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TRANSLATION

BEHAVIOR OF TITANIUM ALLOYS DURING CORROSION UNDER STRESS IN ACID MEDIA

By

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Although the quantity of works devoted to the investigation of the behavior of titanium during corrosion under stress is small, nonetheless it is possible to consider that titanium and its alloys are comparatively little subject to corrosion cracking, especially in water media. It is known that corrosion cracking of titanium and its alloys is observed under the influence of red fuming nitric acid [1], 10% hydrochloric acid [2] (after temperature aging in the region of existence of the β-phase and furnace cooling, i.e., after effectuation of heat treatment promoting separation of impurities on boundaries of grains) and, as was recently fixed by the authors of this article, corrosion cracking of titanium is caused also by a 3% solution of bromine in methylene alcohol. We will indicate in passing that titanium and its alloys are subject to corrosion cracking during high-temperature corrosion in the presence of sodium chloride [3] and also in melted cadmium [4]. Welded seams of titanic alloys are subject to corrosion cracking in chlorinated hydrocarbons at 370° [5].

Side by side with comparatively small inclination to corrosion cracking in aqueous solutions, titanium and its alloys are as is known, subject to embrittlement by hydrogen inclusions [6,7].

Hydrogen can occur in titanium and its alloys during contact corrosion, if they execute role of cathode, during their dissolution in acids. As was shown by investigation of surface of titanium by the method of electron diffraction, during its dissolution in hydrochloric, sulphuric, phosphorous and hydrofluoric acids a hydride film appears on its surface [8,9]. It was considered interesting to investigate, whether external stresses have an effect on penetration of hydrogen, liberated during corrosion, into the depth of the metal and how this is reflected in the behavior of titanium alloys during corrosion under stress.

In this work is investigated the behavior during corrosion under stress of materials with an α -structure, namely alloys of the system Ti-Al (VT5) and titanium (VT1) of industrial issue.

Methodology of Experiment

The material and for the given investigation was sheet VT5 alloy 1.05 mm thick, annealed at a temperature of 700° for 1 hour, and VT1 titanium 0.99 mm thick, annealed at 500° for 1 hour.

For investigation of behavior of welded samples during corrosion under stress was produced argon-arc butt welding of corresponding materials was carried out.[1] Welding of samples of VT5 and VT1 was produced in argon containing 0.23 0/0 nitrogen and 0.05 0/0 oxygen, and (for comparison) in argon containing 0.05 0/0 nitrogen and 0.0038 0/0 oxygen. Expenditure of argon during welding was 8 l/min, arc voltage was 9--117v, and current was 50 to 60 a; diameter of tungsten electrode was 1.6 mm.

Table 1

Chemical composition and mechanical properties of alloys to on the basis of titanium

1 Сплав	Al	Fe	Si	C	O	H	N	2 Предел прочности $\sigma_в$, кГ/мм²	3 Относительное сужение ψ, %	4 Относительное удлинение δ, %
5 ВТ1	—	0,12	0,03	0,065	0,14	0,015	0,024	52,7	49,2	24,2
6 ВТ5	4,7	0,22	0,1	0,07	0,11	0,009	0,028	94,8	40,3	15,1

1) Alloy; 2) Ultimate strength σ_B, kG/mm^2; 3) Relative reduction, 0/0; 4) Relative elongation, 0/0; 5) VT1; 6) VT5.

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[1] Welding was done by G. V. Nazarovyy in the Institute of Metallurgy imeni A. L. Baykova.

Experiments were conducted in solutions of hydrochloric and sulphuric acids of different concentrations, i.e., at different conditions of absorption of hydrogen. Constant in time stretching stress (tension) was realized by means of a lever machine, described by us in detail, earlier[10]. Samples were cut across rolling and had form of discontinuous samples with part width working of 5 mm and length of 50 mm. Before the experiment the samples were cleaned on No. 7 and No. 14 emery paper, degreased by dichlorethane, and then for 6--7 sec. were slighty etched in a solution containing HS1 (d = 1.19 g/cm^3) 340--350 cm^3/1, HNO_3 (d = 1.4 g/cm^3) 55 to 60 cm^3/1 and NaF 50 g/1. After that samples were washed, dried with filter paper and held for approximately 24 hours in an exsiccator. During the experiments the temperature of the working solution was held for 12 hours at 35°, after which the heater was switched off and the temperature was lowered to approximately 20°. Sample was subjected to tension after its potential obtained a value of -0.17v against a normal calomel electrode. This time to imposition stress depending upon solution, varied correspondingly from 10 to 120 min.

