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FOREIGN TECHNOLOGY DIVISION

AIR FORCE SYSTEMS COMMAND

CORROSION OF METALS AND ALLOYS

(SELECTED ARTICLES)

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CORROSION OF METALS AND ALLOYS (SELECTED ARTICLES)

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ISSLEDOVANIYE ELEKTROKHIMICHESKOGO POVEDENIYA TITANA

09 English Title
INVESTIGATION OF ELECTROCHEMICAL BEHAVIOR OF TITANIUM

43 Source
KORROZIYA METALLOV I SPLAVOV (RUSSIAN)

42 Author TOMASHOV, N. D.	98 Document Location
16 Co-Author MODESTOVA, V. N.	47 Subject Codes 20, 11, 07
16 Co-Author PLAVICH, L. A.	39 Topic Tags: electrochemistry, corrosion, titanium, electric potential, anodization, sulfuric acid, titanium oxide
16 Co-Author AVERBUKH, A. B.	
16 Co-Author NONE	

ABSTRACT : Ti is an electronegative metal. The standard electrode potential of its dissolution in the form of divalent ions Ti^{2+} is -1.63 v, and in the form of trivalent ions Ti^{3+}, -1.21 v. Nevertheless, the intense corrosion of Ti, as well as its anodic dissolution in solutions of non-oxidizing acids, occurs in the presence of potentials that are approx. 1 v more positive than the above values, i.e. at -0.45 and -0.25 v. This indicates that the dissolution of Ti during corrosion and anodic depolarization occurs with an exceptionally high anodic inhibition. In studies of the electrochemical behavior of Ti allowance must be made for the thermodynamic possibility of the existence of both the hydride and the oxides of Ti at the surface of Ti over a broad range of potentials, the more so as it is known that not only the oxides but also the hydride of Ti usually inhibit the corrosion rate of Ti in acids. It has also been observed that prior cathodic polarization inhibits in certain cases the anodic dissolution of Ti. In this connection the authors investigate the effect of the hydride layer, forming on Ti during its corrosion or cathodic polarization, on the electrochemical dissolution and oxidation of Ti. To this end, the anodic potentiostatic curves were plotted for Ti with various duration of prior cathodic polarization of its surface. On comparing curves 1 and 2 in Fig. 1 it can be seen that the hydride layer produced during 1 hr of cathodic polarization sharply inhibits the process of the anodic dissolution of Ti: the limiting passivation current is reduced nearly in half. If this prior cathodic polarization is prolonged for 18 hr, however, an opposite effect is produced: the maximum anodic current increases (curve 3). This is due to the loosening and augmentation of true surface area of Ti owing to the absorption of hydrogen. In the region of active anodic dissolution the surfaces of Ti (whether pure or with hydride layer) get oxidized. The degree of this oxidation increases as the potential changes from its normal value to a positive (anodic) value. Studies of the corrosion resistance of Ti oxides show that the

oxides forming in the presence of a potential of +1.0 v in a 3N H_2SO_4 solution, and particularly in diluted 0.5N or 0.1N H_2SO_4 solutions, are relatively resistnat in the region of active anodic dissolution and in conditions of cathodic polarization. In the process of the anodizing of Ti the oxides form on the hydride layer of Ti. The thickness of the hydride layer then is hardly affected. In the course of anodic oxidation, diffusion of Ti ions takes place from the metal across the hydride layer. The relative corrosion resistance of Ti in the solutions of acids in which corrosion occurs with hydrogen depolarization is due to hydride-oxide passivity. Orig. art. has: 11 figures, 1 table. English translation: 22 pages.

Fig. 1. Anodic potentiostatic curves plotted for Ti in 3% H_2SO_4 solution:

1 - titanium with a hydride layer produced after 1 hr of cathodic polarization at $i = 50$ ma/cm^2 and $\sigma \approx 2$ μ;

3 - titanium after 18 hr of cathodic polarization at $i = 5$ ma/cm^2, $\delta \sim 10$ μ.

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Transliterated Title KORROZIONNOYE I ELEKTROKHIMICHESKOYE POVEDENIYE TITANA I EGO SPLAVOV V EKSTRAKTSIONNOY FOSFORNOY KISLOTE

09 English Title CORROSIONAL AND ELECTROCHEMICAL BEHAVIOR OF TITANIUM AND ITS ALLOYS IN WET-PROCESS PHOSPHORIC ACID

43 Source
KORROZIYA METALLOV I SPLAVOV. (RUSSIAN)

42 Author ANDREYEVA, V. V.	**98 Document Location**
16 Co-Author KAZARIN, V. I.	**47 Subject Codes** 20, 07, 11
16 Co-Author KUDRYASHOVA, T. I.	**39 Topic Tags:** corrosion, electrochemistry, titanium, phosphoric acid
16 Co-Author NONE	
16 Co-Author NONE	

ABSTRACT :

The evaluation of the corrosion resistance and electrochemical properties of Ti in wet-process phosphoric acid is of major interest in view of the planned expansion of the production of phosphoric fertilizers in the USSR. Wet-process phosphoric acid is produced by decomposing apatites with H_2SO_4. The experiments with technical Ti as well as with Ti alloys containing 1, 5, 10, 15, 20, 30 and 40% Mo and 10, 20, 30, 40 and 50% Nb were performed in wet-process phosphoric acid (32.1% P_2O_5, 0.2% CaO, 1.67% SO_3, 0.4% Fe_2O_3, 0.4% Al_2O_3, 0.02% MgO, 0.6% SiO_2, 2.28% F, 0.02% Na, 0.02% K, 59.46% H_2O; other elements 5.58%). The principal components of this acid are: H_3PO_4 (up to 50%), H_2SiF_6 (1-3%) and $Fe_2(SO_4)_3$; it is they that markedly affected the corrosion and electrochemical behavior of the metals. The electrochemical studies were performed with the aid of an electronic potentionstat, while the potentials were measured by means of the compensation method with respect to a calomel reference electrode and converted in terms of a normal hydrogen electrode. Findings: the corrosion rate of Ti in phosphoric-acid solutions is a function of the potential. In the presence of specific values of the potential Ti is capable of passing over to passive state. On the basis of the dependence of the density of passivation current on the concentration and temperature, it is possible to establish the regions of concentrations and temperature of phosphoric acid at wich Ti displays satisfactory corrosion resistance. Ti in wet-process phosphoric acid is corrosion-resistant (corrosion rate up to 0.1 mm/year) at up to 40°C. The presence of Fe^{3+} preserves the passive state of Ti at up to 60°C, but at 60°C the corrosion rate then rises to 0.3 g/m^2-hr) (0.6 mm/year). Adding Mo to Ti

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increases the latter's corrosion rate, the more the higher the Mo content of the alloy is, following the relation: $K = 0.354 \exp [0.184\% \text{ (by wt.)}]$, owing to repassivation with respect to Mo as result of the presence of Fe^{3+} ions in the wet-process phosphoric acid. Adding Nb, on the other hand, improves the corrosion resistance of Ti in the acid, and then the corrosion rate decreases following the relation: $K = 0.354 \exp [-0.027\% \text{ (by wt.)}]$.

Original article has: 10 figures. English translation: 10 pages.

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Transliterated Title
MEKHANIZM ZASHCHITY METALLOV OT KORROZII AMMIAKOM

09 English Title
MECHANISM OF PROTECTION OF METALS FROM CORROSION WITH AMMONIA

43 Source
KORROZIYA METALLOV I SPLAVOV (RUSSIAN)

42 Author ROZENFEL'D, I. L.	**98 Document Location**
16 Co-Author PERSIANTSEVA, V. P.	**47 Subject Codes** 11, 07, 20
16 Co-Author NONE	**39 Topic Tags:** corrosion inhibitor, ammonia, steel, surface ionization, hydrolysis
16 Co-Author NONE	
16 Co-Author NONE	

ABSTRACT : Recently, to improve the effectiveness of the corrosion protection of metals in storage and transport, ammonia salts and other compounds capable of releasing ammonia during hydrolysis and dissociation have begun to be added to the standard inhibitors (e.g. $NaNO_3$). It is generally assumed that the mechanism of protective effect may then manifest itself in one of the following phenomena: a) NH_3 displaces the pH of the medium to the region of low corrosive activity; b) NH_3 (or NH_4OH) binds the aggressive component of the medium (e.g. CO_2); c) the mixing of NH_3 salts with $NaNO_3$ leads to the formation of the highly volatile NH_4NO_3. Since these assumptions lacked experimental proof, the authors decided to investigate the protective capacity of NH_3 as a function of its content in the atmosphere, as well as to investigate the effect of NH_3 on the electrochemical behavior of steel. The investigation pertained to NH_3 of 100% relative humidity at 25°C, on varying its concentration by placing in the reaction vessel NH_4OH of various concentrations corresponding to ammonia vapor pressures of from 66.66 to 666.6 n/m^2 (0.5 to 5 mm Hg), with the corrosion being determined as a function of time until the appearance of first signs of corrosion on the steel specimens. These experiments showed that even insignificant concentrations of NH_3 in the atmosphere (266.64 n/m^2 or 2 mm Hg) can effectively protect steel against corrosion. An attendant investigation of the electrochemical behavior of steel in NH_3 atmosphere showed that the presence of NH_3 displaces the steel's potential by 500 mv in the positive direction. The mechanism of the protection of steel by NH_3 is due to the hydration of NH_3 and the concomitant formation of NH_3 ions. The prior adsorp-

tion of hydroxyl ions on the (positively charged) surface of steel makes possible the adsorption of NH_3 ions on the metal surface, which leads to a sharp change in the ionization rate of Fe. These findings are also highly significant to the determination of the mechanism of the protective effect of other amine-class compounds which, in solutions, form cations similar to the NH_3 ion.

Orig. art. has 7 figures and 4 formulas. English translation: 10 pages.

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Transliterated Title ATMOSFERNAYA KORROZIYA STALI, TSINKA, KADMIYA, MEDI I ALYUMINIYA V RAZLICHNYKH PRIMORSKIKH I KONTINENTAL'NYKH RAYONAKH

09 English Title ATMOSPHERIC CORROSION OF STEEL, ZINC, CADMIUM, COPPER, AND ALUMINUM IN VARIOUS MARITIME AND CONTINENTAL REGIONS

43 Source
KORROZIYA METALLOV I SPLAVOV (RUSSIAN)

42 Author BERUKSHTIS, G. K.	98 Document Location
16 Co-Author KLARK, G. B.	47 Subject Codes 11, 04, 08
16 Co-Author NONE	39 Topic Tags: corrosion, atmospheric contamination, steel, zinc, copper, cadmium, aluminum, geographic survey
16 Co-Author NONE	
16 Co-Author NONE	

ABSTRACT: No general theory for the scientific prediction of the rate of atmospheric corrosion of various metals for any arbitrarily taken climatic region has so far been evolved. In this connection, the authors attempted to refine the formula for the mathematical dependence of the rate of this corrosion on external conditions, first derived by N. D. Tomashov and G. K. Berukshtis (Issledovaniya po korrozii metallov. Trudy IFKh AN SSSR, Vyp. VIII, 1960, 6, 69), so as to take into account the effect of corrosion products, rainfall precipitation (wetting of surface) and the contamination of air by SO_2. Specimens of steel, Cu, Zn, Cd and Al were exposed to open air as well as kept in atmospheric booths under conditions simulating storage in unheated warehouses, in various regions of the USSR. Corrosion rate was determined by weighing the specimens before and after the tests over various periods of time (seasons, 1 year, 2 years, 3 years, 4 years, 5 years), and this was combined with regular meteorological observations (hours of fog and sunshine per year, etc.) The products forming at metal surfaces were analyzed for their content of SO_4^{2-} and Cl^- ions and the duration of the wetting of metal (precipitation in hours per year) was recorded. Findings: the corrosion rate of all the five metals may vary markedly depending on environmental factors: thus, for Moscow (industrial district), with its SO_2-polluted atmosphere, as compared with Zvenigorod (rural district), this rate is 1.5 times as high for steel and Cu, 3 times as high for Zn and Al, and 5 times as high for Cd. Thus, SO_2 is a specific aggressor for nonferrous metals and particularly for Cd. For the Baltic Maritime Region, where the amount of chlorides is 40 times as high as in Zvenigorod (rural district), the corrosion rate of Al and Cu is 22 and 3.7 times, respectively, as high as in Zvenigorod, while for steel, Zn and Cd it is either slightly higher or constant, which indicates that chlorides are specific aggressors for such metals as Al and Cu.

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In atmospheric booths this corrosion rate is 1-4 times higher for all the 5 metals (except Al, for which it is the same) than in open air. It is shown that it is fundamentally possible to make scientifically substantiated predictions of the rate of metal corrosion. The findings can be utilized by designers to develop protective coatings for parts of devices and equipment, and will be utilized by the authors themselves to refine the coefficients of conversion of the results of accelerated tests to normal operating conditions. Original article has: 7 figures, 7 tables. English translation: 17 pages.

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U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

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П п	*П п*	P, p	Я я	*Я я*	Ya, ya

* *ye* initially, after vowels, and after ъ, ь; *e* elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

INVESTIGATION OF ELECTROCHEMICAL BEHAVIOR OF TITANIUM

N. D. Tomashov, V. N. Modestova, L. A. Plavich and A. B. Averbukh

Titanium is an electronegative metal. Standard electrode potential of its dissolution in the form of bivalent ions Ti^{2+} is equal to -1.63 V, and in the form of trivalent ions Ti^{3+} -1.21 V (table).

