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## Abstract

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# CORROSION BEHAVIOR OF ALLOYS OF THE TITANIUM-OXYGEN SYSTEM IN SULFURIC ACID SOLUTIONS

*(Presented by Academician A. A. Bochvar on 26 III 1965)*

Titanium is characterized by relatively low corrosion resistance in solutions of $H_2SO_4$ and HCl at concentrations above 10% and at ordinary temperatures. One way to further increase the corrosion resistance of Ti is its rational alloying. Many investigations have been devoted to solving this problem ($^{1-6}$). The authors of these works have shown that, when titanium is alloyed with molybdenum, zirconium, platinum, palladium, silver, and a number of other metals, it is possible to increase its corrosion resistance substantially.

It may be assumed that alloying Ti in order to increase its corrosion resistance is apparently also possible with gases (for example, hydrogen, nitrogen, and oxygen), in amounts permissible, of course, with respect to mechanical properties ($^{7-9}$). Ti has an exceptionally high affinity for oxygen, and the presence of one or another surface compound of titanium with oxygen substantially retards corrosion processes ($^{9-12}$).

In this connection, it is of considerable interest to carry out a study of the corrosion resistance of Ti alloyed with oxygen over a wide concentration range, as a function of alloy composition. This is all the more interesting because a recently conducted ($^{13-16}$) detailed investigation of the phase equilibria of alloys of the titanium-oxygen system in the concentration interval from 1 to 35 at.% oxygen showed that in this system there exists a limited region of solid solutions based on $\alpha$-Ti (up to 9 at.% O) and that previously unknown compounds $Ti_6O$ and $Ti_3O$ with a metallic type of bonding are formed. The compound $Ti_6O$ is stable only below 820-830°, whereas the compound $Ti_3O$ is stable up to the melting temperature. Both compounds are formed as ordered phases, the first from the $\alpha$-solid solution and the second during crystallization from the liquid at a temperature of 1940°.

**Experimental procedure.** To carry out the investigation, alloys were pre-

Fig. 1. Change in corrosion rate (a) compared with the equilibrium phase diagram of the titanium-oxygen system (b). 1 –40% $H_2SO_4$, 2 –70% $H_2SO_4$.

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pared in an arc furnace with a nonconsumable tungsten electrode in an atmosphere of purified argon. The starting materials were iodide titanium (99.9% Ti) and titanium dioxide containing 99.93% $TiO_2$. Oxygen was introduced into the alloys in the form of a master alloy containing 15.8 wt.% oxygen. The master alloy was prepared by melting, in an arc furnace, rods pressed from titanium and fused titanium dioxide.

By the method described above, alloys containing 1, 5, 9, 10, 11, 12, 13, 15, 16, 17, 20, 25, and 36 at.% oxygen were prepared. The cast alloys were annealed at 800° for 100 h and slowly cooled from this temperature.

The corrosion resistance and standard electrode potentials of Ti alloys with oxygen were studied in $H_2SO_4$ of 40 and 70% concentration, i.e., under severe test conditions, under which titanium corrodes intensely.

Samples in the form of cylinders 8 mm in diameter were coated on the side with freshly prepared ED-5 epoxy resin and pressed into a Teflon holder of the same diameter; the working surface was the end face of the sample. Contact between the sample and the current lead was made by means of a spring inside the holder. Before the experiment, the end working surface of the samples was cleaned with emery paper, followed by fine polishing with No. 10 aluminum oxide and washing with distilled water. Before examination, the samples were kept in a desiccator for 17 h.

For an alloy of each composition, curves of the change in potential with time were recorded, as were the duration of the time interval until the moment of activation ($\tau_0$), the value of the potential under dissolution conditions ($E_{\mathrm{H,V}}$), and the corrosion rate, referred to the same residence time of the sample in the active state ($K$). Since the time until activation of the samples was different, the duration of the test, counted from the moment the sample was immersed in the solution, ranged from 5 to 18 h for alloys of different composition.

The volume of the working solution was 170 ml. The experiments were carried out in a thermostat at a temperature of 25°. The corrosion of alloys of the titanium-oxygen system was determined by analysis of the entire solution for the content of titanium ions. The solution was analyzed by the photocolorimetric method with hydrogen peroxide when studying corrosion in 70% acid and with the more sensitive indicator diantipyrylmethane ($^{17}$) when studying corrosion in 40% acid.