Inasmuch as hydrogen in the form of hydrides of titanium is concentrated in a thin surface layer of metal and especially on ribs of the sample, then for removal of steep slopes by the margin of the cuts, separate samples were coated with a galvanic layer of nickel 20 microns thick, after which they were clamped in a steel clamp in such a way that the wide side of the sample was subjected to grinding and polishing. Microsections of alloy VT5 were etched in the following solution: 1 volume HF (d = 1.17 g/cm^3), 4 volumes HNO_3 (d = 1.4 g/cm^3), 4 volumes glycerine. Microsections of titanium were etched in this solution: 1 volume HF, 3 volumes NNO_3 and 3 volumes glycerine.

Results of Investigation

During corrosion under a stress of 72 kG/mm^2 and lower in relatively dilute solutions of hydrochloric (5.3 and 10 0/0) and sulphuric (7.3 and 12.9 0/0)[1] acids, samples of alloy VT5, as distinguished from titanium, undergo brittle failure. Brittle failure of alloy VT5 is observed also in a solution of 60 0/0 (10.67 N) sulphuric acid, where after transient vigorous dissolution for about 10 hours, the corrosion process proceeds at a very low speed, which is stipulated by the formation of little-soluble products of corrosion.

Brittle failure of samples of alloy VT5 is promoted by small stress and low speeds of corrosion. In solutions of 5.3% hydrochloric and 7.3 0/0 sulphuric acids and in a solution 60 0/0 sulphuric acid even with such large stresses as 72 kG/mm^2, samples fail brittlely with the formation of a large quantity of cracks located along the whole length of the sample. The general form of cracks is depicted in Fig. 1, where is presented micrography of a longitudinal section from a sample, standing under a stress of 72 kG/mm^2 in a solution of 5.3 0/0 hydrochloric acid. Failure of the sample set in through 35 days. During the preparation of a microsection, solid greyish-blue hydride layer, well visible under microscope after polishing, was removed. The surface shown on the drawing is located practically directly under the solid hydride layer. The elongated stretched structural components "a" are well-visible hydrides of titanium. Oblique strokes correspond to slip planes along which occurs precipitation of hydrides of titanium, which it is possible to see clearly at large magnification (Fig. 2). We will note that earlier [11, 12] in alloys of the Ti--Al system containing hydrogen introduced into the metal by heating it in an atmosphere of hydrogen, even during the absence of external stress, separation of hydrides of titanium both along slip lines and twinning, and along the grain boundaries was observed.

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[1] These concentrations correspond, respectively, to 1.5 and 2.88 N concentrations of hydrochloric and sulphuric acids.

If steep slopes by the margin of the cut, as described above, and the upper solid hydride layer are removed, then on a longitudinal slide it is possible to see (Fig. 3), without etching of the microsection, a hydride layer by the margin of the sample and filament of hydrides of titanium, stipulated by diffusion of hydrogen into the depth of the metal under influence of stress. In Fig. 3 is given micrography of a longitudinal section of a sample of alloy VT5 after corrosion under a stress of 72 kG/mm^2 in a solution of 60 0/0 sulphuric acid, where the hydride layer by the margin of sample -- in essence by rib of sample -- where hydrogen absorption is especially great, is easily visible.

We will note that side by side with preeminent separation of hydrides of titanium along slip planes, partial separation of hydrides of titanium is observed in a direction perpendicular to the applied stress (in a direction coinciding with the direction of rolling).

Crack in metal, in accordance with preeminent precipitation of hydrides of titanium along the slip planes, are developed also basically along the slip planes, preserving in macroscale a direction perpendicular to the stress (see Fig. 1). Crack pass chiefly along the body of hydrides of titanium.

After two-hour heating of slides of alloy VT5 at 400° in vacuum the superficial hydride layer of metal disappears as a result of diffusion of hydrogen from the surface layer into the depth of the metal, and also of partial removal of hydrogen from metal.