At the same time intense corrosion of titanium, and also its anode dissolution in solutions of nonoxidizing acids, flow at potentials approximately 1 V more positive than above shown values of potentials, i.e., at (-0.45)-(-0.25) V. This indicates that dissolution of titanium during corrosion and anode polarization flows with especially great anode inhibition.

Inhibition of process of anode dissolution of titanium, which occurs not only during corrosion of titanium, with its anode polarization, but also during cathode polarization, is connected with the fact that Ti possesses high affinity to oxygen and to hydrogen.

According to thermodynamic data (see Table 1), formation of titanium hydride TiH is already possible while starting from potential 0.65 V, i.e., even at anode polarization and with increasingly negative values.

Formation of phase oxides on titanium is thermodynamically possibly starting from potential -1.30 V (i.e., even under conditions of cathode polarization) and with increasingly positive values of potentials; thus, in range of potentials from -1.3 to +0.65 V on titanium the formation of both hydrides and oxides is possible.

Potentials E^0 of Certain Reactions on Titanium Electrode.

No. of items	Reaction	E^0, V	Literature source
1	$Ti \rightleftarrows Ti^{2+} + 2e$	−1,63	[1]
2	$Ti \rightleftarrows Ti^{3+} + 3e$	−1,21	[2]
3	$TiH \rightleftarrows Ti + H^+ + e$	+0,65	[3]
4	$TiH_2 \rightleftarrows Ti + 2H^+ + 2e$	+0,45	[3]
5	$TiH \rightleftarrows Ti^{3+} + H^+ + 4e$	−0,73	[3]
6	$TiH_2 \rightleftarrows Ti^{3+} + 2H^+ + 5e$	−0,54	[3]
7	$TiH \rightleftarrows Ti^{3+} + \frac{1}{2} H_2 + 3e$	−0,99	*
8	$TiH_2 \rightleftarrows Ti^{3+} + H_2 + 3e$	−0,91	*
9	$Ti + H_2O \rightleftarrows TiO + 2H^+ + 2e$	−1,30	[2]
10	$2Ti + 3H_2O \rightleftarrows Ti_2O_3 + 6H^+ + 6e$	−1,24	[3]
11	$3Ti + 5H_2O \rightleftarrows Ti_3O_5 + 10H^+ + 10e$	−1,17	[3]
12	$Ti + 2H_2O \rightleftarrows TiO_2 \cdot nH_2O + 4H^+ + 4e$	−0,90	[3]
13	$2TiO + H_2O \rightleftarrows Ti_2O_3 + 2H^+ + 2e$	−1,12	[2]
14	$3Ti_2O_3 + H_2O \rightleftarrows 2Ti_3O_5 + 2H^+ + 2e$	−0,49 −0,33±0,13	[2] [4]
15	$Ti_2O_3 + H_2O \rightleftarrows 2TiO_2 + 2H^+ + 2e$	−0,33±0,22	[4]
16	$Ti_2O_3 + H_2O \rightleftarrows 2TiO_2 \cdot nH_2O + 2H^+ + 2e$	−0,091	[2]
17	$TiH + H_2O \rightleftarrows TiO + 3H^+ + 3e$	−0,65	[3]
18	$TiH_2 + H_2O \rightleftarrows TiO + 4H^+ + 4e$	−0,42	[3]
19	$2TiH + 3H_2O \rightleftarrows Ti_2O_3 + 8H^+ + 8e$	−0,77	[3]
20	$2TiH_2 + 3H_2O \rightleftarrows Ti_2O_3 + 10H^+ + 10e$	−0,56	[3]
21	$TiH + H_2O \rightleftarrows TiO + 2H^+ + \frac{1}{2} H_2 + 2e$	−0,97	*
22	$TiH_2 + H_2O \rightleftarrows TiO + 2H^+ + H_2 + 2e$	−0,84	*
23	$2TiH + 3H_2O \rightleftarrows Ti_2O_3 + 6H^+ + H_2 + 6e$	−1,025	*
24	$2TiH_2 + 3H_2O \rightleftarrows Ti_2O_3 + 6H^+ + 2H_2 + 6e$	−0,93	*

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*Calculated by us.

Presence of hydride on surface of titanium during its brief submersion in acids, for example in hydrofluoric acid, is established by electron diffraction method [5]. Phase hydride layer, appearing with prolonged corrosion of titanium in solutions of sulfuric and hydrochloric acids [6, 7] or all the more during cathode polarization [8], can be observed on microsections.

Phase oxides appear on titanium, as it is known, not only during oxidation in air, anode oxidation, or in solutions of oxidizers, but also during self-passivation in neutral and slightly acidic solutions [9].

During investigation of electrochemical behavior of titanium it is therefore necessary to consider thermodynamic possibility of existence on titanium of both titanium hydride and oxides in a wide range of potentials. It is known all the more that not only oxides, but also titanium hydride usually inhibit the corrosion rate of titanium in acids. Thus, in work of N. D. Tomashov, R. M. Al'tovskiy, and others [10], and the work of Otsuka [11] it was shown that titanium hydride, appearing on its surface during cathode polarization, significantly inhibits corrosion rate of titanium in solutions of small and average concentrations of sulfuric and hydrochloric acids. It is also noted that preliminary cathode polarization in certain cases inhibits anode dissolution of titanium [12].

This work is dedicated to investigation of the effect of hydride layer, appearing on titanium during corrosion or with cathode polarization, on electrochemical dissolution and oxidation of titanium, and also the stability of oxides appearing on titanium in various regions of potentials.

Experimental Part

In order to clarify the state of surface of hydride layer and its effect on anode dissolution of titanium, we plotted anode potentiostatic curves on titanium with various duration of preliminary cathode polarization of surface. For investigation of stability of oxides on titanium we plotted: a) potentiostatic curves of anode oxidized titanium in opposite negative direction with different speed; b) curves of cathode charging; c) galvanostatic curves with alternation of cathode and anode polarization with different preparation of samples (from stripping to submersion in solution or under solution). Furthermore, for clarification of behavior of hydride during anode oxidation we prepared microsections after anode oxidation of titanium and titanium with a hydride layer.

Peculiarities of each experiment are expounded in description of results of investigation.

Titanium samples were produced from BT1 bar. Composition of titanium is the following, % (with respect to mass): 0.03 Fe, 0.06 Cl, 0.03 Si, 0.05 C, 0.03 N, 0.10 O, and 0.00 H.

For relaxation of internal stresses and removal of hydrogen the samples were annealed at 800°C for two hours.

Sample in the form of a cylinder with 12 or 6 mm diameter (in experiments with stripping under a solution) together with a current-conducting lead glued to a polystyrene mandrel by epoxy resin [ED5] (ЭД5). Before the experiment (with the exception of experiments with stripping under solution) samples were cleaned on end face with K3M20 emery cloth, then aluminum oxide powder No. 10. All experiments were conducted with separation of cathode and anode space in solutions of sulfuric acid of special purity.

Potential was measured with the aid of [EMU-3] (ЭМУ-3) electrometric amplifier. For decrease of time constant of instrument the input impedance was lowered to 300 MΩ.

All experiments, with the exception of anodizing, were conducted at a temperature of 25°C. As comparison electrode there was a single-standard calomel electrode. Obtained results are given with respect to a standard hydrogen electrode.

Effect of Hydride Layer and State of its Surface on Shape of Anode Potentiostatic Curves

Let us examine the effect of hydrogenation of titanium on its anode behavior. In Fig. 1 there are given anode potentiostatic curves, taken in 3% solution of H_2SO_4 on titanium (curve 1), on titanium with hydride layer, obtained during one hour of cathode polarization (curve 2) at current density $i = 5$ mA/cm^2 (thickness of hydride layer $\delta \sim 2$ μm) and during 18 hours of cathode polarization (curve 3) with the same current density $i = 5$ mA/cm^2.

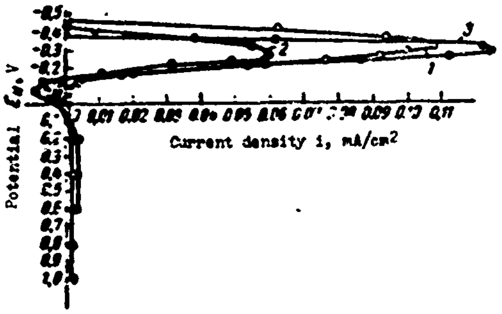

Fig. 1. Anode potentiostatic curves, taken in 3% solution of H_2SO_4: 1 — on titanium; 2 — on titanium with hydride layer, obtained during one hour of cathode polarization at $i = 5$ mA/cm^2 and $\delta \approx$ μm; 3 — on titaniym after 18 hours of cathode polarization at $i_K = 5$ mA/cm^2, $\delta \sim$ μm.

Before plotting potentiostatic curves on titanium without a hydride layer the samples after stripping are washed and for as much decrease of oxidation of sample as possible are immediately immersed in thermostatic working 3% solution of H_2SO_4. After the sample was activated and its potential reached -0.48 V (in approximately 30 min after submersion), we plotted potentiostatic curve on titanium with 15 min holding at point. On titanium with hydride layer we plotted curves after preliminary hydrogenation of titaniym in the same solution (3% H_2SO_4) at density of cathode current 5 mA/cm^2 for an hour. We conducted more prolonged hydrogenation for reduction of dissolution of sample in a more diluted 0.5% of H_2SO_4 also on a freshly cleaned sample for 18 hours. Then the 0.5% solution of H_2SO_4 was replaced by working 3% solution of H_2SO_4, thermostatically controlled beforehand, and we conducted additional cathode polarization (i_K = 5 mA/cm^2) for 10 min. Anode potentiostatic curve was plotted immediately after additional cathode polarization. Thickness of hydride layer in these experiments was ~10 μm.

By comparing curves 1 and 2, it is possible to see that the hydride layer, obtained during one hour of cathode polarization, sharply inhibits process of anode dissolution of titaniym: limiting current of passivation is decreased by almost 2 times. At the same time potential of maximum anode current is somewhat displaced to the positive side. Potential of total passivation is practically not changed. Decrease of limiting anode current of passivation after cathode polarization was noted earlier also in the work of N. D. Tomashov, G. P. Chernova, and R. M. Al'tovskiy [12].

On curves 2 and 3, plotted on titaniym with hydride layer close to passivation potential (Fig. 1), there is observed a small cathode loop. Obviously, the oxide layer, appearing near potential of total passivation, on titaniym with hydride layer in contrast to titanium renders greater inhibition to anode than cathode process of class of hydrogen ions. Therefore, near the passivation potential on titanium with hydride layer the speed of cathode process will be higher than that of anode process, and true cathode current will be greater than true anode. External current, necessary for maintaining the assigned potential, is cathode. This question is examined more specifically in our other work [15].

Increase of duration of preliminary cathode polarization from one hour to 18 hours (curve 3) leads to the opposite effect — increase of maximum anode current. This is explained by loosening of titanium surface under the influence of hydrogenation, by increase of true surface. External view of surface of titanium is changed during prolonged hydrogenation: it becomes darker and rougher. Large specific volume of hydride as compared to titanium and its great brittleness lead to the appearance of microscopic cracks. Appearance and propagation of microscopic cracks are contributed to by high hydrogen content and presence of corrosion process during hydrogenation. If surface layer of loosened hydride is removed, having preserved the basic hydride layer, which is attained by light stripping of samples by aluminum oxide powder, then limiting current of passivation will again be reduced, and anode potentiostatic curve will be similar to curve 2. Loosening of surface under the influence of cathode polarization was noted earlier in [13] during investigation of self-dissolution of titanium and [VT5](BT5) alloy under conditions of cathode polarization.

It is necessary to note that the phase hydride layer, appearing during cathode polarization or corrosion, can be easily revealed thanks to loosening of surface. Thus, with submersion of sample with hydride layer in pickle solution containing HF (for example, HCl of 1.19 g/cm^3 density, 340-350 ml volume, HNO_3 of 1.4 g/cm^3 density, 55-60 ml/l, NaF 50 g/l, water – remainder), it instantly, almost immediately after separation of bubbles, blackens, which is a result of loosening of surface and chipping of titanium hydride owing to the presence of microscopic cracks. After dissolution of phase hydride layer the sample clears up. Rate of dissolution of hydride layer in the shown solution is approximately 1.3 times more than rate of dissolution of titanium for the same time interval, considering from the moment of appearance of bubbles of hydrogen and up to lightening of sample. Blackening of sample vanishes faster, the thinner is the hydride layer, and can serve as criterion of removal of phase hydride layer. Darkening of titanium samples in solutions with the presence of hydride on their surface was noted earlier in work of Otsuka [11].

Increase of maximum anode current on potentiostatic curve 3 (Fig. 1), as increased corrosion rate of titanium hydride in pickle, are caused by growth of true surface of titanium hydride as a result of loosening of surface during prolonged hydrogenation. If, however, we compare behavior of titanium hydride in region of active anode dissolution with equal true surfaces, then titanium hydride will, naturally, ingibit anode dissolution of titanium, as is observed on anode curve 2, obtained for titanium during brief hydrogenation.

Causes of Inhibition of Anode Dissolution of Titanium

Let us examine peculiarities of anode dissolution of titanium. Considering that the anode process of dissolution of titanium in active state flows at potentials (-0.45)-(-0.3) V, which is more positive than equilibrium electrode potential of titanium (-1.21 V) by almost 1 V, it should be considered that even the process of active anode dissolution of titanium flows with exceptionally great overstress (anode inhibition). Thermodynamically, as was noted above, in this region of potentials the existence of both oxides and hydride is possible on the surface of titanium.

