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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Corrosion Behavior of Ti–Nb Alloys in Sulfuric Acid

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Abstract—Specific features of the corrosion behavior of Ti–Nb alloys in a 40% H_2SO_4 solution were studied.

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It is known that the chemical stability and a number of other properties of binary alloys having the form of solid solutions change under the action of a corrosive medium discretely at compositions that are multiples of $n/8$ atomic fractions (n = 1, 2–7) of the more stable component. These alloy compositions are named chemical stability boundaries [1, 2]. According to the existing concepts, the chemical stability boundaries are associated with enrichment of the alloy surface with a more stable component in interaction with a corrosive medium [3, 4].

A quantitative characteristic of dissolution of homogeneous alloys is the coefficient of the selective dissolution of a component, Z_i [5], which is defined as the ratio between the contents of components in the solution and alloy. In the case of a uniform dissolution of the alloy, Z_i = 1 and the ratio of the partial dissolution rates of the components is proportional to the ratio between the contents of the components in the alloy. If the dissolution rates of the components of the alloy markedly differ, then, a mutual influence of the components can be observed at certain compositions for a number of systems [6], and the dissolution rate of a component can be determined by that of another component and may substantially differ from its dissolution rate in the individual state. In selective dissolution of alloys [7–9], a predominant transfer of atoms of the unstable component into solution results in that atoms of the more stable component accumulate on the surface. In the course of dissolution of the alloy, there may occur back deposition of the stable component from solution, accompanied by formation of its own phase on the surface.

The aim of our study was to examine specific features of the corrosion behavior of Ti–Nb alloys forming a continuous series of solid solutions [10] under the conditions in which the individual dissolution rates of the alloy components significantly differ.

EXPERIMENTAL

The alloys were produced from titanium of VT-1 brand and NB-0 niobium. The content of Ti and Nb in the alloys under study was varied as multiples of 5 ± 0.1 at % (see table). A total of 19 alloys and pure Ti and Nb were tested. According to [11], TiNb intermetallides can be formed in alloys containing 47–87 at % Nb. The presence of intermetallides can affect the corrosion behavior of the alloys. Therefore, we studied the microstructure of metallographic sections of alloys containing 40 and 70 at % Nb (at 1000× magnification). It was found that both the alloys have the same structure of a solid solution. The absence of intermetallides in this system was also reported in [12, 13].

The corrosion resistance of Ti and Nb is determined by the stability of passive films in corrosive media [4]. Sulfuric acid with an increased concentration decomposes the protective film of titanium dioxide, and thereby causes its dissolution, whereas niobium is stable in acid media. We chose as a corrosive medium in the study a 40 wt % solution of H_2SO_4 because preliminary experiments demonstrated a noticeable difference in the corrosion behavior of pure metals in this medium: Ti dissolves at a high rate and Nb is almost resistant. The corrosion rate was determined in the study from the loss of mass in g-at m^{-2} h^{-1} and g m^{-2} h^{-1}.

The results of our corrosion tests are listed in the table. It can be seen that the dissolution rates of titanium and niobium in a 40 wt % solution of H_2SO_4 are 1.25 and

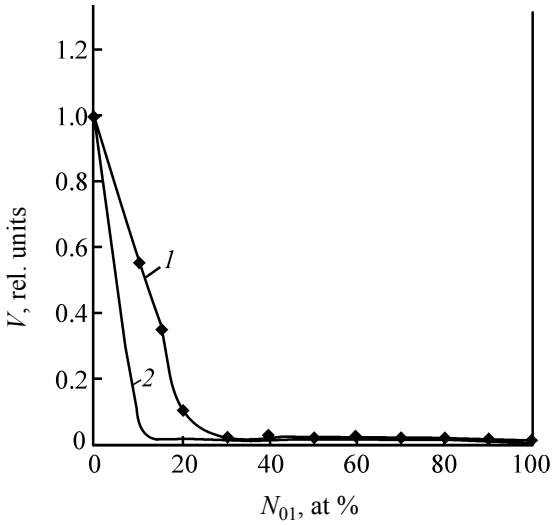

Fig. 1. (1) Corrosion rate V of Ti–Nb alloys and (*2*) niobium content in the surface layer vs. the alloy composition. (N_{01}) Nb content of the alloy; the same for Fig. 2.