Considering the dependence of time to failure of samples on stress (Fig. 4), it is possible to see that it is reduced directly with an increase of load. At equal loads, an increase in concentration of hydrochloric acid from 5.3 to 10 0/0 (straight lines 1 and 2) in accordance with an increase of average speed of corrosion from 5.15 to 9.6 g/m^2 24 hours leads to a reduction of time to failure of samples. The linear dependence of time to failure on load is not characteristic for the usual corrosion cracking and gives a basis to consider that failure of samples is stipulated basically by a decrease in their working section due to corrosion. As one can see from Fig. 5, weight losses of samples to the moment of their failure in a solution of 5.3 0/0 HCl, also are decreased practically linearly with an increase of stress. The weight losses of samples to the moment of failure during tests in a series of other solutions fall on practically the same line.

Fig. 1. Micrography of longitudinal section of sample of alloy VT5 after corrosion under a stress 72 kG/m^2 in a solution of 5.3 0/0 HCl.

a -- hydrides of titanium. P -- direction of applied external stress. X315.

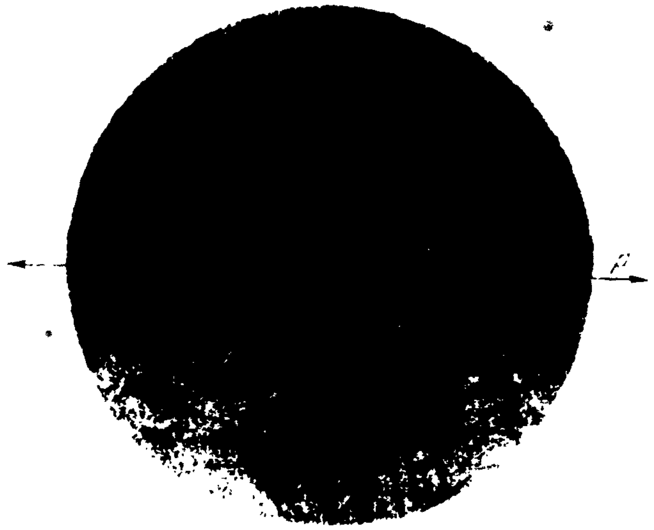

Fig. 2. The same as in Fig. 1 (aside from crack). X 1625.

This attests to the fact that during equal load failure of samples sets in practically at equal weight losses. Within the limits of experimental errors, in the solutions indicated cracks practically do not render an accelerating effect on time to failure of samples.

Formation of many cracks is combined, apparently, with the fact that at a definite state of development of a crack, in spite of concentration of stress in its apex braking sets in/$\overset{\text{in}}{\text{its}}$ development, which makes possible the appearance of new cracks. The braking indicated is probably stipulated by the lowering of the concentration of hydrogen in its apex by the measure of deepening of the crack in the thickness of the metal.

Fig. 3. Micrography of longitudinal section of alloy VT5 after corrosion under stress in a solution of 60 0/0 H_2SO_4 (aside from crack). Section was not etched. X 315.

Cracks obtain essential development only in the last stage of deformation of samples, on sections, marked by dotted lines in Fig. 6, when deformation of samples increases rapidly. Development of cracks in relatively dilute solutions of 5.3 0/0 hydrochloric and 7.3 0/0 sulphuric acids on certain samples at stresses of 65 kG/mm^2 and lower could be observed by the naked eye through transparent walls of the polystyrene vessel at 2--3 days to failure of sample.

Let us note that in solutions of 5.3 0/0 (1.5 N) hydrochloric acid, where average speed of corrosion (5.15 g/m^2 24 hours) is lower than in solutions of 7.3 0/0 (1.5 N) sulphuric acid (6.46 g/m^2 24 hours), in approximately a month sharp lowering of potential in positive direction sets in and the sample is passivated. For restoration of the active state of the sample, it is sufficient to exchange the solution for a fresh one. Changes in the concentration of the acid were immaterial, and activation set in also in the case when the concentration of acid of the fresh solution was equal to that of acid in the decanted solution. One of the main causes of the onset of the passive state was, apparently, the accumulation of ions of tetravalent titanium in the solution.