Let us assume that during dissolution of hydride layer in active region the hydrogen in not oxidized to H^+, titanium is dissolved in the form of ions Ti^{3+}. With rapid dissolution of titanium hydride, for example in very aggressive media, hydrogen will not be diffused inside the metal and, while molarizing [sic], will be removed in the form of gas. With slow dissolution hydrogen can be partially diffused inside the metal and remain connected with titanium by hydride bond.

If we calculate equilibrium potential of dissolution of titanium hydride (isobaric values of formation potential $\Delta Z_{TiH} = 15$ kcal [3], $\Delta Z_{TiH_2} = 20.9$ kcal [3], and $\Delta Z_{Ti^{3+}} = 83.6$ kcal [1], then we obtain the following values of potential for reaction of dissolution of hydride:

$$TiH \rightleftarrows Ti^{3+} + 1/_2H_2 + 3e; \quad E^0 = -0{,}99\ V,$$
$$TiH_2 \rightleftarrows Ti^{3+} + H_2 + 3e; \quad E^0 = -0{,}91\ V,$$

Thus, potentials, observed during anode dissolution of Ti, at ~0.5 V have more positive values than equilibrium potential of dissolution of titanium hydride. It follows from this that under conditions of active anode dissolution of titanium although the presence of hydride on its surface is possible, nonetheless inhibition of anode dissolution of titanium cannot be explained only by the presence of hydride bonding of titanium with hydrogen. It is also necessary to allow the possibility of formation of oxide bond – chemisorption of oxygen – or formation of oxides.

The great inhibition due to interaction of titanium with oxygen in active region is indicated by the fact that limiting current of passivation has relatively small values and depends significantly on concentration of acid. Thus, in 3% solution of H_2SO_4 the current of passivation is equal to only 0.11 mA/cm^2 and even in 10.5% solution of H_2SO_4 it is 0.25 mA/cm^2 [16]. In diluted solutions of sulfuric acid, for example in 0.1% H_2SO_4, anode branch is practically absent and with potentials of anode branch there are observed cathode currents. Together with increase of concentration of acid the solubility of oxides naturally increases. This gives basis to consider that under conditions of anode dissolution the surface of titanium is oxidized and the higher the concentration of acid and, consequently, solubility of oxides, the less the degree in which surface is oxidized and the greater the anode current.

In connection with this we will examine change of density of anode current in time on a titanium electrode in 3% solution of H_2SO_4 with change of potential to the anode side (Fig. 2) and change of potential in time with gradual growth of anode current in the same conditions (Fig. 3). With anode load from stationary potential of titanium (-0.48 V), i.e., during transition from one constant value of potential to another, more positive (see Fig. 2), current instantly increases, then in proportion to increase of degree of oxidation of titanium sample it is lowered in time and is stabilized. It is possible to assume that each potential corresponds to a definite degree of oxidation of surface of sample. Thus, in region of active anode dissolution I (see Fig. 2) during transition from one constant value of potential to another, more positive, curves of change of current in time have the same character as in region of active-passive or completely passive state II. The difference is that current is established the most rapidly in region of active anode dissolution, and the slowest – in region of total passivation.

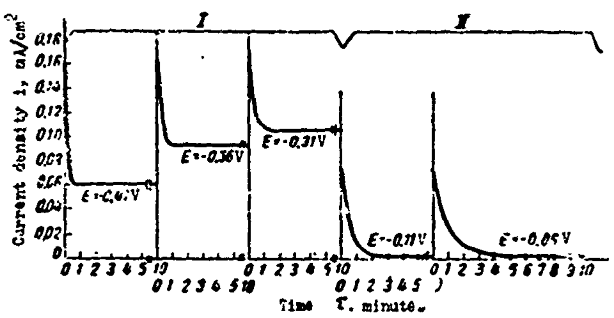

Fig. 2. Change of density of anode current on titanium electrode in time with change of potential to the anode side 3% solution of H_2SO_4, temperature 25°C: I – active region; II – passive region.

Curves of change of potential during change of anode current (Fig. 3) have a different character. With increase of current density the potential on titanium (curve 1) is instantly displaced in a positive direction, then slower, for 2-3 min, in proportion to oxidation of surface, is displaced in the same positive direction. With transition to high values of current the potential is established slower and its changes in time are more considerable. With decrease of current the reverse phenomenon is observed: in the beginning potential is almost instantly displaced in negative direction, then in proportion to destruction of oxide is more slowly

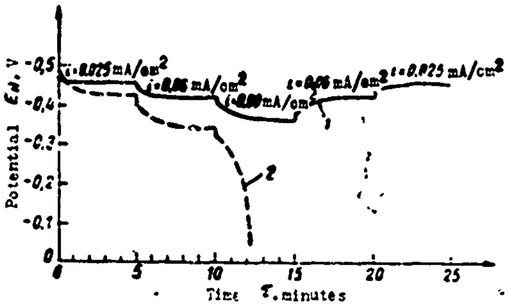

Fig. 3. Changes of potentials of titanium (1) and titanium with hydride layer (2) in time with gradual growth of anode current. 3% solution of H_2SO_4, temperature 25°C.

displaced toward stable value.

With value of current density equal to, for example, 0.06 mA/cm^2, potential of titanium with hydride layer (curve 2) is more positive and is established more slowly than on titanium. With increase of current density to 0.09 mA/cm^2, exceeding limiting current density of passivation on potentiostatic curve of titanium with hydride layer (Fig. 1, curve 2), potential of sample is already continuously displaced in positive direction.

Conducted experiments give basis to consider that titanium and titanium with hydride layer are oxidized in region of active anode dissolution, during which the degree of oxidation (for example, quantity of monolayers of oxide) increases with displacement of potential in positive direction. In solutions of average and higher concentrations of sulfuric acid the continuous dissolution of formed oxide prevents its growth and displacement of potential in positive direction connected with this, thereby ensuring presence of anode branch.

Thus, inhibition of process of anode dissolution on titanium with hydride layer occurs as a result of hydride bonding of titanium with oxygen and oxide bonding of titanium with oxygen. Possibility of simultaneous coexistence of hydride layer and oxide on titanium is confirmed, as will be shown below (see p. 16), by photomicrographs of anode oxidized hydride layer.

Conclusion about the increase of degree of oxidation of sample with displacement of potential from steady-state value to potential of beginning of passivation will fully agree with the assumption expressed earlier by us [13], about the fact that even in conditions of cathode polarization there exists some degree of oxidation of titanium and VT5 alloy, which is decreased with increase of density of cathode current, i.e., with displacement of potential to the negative side.

Considering that standard potential of oxidation of titanium hydride (see Table 1, Nos. 21-24) is very negative, we should consider that titanium hydride is oxidized long before beginning of passivation (cathode polarization, active anode dissolution). Depending upon potential, oxidation can be caused by chemisorbed oxygen or (with more positive values of potential) low-valence oxides.

Near the potential corresponding to maximum current of anode curve on titanium and titanium with hydride layer in the composition of oxide there appears, apparently, more highly valent and much less soluble oxide TiO_2. It is known, for example, that during corrosion in neutral and slightly acidic solutions, and also in conditions of anode polarization to potential +1.0 V, oxide on titanium consists of 1 part Ti_2O_3 and 3-4 parts TiO_2 [9]. Decrease of solubility of surface in connection with appearance of TiO_2 prevents establishment of equilibrium state, with which speed of dissolution of surface oxide on titanium with hydride layer is equal to speed of its formation. Process of anode dissolution develops into process of anode oxidation, which can be seen on the last section of curve 2 (see Fig. 3), corresponding to current density 0.09 mA/cm^2. Shown current density exceeds maximum anode current on potentiostatic curve (Fig. 1, curve 2).

Let us note that titanium will in some degree be connected with hydrogen by hydride bond not only during cathode polarization and stationary potential (-0.48 V), but also in the region of active anode dissolution.

Stability of Anode Oxides on Titanium During Electrochemical Polarization

For investigation of stability of oxides appearing in region of total passivation, we plotted potentiostatic curves of opposite shape, i.e., during displacement of potential of anode oxidized titanium sample in negative direction.

Before plotting the shown curves, freshly cleaned samples were immersed in working 3% or 0.1% solution of H_2SO_4, through which argon was preliminarily admitted for 1.5 h. After that the cell was immediately connected to potentiostat and anode oxidation of sample was conducted at potential 1.0 V for 1.5 h.

Quantity of electricity going into anode oxidation of titanium for 0.1% solution of H_2SO_4 was ~20 μ (millicoulombs), which corresponds to thickness of oxide film ~100 Å (if oxide consists of TiO_2, density is equal to 3.86 g/cm^3, dissolution in 0.1% solution of H_2SO_4 can be disregarded). In 3% solutions of H_2SO_4 the quantity of electricity was considerably greater, which is caused by raised solubility of oxide.

Potentiostatic curves were taken in atmosphere of argon. When plotting curves the potential of sample was rapidly displaced from initial value of 1.0 V to potential 0.1 V and further in negative direction with holding 3 and 15 min at point (Figs. 4 and 5).

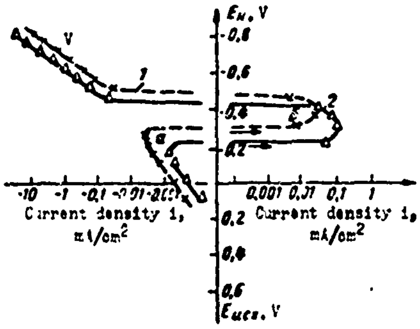

Fig. 4. Opposite shape of potentiostatic curves of titanium, taken in 3% solution of H_2SO_4 on preliminarily anode oxidized titanium (E_H = +1 V) with holding at point: 1 — 3 min; 2 — 15 min; a) cathode loop; b) anode curve; c) cathode curve.

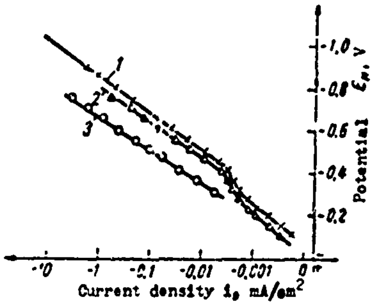

Fig. 5. Opposite shape of potentiostatic curves of titanium in 0.1% solution of H_2SO_4 with holding at point: 1 — 3 min (anode oxidized titanium at E_H = 1.0 V); 2 — 15 min (anode oxidized titanium at E_H = 1.0 V); 3 — 3 min (freshly cleaned titanium).

As can be seen in Fig. 4, on potentiostatic curves, plotted in 3% solution of H_2SO_4 with holding 3 min (curve 1) or 15 min at point (curve 2), there are three sections: cathode loop (a), anode curve (b) and cathode curve (c).[1] In region of cathode loop the cathode currents are insignificant (less than 10 μA/cm^2 even with 3-min holding at point); besides the cathode process of charge of hydrogen ions, here there is also possible the reduction of traces of dissolved oxygen and ions Ti^{4+} appearing with anode oxidation of titanium due to partial dissolution of oxide. Thanks to presence of oxide film and small density of cathode current the formation of titanium hydride in this case is improbable.

Decrease of duration of holding of potential at each point of potentiostatic curve from 15 (curve 1) to 3 min (curve 2) is reflected on the entire shape of potentiostatic curve: cathode loop is increased; transition to anode branch starts later, i.e., with more negative potentials; maximum anode current is correspondingly decreased; basic cathode branch is constructed following anode, occurs at more negative values of potential.

Shown changes indicate that oxides are destroyed slowly and to a considerable degree are preserved in the region of anode dissolution with fast rate of removal of potentiostatic curve.

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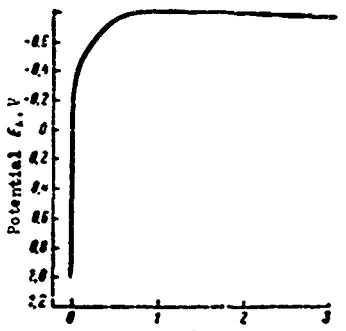
[1] Cathode curves (section c) were plotted with identical speed (3 min at point), in order to trace the effect of oxides, preserved differently with preceding shape of anode curves, taken with 3- and 15-min holdings.

Inasmuch as oxides, as will be shown below, significantly inhibit the cathode process of charge of hydrogen ions, transition from anode branch to cathode with fast rate of removal of curve occurs at somewhat more negative values of potential.

In 0.1% solution of H_2SO_4 (see Fig. 5) the anode branch in all cases (both during 3-min and 15-min holding at point) is completely absent; two cathode sections, observed in 3% solution of H_2SO_4, are connected in a single cathode polarization curve. With decrease of concentration of acid from 3 to 0.1% solubility of oxides is lowered, their stability in region of potentials of anode dissolution is increased accordingly.

Thus, oxides appearing at potential 1.0 V in 3% solution of H_2SO_4 at potentials of active anode dissolution are gradually destroyed. In diluted 0.1% solution of H_2SO_4 in the region of active anode dissolution, oxides are preserved in some form or another.

With potential of activation and potentials of anode branch the reduction of oxides on titanium or titanium hydride is impossible, since corresponding equilibrium potentials are more negative (see Table 1). However, reduction of TiO_2 to more low-valence oxides and even to ions Ti^{3+} is thermodynamically possible.



-Fig. 6. Curve of cathode charging of titanium, preliminarily anode oxidized at E_H = +1.0 V for 1.5 h in 0.1% solution of H_2SO_4; i_K = 100 μA/cm^2.

Fig. 6 shows curve of cathode charging of titanium, obtained in 0.1% solution of H_2SO_4 (in this solution it is possible to disregard chemical dissolution of oxides).