**Fig. 1.** Change in the corrosion rate ($a$) in comparison with the equilibrium

Fig. 2

Figure 2: Fig. 2

phase diagram of the titanium-oxygen system (*b*).
1 –40% $H_2SO_4$, 2 –70% $H_2SO_4$

**Experimental results and discussion.**
Figure 1 gives data on the corrosion resistance (*a*) of Ti alloys with oxygen in comparison with the equilibrium phase diagram (*b*) of the titanium-oxygen system. As can be seen from the figure, all these alloys in 70% $H_2SO_4$ solution have greater corrosion resistance than Ti.

On the corrosion-rate curve in 70% $H_2SO_4$ solution, two minima can be seen at 5 and 15 at.% $O_2$, and two maxima at oxygen contents in the composition ranges 9-13 at.% and around 20 at.%. For alloys with a higher oxygen content, a further decrease in the corrosion rate is observed. Thus, for example, an alloy with 25 at.% oxygen, corresponding to the chemical compound $Ti_3O$, has greater corrosion resistance than an alloy with 20 at.% $O_2$.

Alloys with corrosion minima (5 and 15 at.% oxygen) correspond, respectively, to the $\alpha$-solid solution of oxygen in titanium and to the chemical compound $Ti_6O$.

The maxima of the corrosion rate observed for alloys of compositions 9-13 and around 20 at.% oxygen apparently correspond to the appearance of the two-phase region $\alpha + \gamma$, located to the right and to the left of the compound $Ti_6O$.

In 40% $H_2SO_4$ solutions, the corrosion-rate curve for all alloys lies lower than in 70% $H_2SO_4$, while retaining in general an analogous character, with maxima and minima at approximately the same alloy compositions. However, in contrast to the 70% $H_2SO_4$ solution, in 40% acid pure Ti and Ti with a small amount of oxygen, for reasons not yet explained,

corrodes at a lower rate than the alloys corresponding to the two-phase region $\alpha + \gamma$ (at 12 and 17 at.% $O_2$).

Both in 70% solution and in 40% $H_2SO_4$ solution, the solid solutions of titanium with 5 at.% oxygen, the chemical compounds $Ti_6O$ and $Ti_3O$, as well as an alloy of composition with 36 at.% $O_2$, corresponding to a higher content of the alloying element, prove to be highly corrosion-resistant.

**Fig. 2.** Curves of the change in electrode potential with time for titanium and alloys with oxygen in a 70% $H_2SO_4$ medium.
1–Ti, 2–1%, 3–5%, 4–10%, 5–15%, 6–25% $O_2$.

Figure 2 shows curves of the change in the stationary electrode potential with time for titanium and alloys with different oxygen contents (from 1 to 25 at.% oxygen).

Fig. 3

Figure 3: Fig. 3

As can be readily seen from the figure, the potential of the specimen, corresponding initially to the passive state, gradually shifts in the negative direction as the oxide films are destroyed. Then the specimen passes almost abruptly into the active state. After this, the potential of the specimen shifts somewhat, already in the opposite direction. The indicated slight shift of the potential in the positive direction is apparently due both to facilitation of the cathodic reaction as a result of further destruction of the oxides and the appearance of hydride on the titanium surface, and to retardation of the anodic reaction owing to the formation of titanium hydride.

As can be seen from Fig. 2, and more clearly from Fig. 3, the time for transition of the specimen to the active state initially, in the region of 1-5 at.% $O_2$, increases, and then decreases somewhat. A sharp increase in the time for transition of the alloy to the active state is generally observed for alloy compositions with a two-phase structure. Homogeneous alloys corresponding to the compounds $Ti_6O$ and $Ti_3O$, however, are activated rather quickly.

**Fig. 3.** Dependence of the residence time of the specimen in solution before its transition to the active state on the composition of the alloys.
1–40% $H_2SO_4$, 2–70% $H_2SO_4$.

Here it should be noted that there is a certain similarity with the heat-resistance curves obtained for alloys of the titanium-oxygen system as a function of composition at temperatures of 700 and 800°. On the curves expressing the dependence of the weight gain of specimens on the oxygen content in the alloy, minima were found, i.e., increased heat resistance was present for alloys with 5 and 25 at.% oxygen ($Ti_3O$). The compound $Ti_6O$ is less thermally stable, and when the test temperature is raised already to 700°, there is a considerable increase in the diffusional mobility of the atoms, as a result of which the heat resistance decreases and the corresponding minimum in the oxidation rate is not observed ($^{15}$).