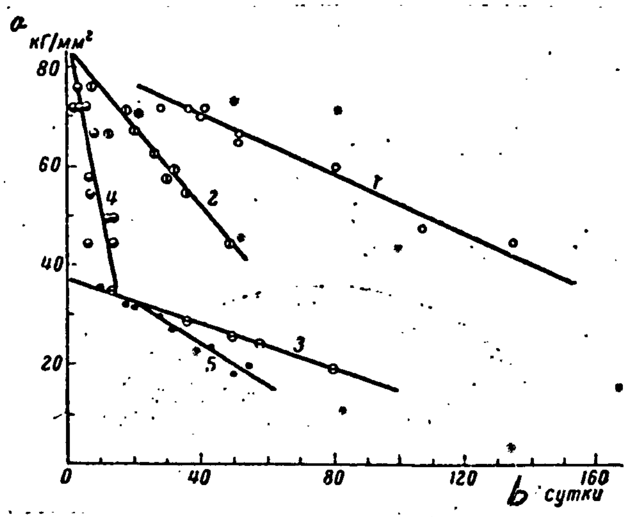

Fig. 4. Time to failure of samples and their welded seams depending upon load:

1 -- VT5 in solution of 5.3 0/0 HCl; 2 -- VT5 in 10 0/0 HCl; 3 -- VT1 in 10 0/0 HCl; 4 -- welded samples in 10 0/0 HCl, VT5 in 10 0/0 HCl; 5 -- VT1 in 10 0/0 HCl. a -- KG/mm^2; b -- 24 hour periods.

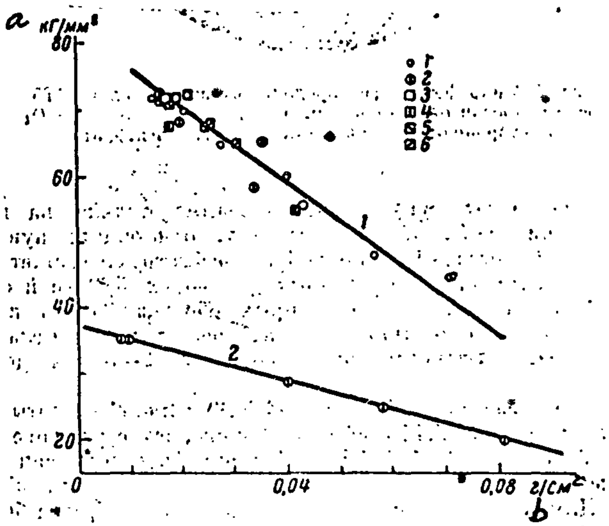

Fig. 5. Weight losses of samples of alloy VT5 (1) and titanium VT1 (2) to moment of failure in solutions. of: 1 -- 5.3 0/0 HCl; 2 -- 10 0/0 HCl; 3 -- 7.3 0/0 H_2SO_4; 4 -- 12.9 0/0 H_2SO_4; 5 -- 40 0/0 H_2SO_4; 6 -- 70 0/0 H_2SO_4; a -- KG/mm^2; b -- g/cm^2. Fact of retardation of corrosion of titanium by ions of tetravalent titanium added to solution of acid was marked in the literature earlier [13].

The character of failure of samples of alloy VT5, as was already indicated, depends on the concentration of acid, and, consequently, from speed of corrosion, as well as on stress. With transition from a solution of 5.3 0/0 to a 10 0/0 solution of hydrochloric acid (Fig. 7) and from a solution of 7.3 to a 40 0/0 solution of sulphuric acid (speed of corrosion, equals 6.46 and 58 g/m^2 24 hours respectively, the time to failure of samples is reduced in accordance with increase of speed of corrosion (curves 1 and 2). Weight losses of samples to moment of failure is practically identical (Fig. 5, 7) and constitutes, in mean, 175 g/m^2.

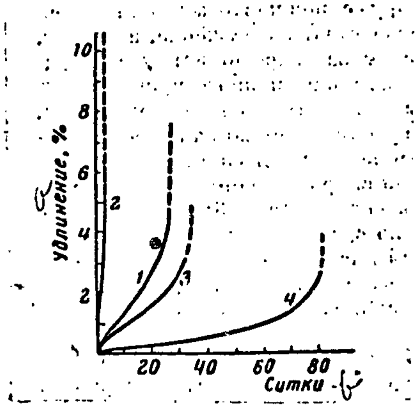

Fig. 6. Deformation of samples of alloy VT5 in time, stress of 72 kG/mm^2: 1--solution 7.3 0/0 H_2SO_4; 2--40 0/0 H_2SO_4; 3--5.3 0/0 HCl; 4--the same, stress of 60 kG/mm^2; a -- elongation, %; b -- 24 hour periods.