Curve of cathode charging was plotted in atmosphere of argon on titanium samples, preliminarily anode oxidized, just as in preceding experiments (see p. 10), at E_H = +1 V for 1.5 h. Solution of sulfuric acid prepared on bidistillate. Cutoff of potentiostat and switch on of constant cathode current with 100 μA/cm^2 density were produced simultaneously with the aid of a switch. Automatic recording of potential was accomplished with aid of H-700 oscillograph.

As can be seen in Fig. 6, a clearly expressed area of reduction of oxide is not observed. This is apparently explained by the fact that the process of partial reduction of oxides is accompanied by simultaneous charging of hydrogen ions. A clearly expressed area of reduction of oxides is also not observed in 3% solution of H_2SO_4. After 2-min cathode polarization the sample remains passive at switching off of current, after 5-min — active.

In order to clarify stability of oxides in conditions of prolonged cathode polarization, samples were alternately exposed to cathode and anode polarization.

For this purpose freshly cleaned titanium samples after a 10-min stay in 3% solution of H_2SO_4 were cathode polarized at constant current density ($i_K = 5$ mA/cm^2) for one hour (Fig. 7, curve 1), then with the aid of a switch the current was instantly changed into anode ($i_a = 0.1$ mA/cm^2) and samples were anode polarized to $E_H = 1.0$ V (curve 2), and then again cathode and anode alternately. Duration of repeated cathode polarization was different in experiments: 5, 15, 20, and 30 min (curves 3a, 3b, 3c, 3d respectively). Curves 4a, 4b, 4c, 4d express change of potential during subsequent anode oxidation of titanium ($i_a = 0.1$ mA/cm^2) after cathode polarization during different time intervals.

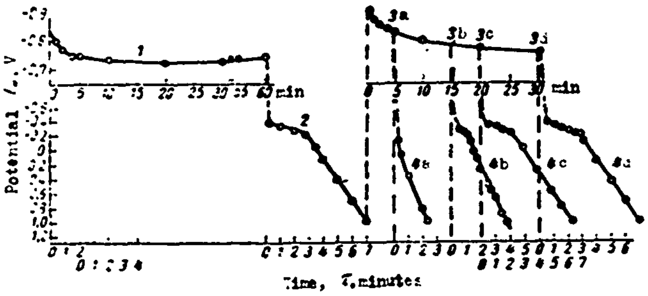


Fig. 7. Change of potential of titanium sample in time in 3% solution of H_2SO_4: 1 — during cathode polarization, $i_K = 5$ mA/cm^2; 2 — during subsequent (in the same experiment) anode polarization, $i_a = 0.1$ mA/cm^2; 3a, 3b, 3c, 3d — during subsequent repeated cathode polarization for 5, 15, 20, and 30 min respectively in each separate experiment; 4a, 4b, 4c, 4d — during repeated anode polarization, conducted after cathode polarization, corresponding to curves 3a, 3b, 3c, 3d.

As can be seen from Fig. 7, during repeated cathode polarization ($i_K = 5$ mA/cm^2), conducted after anode oxidation of sample, potential of sample (curves 3a, 3b, 3c, 3d) lies at more negative values of potential than for titanium, preliminarily anode nonoxidized.

Thus, one may assume that oxides appearing with anode polarization sharply inhibit the cathode process and are completely destroyed, apparently, only with 30-min cathode polarization.

According to curves of repeated anode oxidation 4a, 4b, 4c, and 4d, it is clear that potential of sample after briefer holdings during cathode polarization is displaced in positive direction considerably faster. Thus, for example, after 5-min cathode polarization (curve 3) the potential of sample reaches values 1.0 V in 2.5 min (curve 4), after 30-min of cahtode polarization (curve 3d) in 7 min (curve 4d).

Relatively sloping section on anode curves, corresponding to potentials of active anode dissolution, protrudes the most clearly on curves that, naturally, correspond to least oxidized surface of sample (curves 2 and 4d). On the given section along with dissolution of metal its oxidation occurs simultaneously. With such large current density as 0.1 mA/cm^2, exceeding maximum current of anode potentiostatic curve of cathode polarized titanium (Fig. 1, curve 2), rate of formation of appearing oxide is considerably higher than rate of its dissolution. Therefore, degree of oxidation of surface of titanium continuously increases in time, displacing potential in positive direction.

In similar experiments, conducted in 0.5% solution of H_2SO_4 (Fig. 8), inhibition of cathode process of separation of hydrogen on initial sample (curve 1) is also considerably less than during repeated cathode polarization of oxidized sample (3a, 3b, 3c, 3d, 3e). The shown curves, as curves 4a, 4b, 4c, 4d, and 4e, corresponding to them, in contrast to curves in Fig. 7 are artificially displaced to axis of ordinates ($\tau = 0$). Curves 4a, 4b, 4c, 4d, and 4e, as in the preceding experiment, characterize repeated anode polarization of sample ($i_a = 0.1$ mA/cm^2), conducted immediately after repeated cathode polarization (curves 3a, 3b, 3c, 3d, and 3e) in 4, 15, 30, 45, and 60 min respectively.

As can be seen from Fig. 8, on curves of repeated anode oxidation even after 1 hour cathode polarization in contrast to experiments conducted in 3% solution of H_2SO_4 (see Fig. 7), the relatively sloping section corresponding to potentials of anode dissolution is practically absent. This is apparently caused by low solubility of oxides in 0.5% solution of H_2SO_4 as compared to 3% solution of H_2SO_4.

In Fig. 8 it is also clear that only after one hour of cathode polarization is the shape of repeated anode curve 4e generally similar to initial curve 2, which indicates slower destruction of oxides in 0.5% solution of H_2SO_4 as compared to 3% solution of H_2SO_4.

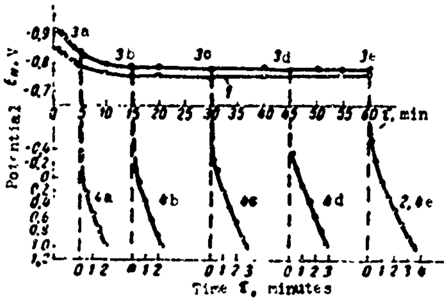


Fig. 8. Change of potential of titanium sample in time in 0.5% solution of H_2SO_4: 1 — during cathode polarization, $i_K = 5$ mA/cm^2, 60 min; 2 — during subsequent (in the same experiment) anode polarization, $i_a = 0.1$ mA/cm^2; 3a, 3b, 3c, 3d, 3e — during subsequent repeated cathode polarization for 5, 15, 30, 45, 60 min respectively in each separate experiment; 4a, 4b, 4c, 4d, 4e — during repeated anode polarization, conducted after cathode polarization, corresponding to curves 3a, 3b, 3c, 3d, 3e.

Considering the above-indicated large effect of concentration of acid on process of destruction of oxides, one should consider that in this process an essential role is played by chemical dissolution of oxides. Initial stage in process of destruction of oxides is apparently the electrochemical reduction of TiO_2 to more low-valence and more easily soluble oxides.

After inclusion of cathode polarization the displacement of potential with respect to time in positive direction on initial, low-oxidized samples (Figs. 7 and 8, curve 1) can be caused both by destruction of surface oxide, appearing immediately after stripping of sample in air, and formation of hydride.

Therefore, it was interesting to clarify the change of overvoltage of hydrogen in time, induced only by hydrogenation, and to compare change of potential of separation of hydrogen in time on oxidized titanium and titanium with hydride layer.

For this purpose there were conducted experiments on a sample, stripped under solution directly before switching on cathode current. Samples were cleaned with the help of horizontally located corundum disk (on ceramic base), having rotary and forward motion, similarly to that described in [17]. Cylindrical sample with currentfeed, preliminarily glued into polystyrene mandrel with ED-5 was then pasted to polished section located in bottom of vessel. The shaft, bearing the corundum disk, was insulated from solution in our installation with the aid of a teflon cover. On the end of the cover the corundum disk was secured by means of a teflon nut. Cathode and anode space of glass vessel was separated with the aid of a cock. Spout of electrolytic key, soldered to wall of vessel, was located a little below the face of working part of sample. Thermostatic control of solution was carried with the aid of a water jacket. It consisted of a glass cylinder and two plexiglas rings, glued to the vessel and glass cylinder with the aid of epoxy resin. Experiments were conducted in argon atmosphere.

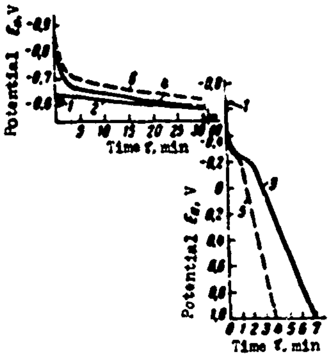


Fig. 9. Change of potential of titanium sample in time in 3% solution of H_2SO_4: 1 – during stripping of sample under solution; 2 – during cathode polarization of sample, conducted immediately after stripping under solution, $i_K = 5$ mA/cm²; 3 – during subsequent anode polarization of sample with hydride layer, obtained during preceding cathode polarization (by 2); $i_a = 0.12$ mA/cm²; 4 – during subsequent cathode polarization of oxidized (by 3) sample with hydride layer, $i_K = 5$ mA/cm²; 5 – during anode polarization of sample preliminarily stripped under soltuion, $i_a = 0.12$ mA/cm²; 6 – during subsequent cathode polarization of oxidized sample, $i_K = 5$ mA/cm².

As can be seen in Fig. 9, potential of sample immediately after stripping under solution (curve 1) is displaced in time in positive direction (curve 2). This displacement of potential on a sample stripped of initial oxides is caused by gradual decrease of overvoltage of hydrogen due to formation of titanium hydride.

Furthermore, in time there can appear another factor, namely loosening of surface of the formed hydride layer. On the sample stripped under solution, thanks to which oxides are removed and hydrogenation is eased, the effect of loosening of surface appears in as early as an hour of cathode polarization. Thus, after preliminary 1-hour cathode polarization the switching on of anode current ($i_a = 0.12$ mA/cm²) leads not to anode oxidation (Fig. 9, curve 3), as is observed after 30 min of preliminary cathode polarization, but to anode dissolution at stabel value of potential (this is not shown on figure).

While comparing curves of change of potential in time during cathode polarization on titanium stripped under solution (Fig. 9, curve 2), oxidized titanium with hydride layer (curve 4), and oxidized titanium (curve 6), it is possible to see that during the first 30 min the greatest inhibition of cathode process is observed on oxidized titanium, less on oxidized titanium with hydride layer, and the least on freshly stripped titanium.

Thus, oxide formed on titanium inhibits the process of charge of hydrogen ions to a still greater degree than oxide formed on titanium with hydride layer. With this the fastest displacement of potential in positive direction is observed on titanium with hydride layer. This is possibly connected with faster destruction of oxide on titanium with hydride layer.

From conducted experiments it follows that in acid media the displacement of potential in time in positive direction, which is observed during cathode polarization of titanium, containing oxides on its surface (appearing, for example, after stripping in air), is caused by:

a) lowering of overvoltage thanks to destruction of oxides;

b) lowering of overvoltage thanks to formation of hydride;

c) increase of true surface in time thanks to its loosening under the influence of hydrogenation.

Inasmuch as potential of separation of hydrogen depends significantly on state of surface of titanium, namely on degree of its oxidation, and preliminary cathode polarization, then it is natural that differences in surface preparation and speed of plotting of cathode polarization curves lead to significant difference in overvoltage of hydrogen (in coefficients a and b in Tafel' equation [18-21].

Anode Oxidation of Titanium and Titanium with Hydride Layer[1]

Anode oxidation of titanium with hydride layer (Fig. 9, curve 3), obtained during 30-min cathode polarization, in initial stage of oxidation (10-15 min) flows at slower displacement of potential in positive direction than on freshly stripped surface of titanium (curve 5), i.e., with less inhibition. In time the rate of displacement of potential in positive direction is delayed, the shown difference is smoothed. Thus, after anode oxidation for one hour ($i_a = 0.12$ mA/cm^2) the potential of titanium and titanium with hydride layer is 4.5 and 4.0 V.

During anode oxidation of titanium, as titanium with hydride layer (Fig. 9, curves 3 and 5), there are observed short-duration local destructions of film, developing in periodic jumps of potential in negative direction. Character of shown jumps of potential of titanium sample in conditions of mixing of 3% solution of H_2SO_4 ($i_a = 0.12$ mA/cm^2) is presented in Fig. 10. In proportion to growth of film the frequency of jumps is decreased, their duration increases. With no mixing of solution the oxide film grows faster, frequency of jumps is sharply reduced.

In order to clarify what occurs with hydride layer in process of anode oxidation, there was conducted anode oxidation of titanium and titanium with hydride layer of 3.5-4 μm thickness. Hydride layer was created by preliminary cathode hydrogenation of titanium samples in 3% solution of H_2SO_4 at current density 15 mA/cm^2 in 1.5 h. Before hydrogenation the samples were pickled in 40% solution of H_2SO_4.

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[1] T. V. Matveyeva cand. chem. sciences, also took part in fulfillment of this section of the work.

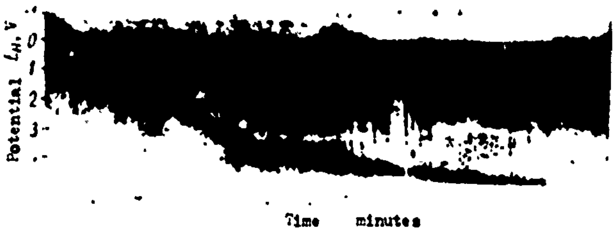

Fig. 10. Change of potential of titanium sample in time in 3% solution of H_2SO_4 at $i_a = 0.12$ mA/cm^2.

