiO_2(hydr.)} + 4\mathrm{H^+} + 4e - 0.86\ \mathrm{V}. \qquad (1)$$

It is known that hydrofluoric acid and acidic electrolytes containing fluoride ions are the most aggressive toward titanium, and, moreover, formation of an oxide film on the surface of titanium is not observed even under anodic polarization in these solutions ([1]). Therefore, the explanation of the difference between the potential of titanium in the active state and its potential during surface stripping by the formation of an oxide film on the titanium surface can also be confirmed by the fact that in a solution of 5% H_2SO_4 + 2% NaF, i.e., in a solution in which the oxide film on the titanium surface is readily soluble, the potential of titanium during stripping and the potential of its active state practically do not differ. It may be assumed that the passivation of titanium after stripping its surface under a sulfuric-acid solution proceeds in two stages. Initially the metal surface interacts mainly with water (according to reaction (1)), the concentration of which ?

of course, considerably higher than the concentration of oxygen. In solutions of sulfuric acid with a concentration above 10%, in which titanium is not stable, adsorption of oxygen on the titanium surface is hindered, as a result of which the formation of the protective film ends at this first stage, which does not provide complete passivation. This assumption is confirmed by the equality of the potentials of titanium in the active state in 10% H_2SO_4 solutions (air atmosphere) and 5% H_2SO_4 (hydrogen atmosphere). At lower sulfuric-acid concentration (5% and below), on the titanium surface, following the formation of an oxide film arising from the interaction of titanium with water, additional adsorption of oxygen occurs and a stable oxide film is formed, ensuring the onset of complete passivity.

Fig. 2. Anodic polarization of Ti in H_2SO_4. 1–27% H_2SO_4. 2–40% H_2SO_4, 3 –50% H_2SO_4, 4–64% H_2SO_4

Fig. 2 shows the curves of anodic polarization of titanium in sulfuric-acid solutions of various concentrations. It is evident from the figure that anodic polarizability in the region of active dissolution of titanium increases with decreasing sulfuric-acid concentration. This may be explained by the fact that, with increasing acid concentration, the solubility of oxygen in the acid decreases ([11]) and the solubility of titanium oxides ([12]), of which the protective oxide film is composed, increases; this film partially covers the surface of titanium in its active state. After the region of active anodic dissolution, the magnitude of which increases with increasing acid concentration, anodic passivity sets in, ac-

Fig. 3. Dependence of the minimum current density necessary for anodic passivity of Ti on H_2SO_4 concentration

Figure 2: Fig. 3. Dependence of the minimum current density necessary for anodic passivity of Ti on H_2SO_4 concentration

companied by a sharp jump in potential to values of +3 to +10 V, with a simultaneous considerable drop in current. This is associated with the formation on the electrode surface of anodic films with high ohmic resistance; at the same time, oxygen evolution also occurs on the electrode. In the region of the passive state of titanium, in contrast to the region of its active dissolution, anodic polarizability increases with increasing acid concentration.

Fig. 3. Dependence of the minimum current density necessary for anodic passivity of Ti on the concentration of H_2SO_4

The formation on the titanium surface of oxide films with high ohmic resistance, preventing the anodic process from proceeding during anodic polarization of titanium in sulfuric-acid solutions, was also shown in works ([2], [3]).

The small region of active anodic dissolution of titanium in sulfuric acid, the considerable drop in current after the onset of anodic passivity (Fig. 2), and also the ability of titanium to form strong, stable protective oxide films both during self-passivation (Fig. 1) and during anodic polarization (Fig. 2), provide grounds for considering anodic protection of titanium in sulfuric acid possible. The possibilities of anodic protection were studied in the regions of maximum corrosion rate of titanium in sulfuric acid (40 and 78%) ([2], [3]). The electrode was lowered into the solution under an anodic current equal to the current minimally necessary for the onset of anodic passivity of ti-

titanium in the given sulfuric acid solution, or somewhat (by 5-10%) greater than it. The magnitude of this current can be determined from the data presented in Fig. 3. As soon as the potential of titanium, as a result of the onset of anodic passivity, reached a value on the order of $+2 \div +3$ V, and oxygen began to evolve on the specimen, the polarizing current decreased so that the potential of titanium lay in the region of values somewhat exceeding the potential of its passive state, i.e., the potential was maintained approximately in the range $+0.5 \div +1.0$ V. Lower potential values may be dangerous because of incomplete passivation and the possibility that titanium may pass into the active state as a result of accidental causes capable of disturbing the passive state. Potential values above 1 V are not dangerous with respect to disturbance of the passive state, but to maintain a higher potential a protective current of higher density is required, which is economically inexpedient. To maintain the potential of titanium in the range $+0.5 \div +1$ V in 78% H_2SO_4 solution after the onset of the passive state, a current density of only $0.5 \div 1.0$ μA/cm^2 was necessary. For 40% H_2SO_4, an even smaller current, $0.1 \div 0.2$ μA/cm^2, was required.

Fig. 4. Corrosion of Ti in H_2SO_4 without protection and with anodic protec-

Fig. 4. Corrosion of Ti in H_2SO_4 without protection and with anodic protection. 1 –40% H_2SO_4 (without protection), 2 –40% H_2SO_4 (with anodic protection), 3 –78% H_2SO_4 (without protection), 4 –78% H_2SO_4 (with anodic protection)

Figure 3: Fig. 4. Corrosion of Ti in H_2SO_4 without protection and with anodic protection. 1 –40% H_2SO_4 (without protection), 2 –40% H_2SO_4 (with anodic protection), 3 –78% H_2SO_4 (without protection), 4 –78% H_2SO_4 (with anodic protection)

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Figure 4 gives the results of corrosion tests of titanium specimens protected anodically and without protection. The corrosion losses (determined by the gravimetric method) of unprotected specimens increased linearly with time. With anodic protection of titanium in both sulfuric-acid solutions studied, corrosion losses were practically completely absent. The insignificant weight losses may be attributed to the initial period of active dissolution of titanium before the onset of anodic passivity. In addition to sulfuric-acid solutions, anodic protection of titanium can undoubtedly also be applied to a number of other solutions in which the passive state of titanium can readily arise as a result of anodic polarization.

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