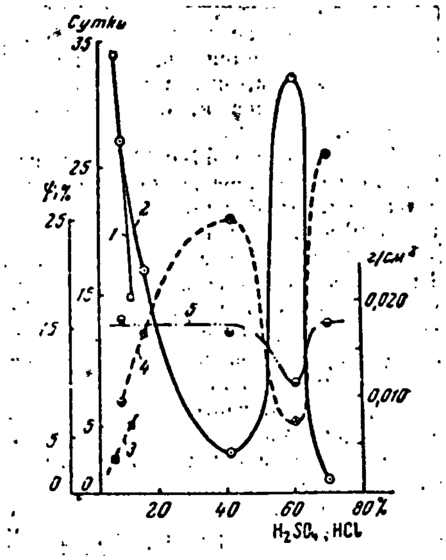

Fig. 7. Dependence of time to failure of samples of VT5 in solutions of hydrochloric (1) and sulphuric (2) acids, relative reduction hydrochloric (3) and sulphuric (4) acids, and weight losses in sulphuric acid (5) on concentration of the respective acids. Stress of 72 kG/mm^2; a -- 24 hour periods; b -- g/cm^2.

At the same time the relative reduction increases with the indicated increase of concentration of acids (curves 3 and 4). In other words, failure is more ductile.

This can be explained by the fact that under an equal load of 72 kG/mm^2, the quantity of hydrogen absorbed to the moment of failure is less for samples in solutions with a high speed of corrosion, for example 40 0/0 H_2SO_4, than, for example, in a solution of 7.3 0/0 H_2SO_4. This should already be known from that fact that thickness of hydride layer to moment of failure of samples corroding in 40 0/0-sulphuric acid is very small (less than 1 micron), while at the same time in samples corroding in a 7.3 0/0-solution of sulphuric acid it constitutes nearly 4.5 microns. We will note that the thickness of the hydride layer after corrosion under a stress of 45 kG/mm^2 in 5.3 0/0 HCl constitutes 7.5 microns.

More ductile failure of samples of alloy VT5 in solutions with high speed of corrosion is promoted also by the circumstance that in these solutions samples are deformed faster (Fig. 6) and failure after a correspondingly shorter time interval. Thanks to this the accelerating influence of deformation on the penetration of hydrogen, and, consequently, on the lowering of relative reduction is, in this case, less. The influence of speed of deformation on the brittleness of alloy VT5, containing hydrogen in a surface layer, is confirmed by the following. Samples underwent preliminary corroding for 25 days without stress in a solution 10 0/0 hydrochloric acid, and were then subjected to tension in air with different speeds of deformation down to failure. Samples elongated for 1 hour had a relative reduction of 12.9 0/0, but elongated for 10 days -- only 6.5 0/0.

We will show that in the same way that an increase of speed of corrosion leads to an increase of relative reduction, so also an increase of stress is accompanied by an increase of relative reduction. This is explained by the fact that with an increase of stress time to failure of samples is reduced and, consequently, time of absorption of hydrogen is decreased.

With a transition from a 40 0/0 to a 60 0/0 solution of sulphuric acid (Fig. 7) time to failure of samples abruptly increases; relative reduction, conversely, is lowered. This is explained by the fact that in the given solution, after approximately 10 hours a sharp braking of the corrosion process sets in, which is connected basically with the formation of insoluble products of corrosion. Fast corrosion of metal in the first hours increases stress and accelerates deformation of the metal; later the corrosion process proceeds under increased stress and small speed of corrosion, promoting penetration of hydrogen into the depth of the metal (Fig. 3) and failure of samples at smaller weight losses, as compared to other solutions (Fig. 7). In a solution of 70 0/0 sulphuric acid, braking of the process by insoluble products of corrosion is not observed. Time to failure of samples, in accordance with the very high speed of corrosion, is lowered, and relative reduction increases.

As distinguished from samples of alloy VT5, samples of titanium VT1 during corrosion under stress in solutions of 10 0/0 HCl, where the average speed of their corrosion (8.3 g/m^2 24 hours) is little distinguished from the speed of corrosion of VT5 (9.6 g/m^2 24 hours), underwent ductile failure even at loads of 20 kg/mm^2. Their relative reduction varied within the limits of 45--51 0/0 and practically was not distinguished from relative reduction during mechanical tests of the original samples in air. Dependence of time to failure on load also has a linear character. Increased inclination of samples of alloy VT5 to embrittlement during corrosion under stress in acids under the conditions when the quantity of absorbed hydrogen is sufficient for the formation of hydrides is, probably, connected with the presence of aluminum. Aluminum, although it decreases somewhat the thickness of the hydride layer, nevertheless, by lowering the ductility of the alloy, promotes thereby the propagation of cracks which appear; besides, under the conditions deformation it, apparently, strongly favors the migration of hydrogen into the metal.