Anodizing was conducted in solution of 18% H_2SO_4 + 10% H_3PO_4 at a temperature of 100°C, density of anode current 1 a/dm^2, for eight hours. With accepted conditions of anode oxidation on the titanium without hydride layer there appears oxide film with thickness about 4 µm.

As can be seen on photomicrograph of cross section of titanium sample, after cathode hydrogenation and subsequent anodizing (Fig. 11) the oxide layer will be formed directly on hydride layer. During this the thickness of hydride layer is not practically changed. Thickness of oxide layer on titanium with hydride layer and on titanium is practically (within limits of errors of experiment) identical. This gives a basis to consider that during anode oxidation of titanium with hydride layer, titanium ions are diffused from it through hydride layer. Hydrogen of hydride layer, if it is oxidized, then it is oxidized in a relatively very small quantity.

Fig. 11. Photomicrograph of cross section of titanium sample after cathode hydrogenation and subsequent anodizing, x1000: 1 — oxide layer; 2 — hydride layer; 3 — titanium.

Less inhibition of process of anode oxidation of titanium with hydride layer, i.e., slower displacement of potential, especially noticeable in initial period of oxidation, can be caused by high conductivity of forming oxide layer owing to the presence in it of some quantity of hydrogen and additional partial current drain on oxidation of hydrogen, thanks to which the growth of oxide in initial moment of time can be delayed, causing accordingly a smaller voltage drop in oxide layer.

In proportion to growth of oxide layer the diffusion of hydrogen from hydride layer will be delayed to a considerably greater degree than diffusion of titanium.

This leads to the fact that further growth of oxide film apparently occurs solely due to diffusion of titanium through hydride layer; layer of hydride is kept constant even during prolonged anodizing.

Hydride-Oxide Nature of Passivity of Titanium

In a wide range of potentials – from 1.3 V to +0.65 V – on titanium electrode in aqueous solutions from a thermodynamic point of view the formation of both oxides and hydrides is possible. Above mentioned experimental data of investigation of electrochemical behavior of titanium indicate that titanium hydride, just as oxides, significantly inhibits anode dissolution of titanium. Surface of titanium, as surface of titanium with hydride layer is oxidized, in a wide range of potentials, namely not only in passive and passive-active region, but also in region of active anode dissolution, and partially during cathode polarization. Degree of oxidation will be different starting from chemisorbed oxygen with sufficiently negative potentials of electrode to oxide layers, measured by tens and hundreds of angstroms in region of total passivity and by several microns in process of anodizing with very positive potentials. Simultaneous coexistance of hydride and oxide layers may be seen visually on microsections of anodized titanium with preliminarily applied hydride layer.

In usual conditions of corrosion, i.e., with the absence of external polarization state of surface of titanium, besides temperature, will also depend on nature and concentration of solution of electrolyte.

With corrosion in diluted sulfuric acid (less than 5%) and at low temperatures (25°C) on titanium stripped under solution there appears basically oxide, consisting of 1 part Ti_2O_3 and 3-4 parts TiO_2 [9], and hydride is practically not formed.

In more concentrated solutions, where oxides are dissolved better, corrosion of titanium is possible mainly with hydrogen depolarization and partial absorption of hydrogen with formation of hydride. Hydride layer will grow at a rate attenuating in time [8]. In proportion to increase of hydrogen content in surface layer the anode process of dissolution of titanium will be inhibited to known limit and cathode process of separation of hydrogen will be facilitated. During this the potential can be displaced in positive direction, and in separate cases passivity can set in.

In aggressive media, where rate of dissolution of titanium is very great, for example with the presence of HF, thickness of surface hydride layer is insignificant and is rapidly stabilized in time, if composition of solution is kept constant. In such aggressive media the presence of hydride on surface of titanium is fixed only by electron diffraction method [5].

If we lower into aggressive solution a titanium sample with hydride layer, preliminarily created on it, exceeding thickness of hydride layer in stationary conditions of dissolution of titanium in given solution, then the hydride layer will be rapidly dissolved.

In other words, thickness of hydride layer appearing at corrosion of titanium with hydrogen depolarization at given temperature will depend on concentration of acid, nature of anion, and duration of holding. Displacement of electrode potential to more negative values (cathode polarization) increases probability of formation of hydride, while lowering its degree oxidation.

Thus, for titanium, distinguished by very negative value of standard electrode potential and, consequently, by high degree of thermodynamic instability, there is observed relatively high stability of it in diluted solutions caused by presence of passive state. Our investigations permit making the conclusion that passivity of titanium (i.e., increased retardability of flow of anode processes) in many respects is determined by inhibition of anode process simultaneously due to chemical bonding of titanium with oxygen (chemisorption of oxygen, formation of oxides) and chemical bonding of titanium with hydrogen (chemisorption of hydrogen, formation of hydrides), i.e., carries the character of hydride-oxide passivity.

Conclusions

1. There is investigated the effect of preliminary cathode polarization on anode dissolution and anode oxidation of titanium, and also stability of oxides on titanium in a wide range of potentials — in region of potentials of active anode dissolution and during cathode polarization of titanium in solutions of sulfuric acid.

2. Anode dissolution of titanium with hydride layer flows with greater inhibition than without hydride layer (smaller limiting current of passivation). Only after prolonged cathode polarization owing to loosening and increase of true surface on titanium with hydride layer is there observed greater limiting anode current than on titanium.

3. In region of active anode dissolution the surfaces of titanium and titanium with hydride layer are oxidized. Degree of oxidation of surface increases at displacement of potential from its steady-state value to positive (anode) side.

4. Oxides, forming at potential of +1.0 V in 3% solution of H_2SO_4, and especially in diluted 0.5% or 0.1% solution of H_2SO_4, are relatively stable in region of active anode dissolution and in conditions of cathode polarization. During their destruction on essential role is played by factor of chemical dissolution. First stage of destruction is possibly their electrochemical reduction to low-valence, more easily soluble oxides.

5. In anodizing process of titanium with hydride layer, oxide will be formed on hydride layer. Thickness of hydride layer is practically not changed. In process of anode oxidation there occurs diffusion of titanium ions from metal through hydride layer.

6. Relative stability of titanium in solutions of acids, where corrosion flows with hydrogen depolarization, is caused by hydride-oxide passivity.

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CORROSIONAL AND ELECTROCHEMICAL BEHAVIOR OF TITANIUM AND ITS ALLOYS IN WET-PROCESS PHOSPHORIC ACID[1]

V. V. Andreyeva, V. I. Kazarin, and T. I. Kudryashova

It is known what huge value we give at present in our country to the expansion of production of phosphorous fertilizers. For production of fertilizers, containing phosphorous, phosphoric acid is necessary. In the production of phosphoric acid, as in any chemical production, there is used equipment manufactured from corrosion resistant material, for correct and long-term operation of which it is necessary to consider not only its properties, but also the specific character of corrosionally active medium.

Titanium and its alloys have begun to occupy an ever increasing place as structural materials in the production of chemical equipment. Evaluation of their corrosion resistance and electrochemical properties in wet-process phosphoric acid presents much interest.

In this article there are cited results of investigation of corrosion resistance and electrochemical properties of commercial titanium and its alloys with molybdenum (up to 40%) and niobium (up to 50%) in wet-process phosphoric acid, derived with decomposition of apatites with sulfuric acid and utilized mainly for production of fertilizer.

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[1] M. T. Anisimova took part in the work.

Methods of Investigation

We investigated commercial titanium (composition: 0.15% Fe, 0.03% Si, 0.05% C, 0.03% N_2, less than 0.1% O_2), titanium alloys with molybdenum (composition with respect to charge: 1, 5, 10, 15, 20, 30, and 40% Mo) and niobium (composition with respect to charge: 10, 20, 30, 40, and 50% Nb).

A large part of the experiments were conducted in wet-process phosphoric acid (32.1% P_2O_5, 0.2% CaO, 1.67% SO_3, 0.4% Fe_2O_3, 0.4% AL_2O_3, 0.02% MgO, 0.6% SiO_2, 2.28% F, 0.02% Na, 0.02% K, 59.46% H_2O, remaining elements 5.58%) from the Voskresenskiy chemical combine. Basic components of wet-process phosphoric acid — H_3PO_4 (up to 50%), H_2SiF_6 (from 1 to 3%), and $Fe_2(SO_4)_3$. They had considerable effect on corrosional and electrochemical behavior of metals. During investigation of titanium alloy with 40% molybdenum a number of electrochemical experiments were conducted in solutions of pure phosphoric acid (up to 87%), and also in solution of 87% acid with additions of NaF (up to 1%) and $Fe_2(SO_4)_3$ (1%).

Electrochemical investigations were conducted with the aid of electron potentiostat [1, 2], and potentials were measured with the aid of compensating method relative to calomel comparison electrode and converted relative to a normal hydrogen electrode.

Corrosion investigations at constant potentials were conducted by means of prolonged holding of metal sample (preliminarily weighed with an accuracy up to 10^{-5} g) at constant potential from 30 min to 1 h, maintained with the aid of electron potentiostat [2]. For maintaining the assigned temperature we used thermostats, equipped with electronic relay.

Corrosion Resistance and Electrochemical Properties of Titanium in Solutions of Phosphoric Acid

Corrosion resistance of titanium in solutions of phosphoric acid is examined in [1, 3-5], in which there is shown small corrosion of titanium (up to 30% H_3PO_4) at low temperatures. At elevated temperatures the corrosion rate was considerable. Earlier there was shown possibility of passivation of titanium in solutions of phosphoric acid and its protection by anode polarization [6, 7].

In this report there are cited data of corrosion rate of commercial titanium depending upon potential at 100°C for three concentrations (40, 60, and 87%) of phosphoric acid (Fig. 1). In Fig. 1 it is clear that with displacement of potential

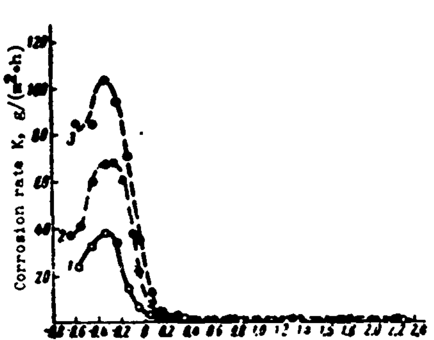

Fig. 1. Dependence of corrosion rate of titanium on potential in solutions of H_3PO_4 of various concentration at 100°C:
1 — 40% H_3PO_4; 2 — 60% H_3PO_4;
3 — H_3PO_4.

in positive direction from -0.6 V the corrosion rate of titanium at first increases, reaching maximum at potential -0.3 V, and then drops to minimum value at potential 0.2 V. From this and more positive potential the region of passive state is started. Corrosion rate in passive state is small and is increased with increase of temperature and concentration of phosphoric acid. Thus, at 100°C in 40% solution the corrosion rate is located within limits of 0.1 $g/(m^2 \cdot h)$, then as in 87% acid it is increased to 1 $g/(m^2 \cdot h)$, which is connected with increase of rate of dissolution of protective oxide films. In 87% phosphoric acid the maximum corrosion rate of titanium at potential of passivation in active region is 106 $g/(m^2 \cdot h)$.

Potentiostatic curves of titanium polarization indicate that maximum current density of passivation corresponds to maximum corrosion rate at potential of passivation equal to -0.3 V. Titanium changes into solution in the form of trivalent ions, whereas in passive state — in the form of tetravalent ions.

Potential of passivation was scarcely changed with change of acid concentration, but potential of activation, i.e., potential, with more negative value of which there is observed growth of corrosion rate, was displaced to positive values with increase of acid concentration. Thus, at 100°C for 40, 60, and 87% phosphoric acid the potential of activation was equal to -0.07, 0.02, 0.1 V respectively.

Corrosion rate of titanium in 87% phosphoric acid at 100°C in active state in steady-state conditions (without external polarization) is equal to 85 $g/(m^2 \cdot h)$, i.e., 1.25 times less than maximum possible at potential of passivation. There was approximately the same relationship at other concentrations of H_3PO_4. With the absence of oxidizers in solution, reduced in region of shown potentials, it is possible to calculate maximum corrosion rate by current density of passivation.

Figure 2 shows dependence of current density of passivation of commercial titanium on concentration and temperature of phosphoric acid. Results show that in double logarithmic coordinates data are packed into straight lines with one slope

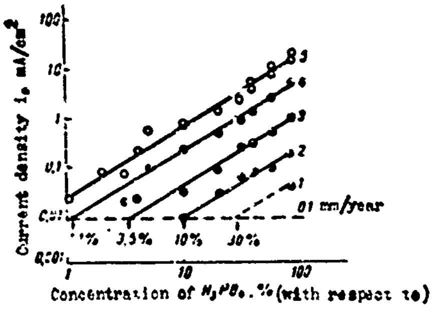

Fig. 2. Dependence of current density of passivation of titanium on concentration and temperature of H_3PO_4: 1 – 23°C; 2 – 40°C; 3 – 60°C; 4 – 80°C; 5 – 100°C.

(n = 1.45). This in turn permits extrapolating them over current density, equal to μA/cm², which is equivalent to 0.1 mm/year, taking into account that 1 g/(m²·h) corresponds to 167 μA/cm² during dissolution of titanium in the form of trivalent ions. Hence it is possible to establish region of stability of commercial titanium by concentration and temperature of solution Titanium is stable at room temperature (corrosion rate less than 0.1 mm/year) at concentration of H_3PO_4 up to 30%, at 40°C – up to 10%, at 60°C – up to 3.5%, and at 80°C – up to 1.1% without fear of possibility of activation during accidental cathode polarization, since all data on current density of passivation are derived after preliminary activation of titanium by cathode current.