0.006 g m^{-2} h^{-1}, i.e., the ratio between the dissolution rates of the individual components is $k = V_{Ti}/V_{Nb} = 208$. By the type of dissolution, the alloys can be divided into two groups (Fig. 1). Alloys of the first group are resistant alloys containing ≥30 at % Nb which dissolve at a rather low rate weakly dependent on the alloy composition and have a stability corresponding to that of pure niobium. The second group are unstable alloys containing less than 30 at% niobium. An increase in the Nb content within the range 5–25 at % leads to a linear decrease in the corrosion rate of the alloys. Thus, a sharp change in the corrosion resistance (appearance of a chemical stability boundary) upon an increase in the content of the more stable component was not observed in the case in question.

To find out for unstable alloys whether Ti is selectively dissolved or both the components are dissolved in proportion to their volume content, we analyzed for the content of Ti^{3+} ions the solutions obtained upon the corrosion tests. The content of these ions was determined calorimetrically with the use of hydrogen peroxide H_2O_2 which forms colored compounds with titanium. Below are presented results of analyses of the solutions and changes in the sample masses, Δm, after corrosion tests of alloy nos. 3 and 5, which contain 10 and 20 at % Ni, respectively:

Alloy no.	Amount of titanium in solution, g	Δm, g
3	0.0436	0.0426
5	0.0038	0.0033

It can be seen that the corrosion of unstable alloys is accompanied by dissolution of only titanium, i.e., there occurs "detitanization" of the alloy and accumulation of the more stable component, niobium, on the surface. The steady-state composition of the surface layer of the alloy can be calculated [15]:

$$N_1 = \frac{V_2 N_{01}}{V_1 + (V_2 - V_1)N_{01}} = \frac{kN_{01}}{1 + (k-1)N_{01}}, \qquad (1)$$

where $N_{01}$and N_1 are the contents of the more stable component Nb in the alloy and in the surface layer (at. fractions), respectively; V_1 and V_2, partial dissolution rates of niobium and titanium; and k, ratio of the partial dissolution rates of titanium and niobium. The results of

Corrosion rate of Ti–Nb alloys and niobium content of the surface layer C(H_2SO_4) 40 wt %

Alloy no.	Content, at %		Corrosion rate		N_1, at. fraction
	Nb	Ti	g m^{-2} h^{-1}	g-at n^{-2} h^{-1}	
1	0	100	1.250	0.0260	0
2	5	95	0.995	0.0205	0.917
3	10	90	0.769	0.0156	0.959
4	15	85	0.462	0.0090	0.974
5	20	80	0.135	0.0026	0.982
6	25	75	0.075	0.0013	0.986
7	30	70	0.026	0.0004	0.989
8	35	65	0.032	0.0005	0.992
9	40	60	0.036	0.0006	0.993
10	45	55	0.030	0.0005	0.995
11	50	50	0.029	0.0005	0.996
12	55	45	0.022	0.0003	0.996
13	60	40	0.031	0.0004	0.997
14	65	35	0.024	0.0003	0.998
15	70	30	0.020	0.0003	0.998
16	75	25	0.015	0.0002	0.999
17	80	20	0.016	0.0002	0.999
18	85	15	0.014	0.0002	1.0
19	90	10	0.013	0.0002	1.0
20	95	5	0.015	0.0002	1.0
21	100	0	0.006	0.0001	1.0

a calculation of the Nb content of the surface layer are listed in the table, and Fig. 1 shows the dependence $N_l = f(N_{01})$ (curve *2*). It can be seen that, at a low content of niobium in the alloy, $N_{01} = 0.05$ (95 at % Ti), and ratio between the partial dissolution rates of the components, $k = 208$, the content of niobium in the surface layer is $N_l = 0.917$ (8.3 Ti), i.e., a rather strong enrichment of the surface layer with niobium is observed under the given conditions. This must lead to a sharp decrease in the dissolution rate of the alloy. However, no sharp deceleration of the dissolution of the alloy was observed. This possibly occurs because, at a large difference between the dissolution rates of the components and a low content of the more stable component in the alloy, the surface layer is formed under nonequilibrium conditions and a rather defective layer appears on the surface of the alloy. This layer is enriched with atoms of the more stable component with a distorted crystal lattice, which exerts a kind of accelerating catalytic influence on the dissolution of the less stable component.