It may be assumed that at room temperature, on alloys close in composition to 5 at.% oxygen, and on the compounds $Ti_6O$ and $Ti_3O$, the oxide films will have a relatively small thickness in comparison with the inhomogeneous two-phase alloys. They should therefore dissolve in the acid in a shorter time. For this reason, the time for the specimens with 5, 15, and 25 at.% oxygen to pass into the active state is considerably shorter than for alloys with a two-phase structure, for example the alloys with 11 and 20 at.%.

Figure 4 presents the curve of the change in the potential of a specimen, recorded as its most negative value, as a function of the composition of the alloys of the titanium-oxygen system. On this curve a clearly expressed minimum is observed, i.e., the most positive value of the potential, at 5 at.% oxygen in the alloy. It

Fig. 4. Dependence of specimen potential in solutions of 40% (1) and 70% $H_2SO_4$ (2) on the oxygen content in the alloys

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should be noted that the potential minimum at 5 at.% oxygen is also observed if the ordinate axis is used to plot the relatively stable value of the potential recorded 5 h after immersion of the specimen in the solution (−0.2 V). At this oxygen concentration in the alloy, a reduced corrosion rate is also found (see Fig. 1). However, complete parallelism between corrosion resistance and the value of the stationary potential is not observed, since the latter depends simultaneously on the kinetics of both anodic and cathodic processes ([18]).

**Fig. 4.** Dependence of the potential of the specimen in solutions of 40% (1) and 70% $H_2SO_4$ (2) on the oxygen content in the alloys

The sharp decrease in the corrosion rate of Ti upon the introduction of 5 at.% $O_2$, as well as at higher contents of it, gives grounds to suppose that the formation, by one route or another, of a surface layer of such an alloy on Ti can substantially increase its corrosion resistance.

As a result of the investigation, the following conclusion may be drawn. 1. It has been shown that in 70% $H_2SO_4$ solutions all Ti alloys with oxygen are more corrosion-resistant than Ti. 2. Of considerable interest is the fact that, when oxygen is introduced up to 5 at.%, the corrosion resistance of titanium increases severalfold.

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## CITED LITERATURE

1. N. D. Tomashov, G. P. Chernova, R. M. Al' tovskii, ZhFKh, **35**, issue 5, 1068 (1961).

2. N. D. Tomashov, R. M. Al' tovskii et al., in: *Corrosion and Protection of Structural Materials*, 1961, p. 173.

3. R. M. Al' tovskii, N. N. Tomashova, ZhP Kh, **37**, No. 126 (1964).

4. V. V. Andreeva, G. P. Danilova, Ya. M. Tsirkes, *Strong Corrosion-Resistant Alloys Based on Titanium*, ser. 19, MT-56-452/9, 1956.

5. V. V. Andreeva, V. I. Kazarin, DAN, **128**, No. 4, 748 (1959).

6. V. V. Andreeva, A. I. Glukhova, ZhP Kh, **35**, 1771 (1962).

7. N. D. Tomashov, R. M. Al' tovskii et al., in: *Corrosion and Protection of Structural Materials*, 1961, p. 151.

8. R. Y. Otsuka, *J. Metals*, **9**, No. 1, 73 (1957).

9. N. D. Tomashov, R. M. Al' tovskii, *Corrosion and Protection of Titanium*, 1963.

10. N. D. Tomashov, G. P. Chernova et al., *Zav. lab.*, No. 3, 299 (1963).

11. N. D. Tomashov, R. M. Al' tovskii, M. N. Kushnerov, DAN, **141**, No. 4, 913 (1961).

12. N. D. Tomashov, V. N. Modestova, L. A. Plavich, in: *Corrosion and Protection of Metals*, Moscow, 1965.

13. I. I. Kornilov, V. V. Glazova, DAN, **150**, No. 2, 313 (1963).

14. I. I. Kornilov, V. V. Glazova, DAN, **154**, No. 3, 638 (1964).

15. I. I. Kornilov, V. V. Glazova, *Izv. AN SSSR, OTN, Metallurgy and Mining*, No. 3 (1964).

16. I. I. Kornilov, V. V. Glazova, *Fiz. met. i metalloved.*, **18**, issue 3 (1964).

17. L. Ya. Polyak, ZhAKh, **37**, issue 2, 206 (1962).

18. N. D. Tomashov, *Theory and Protection of Metals*, Izv. AN SSSR, 1959.

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