Electrochemical and Corrosional Behavior of Titanium and its Alloys with Molybdenum and Niobium in Wet-Process Phosphoric Acid

Earlier [8] it was noted that in acid solutions with the presence of various passivators when plotting potentiostatic curves of polarization in region of transition of titanium into passive state there is observed a negative loop, characterizing growth of oxidizing properties of given solution with respect to the solution not containing passivator; values of stationary potentials in conditions of experiment exceed the value of activation potential, i.e., metal is in passive state.

When plotting potentiostatic curves for commercial titanium in wet-process phosphoric acid at temperatures 25, 40, 60, and 80°C (Fig. 3) there were revealed cathode negative loops, appearance of which is connected with reducing process of Fe^{3+} in F^{2+} on passivating surface of titanium. Stationary potential in this case can lie in passive or active region depending upon temperature and time, and due to presence of fluosilicic acid in solution the corrosion rate of titanium in active region of potentials can reach large values. In Fig. 4 there is shown dependence of corrosion rate of commercial titanium on potential in wet-process phosphoric acid at temperatures 40, 60, and 80°C, from which it is clear that

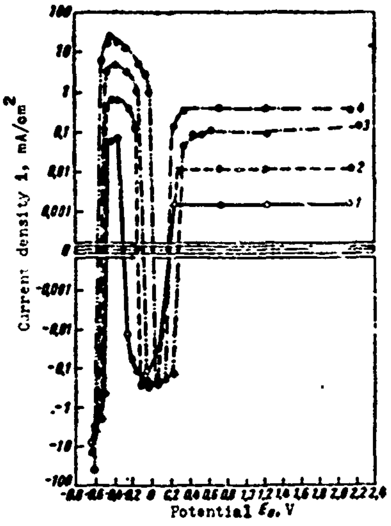

Fig. 3. Potentiostatic curves of polarization of titanium in wet-process H_3PO_4 at various temperatures: 1 – 25°C; 2 – 40°C; 3 – 60°C; 4 – 80°C.

corrosion rate in passive state right up to 40°C is approximately equal to 0.1 mm/year, at 60°C it is 0.3 $g/(m^2.h)$ (0.6 mm/year), and at 80°C reaches 2.5 $g/(m^2.h)$ (5 mm/year). Corrosion of titanium in active state at potential more negative than 0.2 V takes large dimensions, being increased with temperature from 5 $g/(m^2.h)$ at 40°C to 104 $g/(m^2.h)$ at 80°C. It is necessary to note the uniform character of corrosion both in active and in passive regions. Thus, as data mentioned above show, corrosion rate of titanium in solutions of wet-process phosphoric acid even in passive state at temperatures above 40°C is quite high, that limits its application. We proposed to increase corrosion resistance of titanium by alloying with molybdenum or niobium, since earlier [1] there was shown increase of corrosion resistance by additions into titanium of molybdenum in pure solutions of phosphoric acid.

Figure 5 shows dependence of corrosion rate of titanium and titanium alloys with 10 and 40% molybdenum upon potential in wet-process phosphoric acid at 60°C.

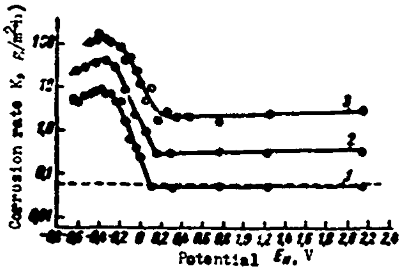

Fig. 4. Dependence of corrosion rate of titanium on potential in wet-process H_3PO_4 at various temperatures: 1 – 40°C; 2 – 60°C; 3 – 80°C.

From the figure it is clear that corrosion rate is decreased with increase of molybdenum content in alloy in region of active state (from -0.6 V to zero) and is increased in region of passive state (above 0.3 V). Thus, for titanium and its alloys with molybdenum (with high molybdenum content) there are observed two regions, in which their behavior is different. Depending upon temperature of wet-process phosphoric acid there is realized some behavior of metal or another, which can be indicated by change of potential in time.

Change of potential of titanium and its alloy with 40% molybdenum in time in wet-process phosphoric acid at various temperatures is shown in Fig. 6.

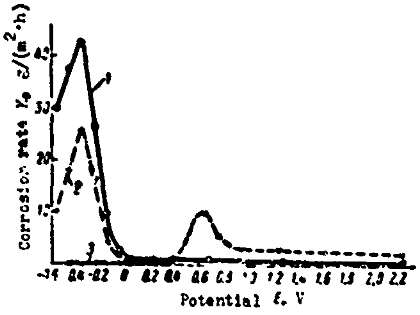

Fig. 5. Dependence of corrosion rate of titanium and titanium alloys with molybdenum upon potential in wet-process H_3PO_4 at 60°C: 1 — titanium; 2 — Ti + 10% Mo; 3 — Ti + 40% Mo.

Potential of titanium alloy with 40% molybdenum rapidly reaches steady-state value and with increase of temperature from 25 to 100°C is displaced somewhat to less positive values (curves 1, 2, 3, 4, and 5), remaining within limits of 0.34-0.45 V; corrosion rate of alloy increases with this (curve 11). Potential of titanium at temperature up to 60°C lies in region of passive state (curves 6, 7, and 8), and according to results of prolonged tests (100 h) the corrosion rate is 0.05 and 0.3 $g/(m^2 \cdot h)$ at 40 and 60°C respectively. At 80 and 100°C (curves 9 and 10) the potential of titanium as early as in the first minutes reaches large negative values (-0.6 V), i.e, titanium spontaneously passes into active state, during which the corrosion rate, for example at 100°C, composes about 400 $g/(m^2 \cdot h)$. Thus, effect of temperature on corrosion rate of titanium and its alloys both in passive and active states is considerable.

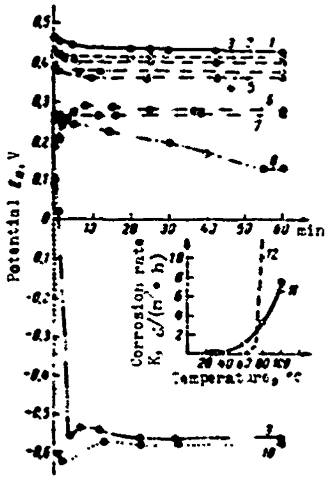

Fig. 6. Change of potential of titanium and its alloys with 40% molybdenum in time in wet-process H_3PO_4 at various temperatures: 1, 2, 3, 4, 5 — titanium alloy with 40% molybdenum 25, 40, 60, 80, and 100°C respectively; 6, 7, 8, 9, 10 — commercial titanium at 25, 40, 60, 80, and 100°C respectively; 11 and 12 — curves of dependence of corrosion rate of titanium alloy with 40% molybdenum and titanium respectively upon temperature.

In Fig. 7 there are presented results of dependence of corrosion rate of titanium and its alloys with 40% molybdenum upon opposite temperature in various conditions. Horizontal dotted line on figure shows corrosion rate 0.05 $g/(m^2 \cdot h)$, which is accepted permissible for structural materials in chemical machine building.

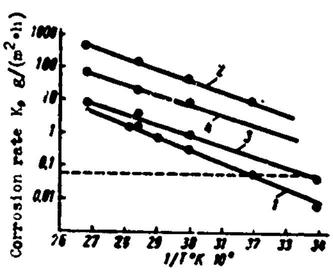

Fig. 7. Dependence of corrosion rate of titanium and titanium alloys with 40% molybdenum in active and passive states upon opposite temperature in wet-process H_3PO_4; 1 — titanium in passive state at E_H = +0.2 V; 2 — titanium in active state at E_H = -0.3 V; 3 — Ti + 40% Mo at stationary potentials $E_H \approx +0.4$ V); 4 — Ti + 40% Mo at E_H = +0.7 V.

Curve 1 reflects change of corrosion rate of titanium in passive state at 0.2 V from 1/T whereas curve 2 corresponds to active state at -0.3 V. Intersection of curve 1 with dotted line shows possibility of use of titanium up to 40°C. At higher temperature the corrosion rate of titanium exceeds permissible value and danger of transition into active state increases (curve 2). Even at room temperature the corrosion rate of titanium in active state composes more than 2 g/(m^2·h).

Corrosion rate of titanium alloy with 40% molybdenum in steady-state conditions (at stationary potentials with no external polorization) is less than 0.1 g/(m^2·h) only at temperature up to 30°C, above it the corrosion rate increases and at 100°C 7.5 g/(m^2·h). Maximum corrosion rate of alloy (curve 4), observed at more positive potential (0.7 V), is an order higher than at usual test conditions.

For clarity on Fig. 8 there is shown corrosional behavior of titanium alloy with 40% molybdenum in a wide region of potentials (curve 1) together with potentiostatic curve 2, plotted in the same solution at 80°C in wet-process phosphoric acid. With comparison of these curves it is clear that in region of negative potentials, where there is noted cathode reduction of hydrogen ion and ion of trivalent iron right up to 0.2 V, corrosion rate of alloy is insignificant, whereas at positive values of potentials corrosion increases and at 0.7 V reaches maximum [about 20 g/(m^2·h)]; then it is lowered to 8.5 g/(m^2·h) and remains constant in a wide region of potentials. Thus, displacement of potential to more positive values than 0.2 V leads to considerable dissolution of titanium alloy with molybdenum due to phenomenon of overpassivation [1, 6], inherent to molybdenum (at these potentials).

Effect of separate components of solution on electrochemical behavior of alloy Ti + 40% Mo may be seen in Fig. 9, where there are given potentiostatic curves of polarization, plotted in 87% solution of phosphoric acid at 100°C and with consecutive addition of 1% $Fe_2(SO_4)_3$ and 1% NaF. Potentiostatic curve 1 for pure

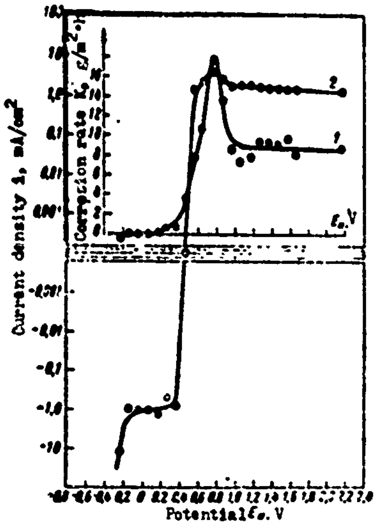

Fig. 8. Dependence of corrosion rate (1) and current density (2) of titanium alloy with 40% molybdenum upon potential in wet-process H_3PO_4 at 80°C.

solution of 87% phosphoric acid in cathode region shows reduction of hydrogen ions and position of stationary potential in the absence of external polarizing current close to zero. With displacement of potential more positive than 0.2 V there is observed considerable increase of anode current density, corresponding to increase of corrosion. Addition of 1% iron sulfate (oxide) to solution leads to the appearance of limiting current of diffusion of reduction of trivalent iron into bivalent and to the displacement of stationary potential to 0.4 V (curve 2), at which there already appears corrosion of alloys with raised molybdenum content. Further shape of curve almost coincides with the preceding. Potentiostatic curve 3 shows the joint effect of trivalent iron and fluorine ion. In the presence of fluorine ion there appears an active loop in the region of negative potentials from -0.2 V to zero, changing to negative loop characterizing reduction of trivalent iron on passivated surface of alloy.

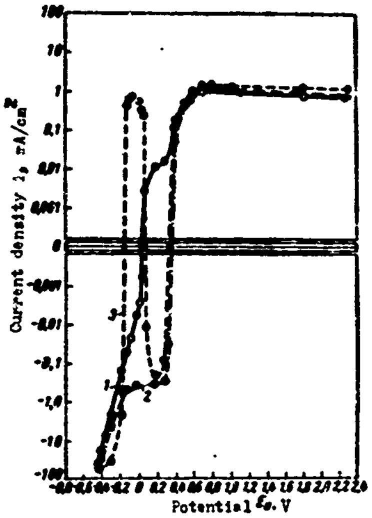

Fig. 9. Potentiostatic curves of polarization of titanium alloy with 40% molybdenum in 87% solution of H_3PO_4 with additions of $Fe_2(SO_4)_3$ and NaF at 100°C: 1 – solution of 87% H_3PO_4; 2 – solution of 87% H_3PO_4 + 1% $Fe_2(SO_4)_3$; 3 – solution of 87% H_3PO_4 + 1% $Fe_2(SO_4)_3$ + 1% NaF.

Thus, additions of molybdenum to titanium decrease corrosion rate of titanium in 87% phosphoric acid in active state, but increase corrosion in passive state. Depending upon composition of electrolyte there will appear some behavior of titanium and its alloys or another.

In Fig. 10 there are presented results of corrosional behavior of binary alloys based on titanium with additions of molybdenum and niobium in wet-process phosphoric acid at 60°C (100 h tests). Alloying with niobium, in contrast to molybdenum, decreases corrosion rate and with 50% content of niobium in alloy it composes 0.1 g/(m²·h), i.e., is decreased by three times.