The absence of a pronounced stability boundary in the system of alloys of the type of binary solid solutions at a noticeable difference between the corrosion rates of pure components has also been observed for the Cu–Ni system in a S_2Cl_2 solution [2]. The sulfur chloride is not an electrolyte and, therefore, there is no ion exchange between the alloy surface and the corrosive medium.

Assuming that the partial dissolution rates of the alloy components, we can calculate the corrosion rate of an alloy at a certain composition by taking into account the possibility of enrichment of the alloy surface with a more stable component [15]. The total corrosion rate of an alloy, V, can be represented as a sum of the dissolution rates of the alloy components, with their atomic fraction on the surface taken into account:

$$V = V_1N_1 + V_2(1 - N_1) \quad (2)$$

Substituting N_l from (1) into (2), we obtain

$$V = \frac{V_1V_2}{V_1 + (V_2 - V_1)N_{01}} = \frac{V_2}{1 + (k - 1)N_{01}}, \quad (3)$$

It can be seen that the type of the dependence $V = f(N_{01})$ is determined by the ratio k between the dissolution rates of the individual components of the alloy. To enable comparison of the calculated and experimental values of V, the corrosion rate was expressed in relative units, with the corrosion rate of pure Ti taken to be unity in both cases.

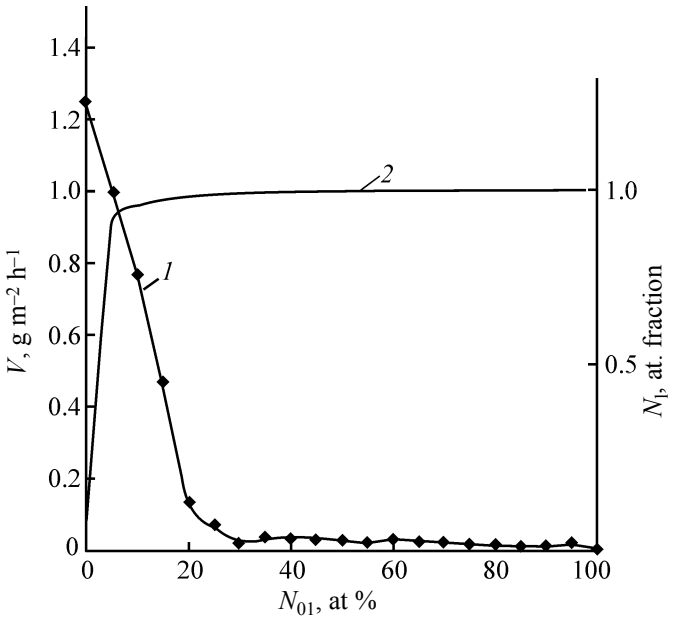

Fig. 2. Corrosion rate V of Ti–Nb alloys vs. the alloy composition.

Figure 2 shows how the calculated (curve *1*) and experimental (curve *2*) values of V depend on the alloy composition. It can be seen that the dependences are symbate. In the range of corrosion-resistant alloys, the curves almost coincide. In the range of unstable alloys (up to 30 at %), the calculation gives underestimated values of the corrosion rate, compared with those experimentally obtained. This is due, as shown above, to the defectiveness of the surface layer, which is characterized by a poorer protection efficiency and thereby fails to sharply decelerate the alloy dissolution.

CONCLUSIONS

(1) It was found that the corrosion resistance of Ti–Nb alloys in a 40% H_2SO_4 solution linearly decreases as the niobium content increases within the range 5–25 at %.

(2) It was shown that, at a large difference between the dissolution rates of the individual components, a defective layer of the more resistant component is formed on the surface. This layer does not sharply decelerate the alloy dissolution.

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