Welded samples of alloy VT5 during corrosion under stress in 10 0/0 HCl (see Fig. 4) failed along the weld metal approximately four times faster than unwelded samples, which is stipulated basically by the high speed of corrosion of the weld metal. Welded samples of titanium under a load of 25 kG/mm^2 failed 1.5 times faster than unwelded. At stresses over 30 kG/mm^2 failure occurred not along the seam, but in the base metal; thanks to its large deformation. Application of purest argon and vacuum annealing of welded samples of alloy VT5 at a temperature of 800° for two hours increased time to failure of samples only by approximately 25 0/0.

Conclusions

1. The long-time influence of dilute hydrochloric and sulphuric acids on alloy VT5 and titanium, and also of 60 0/0 sulphuric acid on alloy VT5, leads to the formation on them of a solid hydride layer of a greyish-blue color.

2. Stress under the conditions of corrosion in the conditions shown above promotes pentration of hydrogen into the depths of alloy VT5 and titanium. On alloy VT5 the precipitation of hydrides of titanium, clearly emerges chiefly along the slip planes and partially in a direction perpendicular to that of applied external stress.

3. As distinguished from titanium VT1, the failure of samples of alloy VT5 in dilute hydrochloric and sulphuric acids is relatively brittle. Cracks are developed chiefly along the slip planes, preserving in macroscale a direction perpendicular to the stress. The indicated behavior of alloy VT5 is stipulated, apparently, by the presence of aluminum.

4. During corrosion under stress of alloy VT5 an increase of speed of corrosion with an increase of concentration of acid or an increase of stress with a constant concentration of acid leads to a more ductile failure of samples with practically equal weight losses. This is caused basically by the smaller quantity of hydrogen absorbed up to the moment of failure of samples in solutions with a high speed of corrosion or with imposition of large stresses. Cracks

caused by the formation of hydrides of titanium have little influence on time to failure.

During corrosion under stress in 10 0/0 hydrochloric acid, welded samples of titanium and especially of alloy VT5 were destroyed significantly faster than unwelded samples.

Literature

1. G. F. Kiefer, W. W. Harple. Metal Progress, 1953, 63, 74--76.

2. M. G. Fontana. Industr. and Engng. Chem., 1956, 48, 9, Part 1, A 59--60.

3. Progress Report, TML-88, Battle [sic] Memorial Inst. Titanium Metallurgical Lab., Columbus, Ohio, 1957, Nov 20, p. 54.

4. R. D. W. Strough, F. W. Fink, P. S. Peaples. TML-84, Battle [sic] Memorial Inst., Titanium Metallurgical Lab., Columbus, Ohio, Sept. 1957, 15, p. 54.

5. R. Meredith. W. L. Artrz. Welding Journal, 1957, 36, No. 9, 415.

6. G. A. Lenning, C. M. Craighead, R. J. Saffe. J. Metals, 1954, 6(3), p. 367.

7. K. Z. Claus, Metallkunde, 1958, 49, Heft 4, 203.

8. S. Ogawa, D. Wetanabe. Science Reports of the Research Institute, Tokoku University, 1955, 7A, 184.

9. G. R. McKinsey, M. Stern, P. A. Perkins. Transactions of American Society for Metals, 1958, 50, 438.

10. N. D. Tomashov, V. N. Modestova, G. K. Blinchevskiy. Works of the Institute of Physical Chemistry of the Academy of Sciences USSR, issue. 7. Investigation on corrosion of metals, 1959, 5, 64.

11. Thien-shin Liu, M. A. Steinberg. Transactions of American Society for Metals, 1958, 50, 455.

12. A. M. Yakimova. Influence of hydrogen and oxygen on properties of titanium alloys. Candidate dissertation, 1959. Institute of metallurgy of the Academy of Sciences USSR.

13. V. V. Andreyeva, V. I. Kazarin. Reports of the Academy of Sciences USSR, 1959, 128, 4, 748.

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