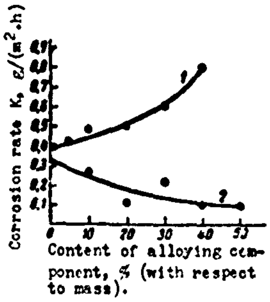

Fig. 10. Dependence of corrosion rate of binary alloys based on titanium with additions of molybdenum and niobium in wet-process H_3PO_4 at 60°C upon content of alloying addition in alloy: 1 – titanium alloy with molybdenum; 2 – titanium alloys with niobium.

Effect of niobium and molybdenum on corrosion rate K of alloys can be expressed by the following relationships: for molybdenum K = 0.35 exp [0.0184% (with respect to mass)], and for niobium K = 0.35 exp [-0.0276% (with respect to mass)].

Conclusions

1. Corrosion rate of titanium in solutions of phosphoric acid depends on potential. With definite values of potential titanium is able to pass into passive state. Proceeding from dependence of current density of passivation upon concentration and temperature it is possible to establish regions of concentrations and temperature of phosphoric acid, in which titanium possesses satisfactory corrosion resistance.

2. Titanium in wet-process phosphoric acid is stable (corrosion rate up to 0.1 mm/year) to 40°C. Presence of trivalent iron keeps titanium in passive state for a long time up to 60°C; however, corrosion rate at 60°C increases to 0.3 $g/(m^2 \cdot h)$ (0.6 mm/year).

3. Addition of molybdenum to titanium increases corrosion rate of the latter more, the higher the content of molybdenum in alloy, according to relationship: K = 0.354 exp [0.184% (with respect to mass)]. Lowering of stability of titanium alloys with molybdenum in wet-process phosphoric acid is connected with achievement of conditions of overpassivation by molybdenum due to presence of ions of trivalent iron in acid.

4. Addition of niobium improves corrosion resistance of titanium in wet-process phosphoric acid, besides the corrosion rate is decreased according to relationship: K = 0.354 exp [-0.027% (with respect to mass)].

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MECHANISM OF PROTECTION OF METALS FROM CORROSION WITH AMMONIA

I. L. Rozenfel'd, and V. P. Persiantseva

Ammonia is widely used for protection of steel from corrosion in the entire series of productions. For example, in enterprises on cracking of petroleum for preventing corrosion caused by hydrogen sulfide or hydrogen chloride, which appears as a result of hydrolysis of magnesium chloride, present in aqueous phase of petroleum; for protection of boilers and capacitors for the purpose of regulation of alkaline conditions of water and neutralization of carbonic acid available there.

Recently for increase of effectiveness of protection of metals from corrosion during storage and transportation it is recommended to add ammonium salts or other compounds, able to separate ammonia in process of hydrolysis and sissociation, to applied inhibitors (for example, sodium nitrite).

Mechanism of protective action can appear with this in one of the following phenomena.

a) ammonia shifts pH of medium into region of small corrosivity [1, 2]; b) ammonia (or ammonium hydroxide) bonds aggressive component of medium (for example, CO_2) [1, 2]; c) mixing of ammonium salts with sodium nitrite causes formation of ammonium nitrite, possessing great volatility [3].

The shown assumptions were not checked experimentally. In connection with this it was interesting to investigate protectability of ammonia depending upon its content in atmosphere, and also to study the effect of ammonia on electrochemical behavior of steel. The derived information is very useful for determination of mechanism of protective action of ammonia and other compounts of the amine class, forming cations, to ammonium ion, in solution.

Dependence of Protective Properties of Ammonia Upon its Concentration in Atmosphere

Protective properties of ammonia (were studied at 100% relative humidity and temperature 25°C. Concentration of ammonia in air atmosphere was regulated by location in reaction vessel of ammonium hydroxide of various concentration, corresponding to vapor pressure of ammonia from 66.66 to 666.6 N/m^2 (0.5 to 5 mm Hg).

Protective properties of ammonia were determined by time to appearance of first corrosion damages on samples. Derived results are presented in Fig. 1. As follows from the figure, even small concentrations of ammonia in solution increase time to appearance of corrosion on steel. However, up to a definite concentration of ammonia in atmosphere the observed increase of time to appearance of corrosion damages is very insignificant. Sharp increase of time to appearance of corrosion sets in at pressure of ammonia in atmosphere close to 200 N/m^2 (1.5 mm Hg). At pressure 266.64 N/m^2 (2.0 mm Hg) the time to appearance of corrosion increases to 50-60 days. Thus, from our experiments it follows that even insignificant concentrations of ammonia in atmosphere on the order of 200 N/m^2 (1.5 mm Hg) strongly retard the appearance of corrosion on steel. Long-term and successful protection from corrosion is observed, judging by results of our experiments, in those cases when concentration of ammonia in atmosphere reaches 266.64 N/m^2 (2.0 mm Hg).

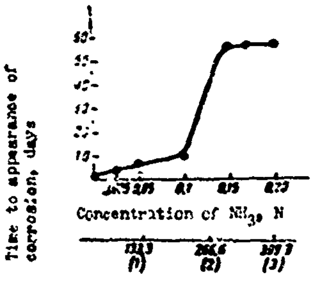


Fig. 1. Dependence of protective properties of ammonia upon its vapor pressure in atmosphere (for steel).

In view of the fact that in process of protection of metals from corrosion there is not ensured complete airtightness of system, it is important to study corrosion in conditions of possible leakage of ammonia from system. For this purpose experiments were performed in such a way that concentration of ammonia in atmosphere of reaction vessel was regulated by exit velocity of ammonia from reservoirs with holes of different diameter. Experiments showed that duration of protection by ammonia highly depends on time, during which the above-indicated pressure of ammonia is reached. For atmospheres in which relative humidity is equal to 100%, it is necessary that protective pressure [higher than 266.64 N/m^2 (>2 mm Hg)] would be reached after not more than 10 h.

Figure 2 contains data on effect of rate of saturation of atmosphere by ammonia and rate of its removal from reaction vessels to corrosion of steel. In the left part of figure there are curves of rate of saturation of atmosphere by ammonia in various reaction vessels. In these vessels there were located steel samples, for which observation was conducted. Curve 1 characterizes slow saturation of space of vessel by ammonia. In this vessel in the first 10 hours concentration of ammonia did not even reach 266.64 N/m^2 (2 mm Hg). During this time on samples there was observed appearance of corrosion damages.

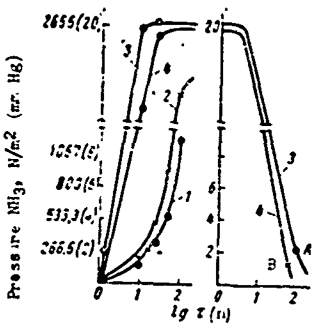


Fig. 2. Effect of rate of saturation of atmosphere by ammonia and rate of its removal from reaction vessel to corrosion of steel: 1 — appearance of corrosion in first twenty-four hours; 2 — absence of corrosion; 3 — absence of corrosion to point A; 4 — absence of corrosion to point B.

In the second vessel (curve 2) saturation of atmosphere by ammonia occurred at a high rate. For the first twenty-four hours pressure of ammonia in vessel reached almost 533.28 N/m^2 (4 mm Hg). In this case the samples were not exposed to corrosion destructions. We did not observe corrosions on samples placed in vessels, in which saturation of atmosphere by ammonia occurred still more rapidly (curves 3 and 4).

From conducted experiments it follows that in conditions of 100% relative humidity the prevention of corrosion on steel is possible only when saturation of atmosphere by ammonia goes at a sufficiently high rate, ensuring achievement of concentration of ammonia in the first twenty-four hours about 533.28 N/m^2 (4 mm Hg) [for the first 10 hours not lower than 266.64 N/m^2 (2 mm Hg)].

It was further interesting to clarify at what conditions disturbance of passive state of metal, acquired under the influence of ammonia will occur. For this purpose ammonia was gradually removed from two vessels (curves 3 and 4), during which change of concentration of ammonia in atmosphere and change of state of surface of steel were fixed. It turned out that disturbance of passive state of surface and the appearance of corrosion on samples due to this are observed in that case when concentration of ammonia in atmosphere of vessel is lowered to 266.64 N/m^2 (2 mm Hg) and less. On the sample placed in vessel (curve 3), from which ammonia is removed at a smaller rate, corrosion appeared in 186 days. On the sample located in vessel (curve 4), from which ammonia is removed at a higher rate than from the preceding vessel, corrosion appeared in 96 days (see Figure 2 — right side, curves 3 and 4).

Thus, these experiments show that concentration of ammonia in atmosphere below 266.64 N/m^2 (2 mm Hg) does not ensure reliable protection of steel in conditions of 100% relative humdity. Duration of protection of steel by ammonia depends on degree of airtightness of system, ensuring preservation of concentration of ammonia in it not lower than the minimum protective concentration, equal to 266.64-533.28 N/m^2 (2-4 mm Hg).

With the process of saturation of atmosphere by ammonia there is connected the protective action of other compounds, in which there is no free ammonia, but which are able to separate it into atmosphere due to dissociation or hydrolysis (various mixtures of sodium nitrite with ammonium salts). The latter is confirmed by processes of hydrolysis of ammonia carbonate of copper, possessing high protective properties for steel, and also kinetics of separation of nitrite-ion from different mixtures.

Carbonate ammoniate of copper with the presence of water is subjected to hydrolysis according to system

$$3{,}9Cu(NH_3)_2CO_3 + H_2O \rightleftarrows 7{,}8NH_3 + CO_2 + Cu(OH)_2 + 2{,}8CuCO_3.$$

Forming ammonia is the only carrier of protective properties in this compound; separation of it into atmosphere stipulates the ability of this compound to prevent corrosion of steel.

Investigation of mixtures of inorganic salts, consisting of sodium nitrite and ammonium salts, in which formation of volatile nitrous compounds is possible, and in connection with this improvement of their protective properties in vapor phase as compared to sodium nitrite alone, showed that no noticeable change of concentration of nitrite-ion in atmosphere as compared to mixture, where formation of volatile nitrite compounds is excluded, is observed.

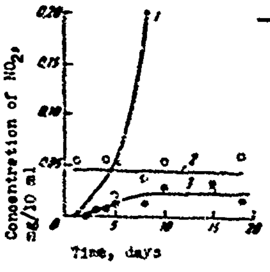


Fig. 3. Change of concentration of nitrite-ion in water in time: 1 — urotropine 8.1 g + $NaNO_2$ 8.1 g; 2 — $NaNO_2$ 8.1 g + $(NH_4)_2PO_4$ 5.25 g + $NaHCO_3$ 1.63 g; 3 — $NaNO_2$ 8.1 g + $NAHCO_3$ 6.9 g.

In Fig. 3 there is presented dependence of concentration of nitrite-ion in water, saturation of which by this ion occurs as a result of separation of nitrous compounds from two different mixtures. These mixtures are distinguished by the fact that one of them includes a compound able to form ammonium nitrite; furthermore, this mixture is able to separate ammonia into atmosphere due to hydrolysis (curve 2). In the other mixture components are able to separate ammonia into atmosphere and volatile nitrite compounds are absent (curve 3).

As follows from figure, concentration of NO_2 ion in both cases is of the same order. Considering this, there are no bases to consider that increase of effectiveness of mixture is connected with formation of volatile compounds with nitrite-ion. It is obvious that higher protective properties of mixture of ammonium nitrite and phosphate are caused by additional separation of ammonia into atmosphere due to hydrolysis of compounds.

A somewhat different mechanism of protection is observed with application of mixture of sodium nitrite with urotropine. Concentration of nitrite-ion in atmosphere is noticeably increased as compared to concentration of nitrite-ion with application of sodium nitrite or above or mixture of it with ammonium phosphate and bicarbonate (see Fig. 3, curve 1). In this case, obviously, there is actually observed formation of volatile nitrite compounds, able to saturate the atmosphere with its own vapors and to increase concentration of nitrite-ion on metallic surface. Obviously, this is the basic factor determining higher protectability of urotropine mixtures based on sodium nitrite as compared to mixtures of sodium nitrite with ammonium salts. This indicates the fact that basic function in many mixtures is fulfilled by nitrite-ions, which possess high passivating properties.

While examining protective properties of various salts, mechanism of action of which is connected with separation of ammonia into atmosphere it should be noted that as volatile inhibitors it is possible to apply any mixture that is able to separate ammonia into atmosphere. Effectiveness and duration of protection of such mixtures and compounds will depend on pressure of ammonia in atmosphere and character of products of reaction of hydrolysis.

Proceeding from above-stated data, mixtures, ensuring vapor pressure of ammonia in closed space 266.64-533.28 N/m^2 (2-4 mm Hg), will effectively protect steel from corrosion. Compounds not ensuring such vapor pressure are unsuitable for prolonged protection.

Electrochemical Behavior of Steel in Atmosphere of NH_3

Investigation of potential of steel in atmosphere of ammonia was conducted in thin layers of electrolyte with spontaneous hitting of ammonia on electrode surface

[4]. Ammonia was separated into atmosphere from ammonium hydroxide, placed on bottom of reaction vessel. Electrolyte was deposited at electrode in one case after influence of ammonia on electrode in 42 and 72 hours, in another case — before influence of ammonia on electrode. Derived data on presented in Fig. 4.

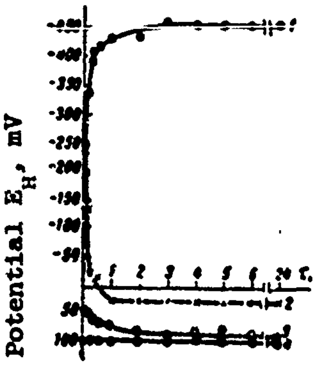


Fig. 4. Effect of ammonia in atmosphere on electrode potential of steel: 1 — without ammonia under a film of electrolyte of 160 μm thickness; 2 — without preliminary influence of ammonia on electrode; saturation of ammonia through film of electrolyte; 3 — influence of ammonia on electrode for 48 hours before putting electrolyte on it; 4 — influence of ammonia on electrode for 72 hours before putting electrolyte on it.

As follows from the figure, influence of vapors of ammonia in both cases causes stable improvement of electrode. With preliminary influence of ammonia on electrode the improvement reaches 550 mV. Somewhat less shift is observed during influence of ammonia through a film of electrolyte; however, even in this case the potential is changed 500 mV. Such change of potential is observed in an hour after placing electrode in an atmosphere of ammonia. Thus, in contrast to other volatile inhibitors [5] the protective action of ammonia is not changed depending upon whether it gets on surface before or after condensation of electrolyte on metal.

Kinetics of electrochemical reactions were studied in solution of ammonia with concentration corresponding to that which ensures effective protection in vapor phase (0.2%). Investigations showed that the presence of ammonia in solution does not practically affect kinetics of cathode reaction (Fig. 5). Speed of cathode process starts to differ from its speed in initial solution only at potential 650-750 mV, at which process of separation of hydrogen flows. The latter is connected with decrease of concentration of hydrogen ions in solutions containing ammonia.

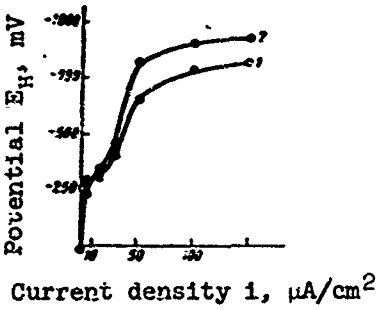


Fig. 5. Cathode polarisation of steel: 1 — in initial electrolyte (30 m/g NaCl + 70 mg/l Na_2SO_4), pH = 7; 2 — in initial electrolyte + 0.2% solution of NH_4OH, pH = 10.35.

Investigation of kinetics of anode reaction of ionization of metal (Fig. 6) showed that the effect of ammonia and caustic soda on speed of anode process is different (experiments were performed at pH = 10.35). At low currents of polarization in solution of ammonia the rate of anode process is strongly inhibited. In the presence of ammonia it is possible to displace potential to 900 mV in such a manner that electrode would not be activated. In the presence of NaOH such deceleration of anode process does not occur. In solution of ammonia the surface is passivated in a wide range of potentials due to adsorption of ammonia. This leads to the fact that rate of anode dissolution of iron in the presence of ammonia is many times less than in the presence of caustic soda. Stronger inhibition of anode reaction in the presence of ammonia is indicated by large shift of stationary potential (see Fig. 6).

Thus, from electrochemical investigations the conclusion can be made that protective properties of ammonia are caused by the presence in solution not so much of ions of hydroxyl, as NH_3.

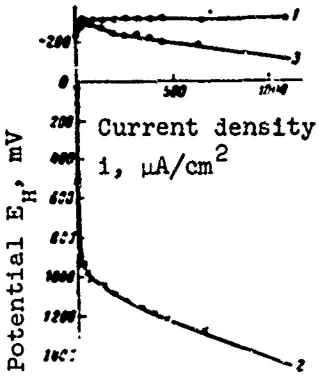


Fig. 6. Anode polarization of steel: 1 — in initial electrolyte (30 mg/l NaCl + 70 mg/l Na_2SO_4); 2 — in initial electrolyte + 0.2% solution of NH_4OH, pH = 10.35; 3 — in initial electrolyte + NaOH, pH = 10.35.

In what form does ammonia participate in inhibition of corrosion process?

Let us first consider the entire construction of ammonia molecule and possible forms of its existence in water. Molecule of ammonia has the form of a tetrahedron with atom of nitrogen at vertex and angle between hydrogen compounds equal to 108°. Since electrons of bonds N-H are quite strongly displaced from hydrogen to nitrogen, then ammonia molecule is characterized by considerable polarity (length of dipole 0.31 Å). Figure 7 shows diagram of structure of ammonia molecule.

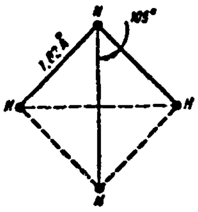
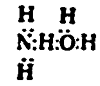


Fig. 7. Diagram of structure of ammonia molecule.

In water NH_3 can be hydrated with formation of hydrogen ids nds of two types:

$$\overset{H}{\underset{\ddot{H}}{H{:}\ddot{N}}}{:}\overset{H}{H{:}\ddot{O}} \qquad (1)$$



$$\overset{H}{\underset{\ddot{H}}{\ddot{N}}}{:}\overset{H}{H{:}\ddot{O}}{:}H. \qquad (2)$$

Since hydrogen is polarized more in water than nitrogen, and also since proton affinity of nitrogen is higher than for oxygen, second type of hydration of ammonia is less probable.

Thus, if we take hydration of ammonia according to system (1), in aqueous solutions of ammonia the following equilibriums will be possible:

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^+ + OH^-, \qquad (3)$$

when $K_1 = 2 \cdot 10^{-5}$. However, there is not excluded dissociation of ammonium ion according to system

$$NH_4^+ \rightleftarrows NH_3 + H^+ \qquad (4)$$

when $K_2 = 6 \cdot 10^{-10}$.

when $K_2 = 6 \cdot 10^{-10}$.

Consequently, in aqueous solution of ammonia there exist molecules of ammonium hydroxide, ammonium ions, OH ions, and also molecules of free ammonia.

Considering constant of reactions (3) and (4), quantity of ammonia molecules should be predominate over quantity of ammonium and ammonium hydroxide ions.

It is necessary to clarify which of the particles present in solution can be adsorbed chiefly on surface of iron. Taking point of zero charge of steel equal to -0.38 V [6], we came to the conclusion that stationary potential of steel lies in region of positive values and, consequently, surface of steel is charged positively. In these conditions the positively charged ammonium ions without additional allowances are probably not able to be adsorbed on surface of steel. Regarding neutral molecules of NH_3, considering results of investigation by Hackerman [7], according to which compounds that form hydrogen bonds with nitrogen at 108° angle, as is observed for ammonia, possess low adsorptability, it is doubtful whether change of corrosivity of steel in the presence of ammonia can be connected with adsorption of these molecules. Adsorption of molecules of ammonium hydroxide is unlikely, existence of which in undissociated form some researchers subject to doubt [8]. Thus, change of electrochemical and corrosional characteristics of steel in solutions of ammonia is obviously, connected with presence of ammonium ions, forming with hydration.

In what form can this positively charged ion passivate surface of steel also having positive charge? With respect to form the ammonium ion is a regular tetrahedron with nitrogen in the center. Due to generalization of free pair of electrons by nitrogen of ammonia molecule and hydrogen ions the nitrogen of ammonium ion acquires positive charge. In virtue of this the approach of ion to positively charged surface, as was already indicated, is hampered and, one would think, its adsorption by metal is excluded. However, if we allow that in the beginning there are adsorbed hydroxyl ions present in solution, which cause recharge of surface, then adsorption of ammonium ions also becomes possible.

Thus, hydroxyl ions as if facilitate adsorption of ammonium ions which basically promote passivation in a wide range of potentials.

Conclusions

1. There is studied mechanism of protection of steel from corrosion with the aid of ammonia and volatile inhibitors, composition of which includes ammonium salts. It is shown that protection of steel from corrosion by volatile inhibitors

is caused by separation of ammonia into atmosphere, and not by other passivating anions.

In mixtures of sodium nitrite with ammonium phosphate and bicarbonate, nitrites act basically as contact inhibitor, and ammonia, separated as a result of hydrolysis, strengthens protection only in those places where there is no direct contact of nitrite with metal surface.

2. There is determined minimum pressure of ammonia in atmosphere, ensuring protection of steel. Any compound able to create pressure of ammonia not less than 266.64 N/m^2 (2 mm Hg) in atmosphere can protect steel from corrosion at 100% relative humidity.

Shown pressure of ammonia in system should be reached in not more than 10 hours and be kept not lower than this level during the entire time of storage of metal.

3. There are studied stationary potentails of steel and kinetics of electrochemical reactions in electrolytes, containing ammonia.

It is shown that in the presence of the minimum necessary concentrations of ammonia in atmosphere the potential of steel is displaced 500 mV to positive side. At identical value of pH, electrolytes containing ammonia shift the potential of steel to the more positive side than those containing NaOH. There is a fundamental difference in the effect of sodium alkali and ammonia on kinetics of anode process. Passive state of iron in the presence of ammonia is preserved in a wide range of potentials. With simple alkalinization of medium anode polarization does not cause noticeable passivation of electrode surface.

Mechanism of protection of steel by ammonia is caused by hydration of ammonia with formation of ammonium ions. Preliminary adsorption on steel surface, having positive charge, of hydroxyl ions makes possible the adsorption of ammonium ions by metallic surface, which leads to sharp change of speed of ionization of iron.

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ATMOSPHERIC CORROSION OF STEEL, ZINC, CADMIUM, COPPER, AND ALUMINUM IN VARIOUS MARITIME AND CONTINENTAL REGIONS

G. K. Berukshtis and G. B. Klark

Effect of climatic factor and air contamination on rate of atmospheric corrosion was studied by many researchers. Recently there was obtained a large amount of data on corrosion rate of various metals in the most diverse climatic regions of the Earth. It is shown that depending upon external conditions the rate of atmospheric corrosion of metals can be changed in very wide limits, tens and even hundreds of times [1]. However, until recently there was not made any generalizations making it possible to scientifically predict rate of atmospheric corrosion of various metals for any arbitrarily selected climatic region.

First attempts to calculate rate of atmospheric corrosion of metals with respect to meteorological characteristics and air contamination by fuel gases were made at the same time in USSR by N. D. Tomashov and G. K. Berukshtis [2] and in the United States by P. I. Sereda [3]. Soviet scientists considered rate of atmospheric corrosion of steel as a function of temperature, relative to atmospheric humidity and number of days with atmospheric preciptitation, i.e., those meteorological factors which determine total duration of wetting of metal in open atmosphere. True duration of wetting of metal in atmosphere of various climatic regions was determined also by models of microcorrosion elements copper — iron, exposed at corrosion stations of Institute of Physical Chemistry [IFKh] (ИФХ), Academy of Sciences of USSR.

In calculation formula, given in [2], duration of wetting was not considered, by us since with identical duration of wetting the value of corrosion can be different [4]. Effect of air contamination by sulfurous gas was considered in calculation formula by empirical coefficient.

In works of American researchers the rate of atmospheric corrosion was examined as a function of temperature, concentration of sulfurous gas, and duration of wetting, which was determined by a special transducer exposed in the open air for a long time [5].

This investigation was conducted for the purpose of further more precise definition of form of mathematical dependence of rate of atmospheric corrosion of metals upon external conditions. In the article there are cited data on rate of atmospheric corrosion of five technically important metals: steel, zinc, cadmium, copper, and aluminum in various climatic regions of USSR with exposure in open air and in atmospheric booths, simulating condition of storage in unheated storehouses.

There is examined the new method of calculation of corrosion rate of metals with respect to meteorological characteristics, taking into account the effect of products of corrosion and air contamination by sulfurous gas.

Method of Testing

Investigated samples are 80 × 50 × 1 mm plates of steel, copper, zinc, cadmium, and aluminum. Conditions of test are expounded in detail in [6]. It was of interest to clarify the effect of position of surfaces of samples on rate of corrosion. For this purpose one of the sides of each sample (turned to the sky or to the ground) was insulated with [BF-6] (БФ-6) varnish.

There were conducted short- and long-term tests. Short-term tests were conducted in order to clarify the effect of meteorological conditions on rate of atmospheric corrosion. For this the samples were exposed to tests in all the investigated regions in various seasons of the year (in February, April, June, August, October, and December) for a period of two months. Long-term tests were conducted in order to determine the effect of products of corrosion of metals, forming in various conditions, rate of atmospheric corrosion of the latter. Duration of testing was five years with intermediate removal of part of the samples in one, two, three years, and five years. At each period there were exposed three parallel samples. In this investigation there is published data for one year of tests.

Basic criteria of evaluation of corrosion resistance of tested metals were the following: loss of mass of metal for the period of tests (g/m^2), quantity of corrosion products remaining on surface of metal after tests (g/m^2), and change of appearance of metal (color and character of layers of corrosion products).

During the entire period of corrosion tests there were conducted meteorological observations, results of which are cited below.

Furthermore, during entire period of tests we made analysis of air for content of sulfurous gas and chlorides. Methods of analysis are expounded in literature [7]. Corrosion products forming on surface of metals were analyzed for content in them of ions SO_4^{2-} and Cl^-.

We recorded duration of wetting of metal. For this purpose we used a model of microcorrosion element [8].

Climatic Characteristics and Contamination of Air in Regions of Location of Corrosion Stations

In Table 1 there are given basic meteorological characteristic of regions of location of corrosion stations.

Meteorological Characteristics of Regions of Location of Corrosion Stations of USSR in Period of Tests 1959-1960

Station	Average annual temperature, °C	Average annual humidity, %	Duration of solar radiance after a year, h.	Oscillation of wind velocity for a year, m/s	Number of days with fog for a year	Number of days with precipitation (rain, dew, thaw) for a year	Number of days with precipitation in the form of rain for a year	Tentative duration of wetting of metal for a year, h
Northern maritime region......	1.6	75	1275	5—12	26	172	168	2133
Moscow (industrial region)....	6	69	960	1—2	—	169	172	1342
Zvenigorod (rural region)....	4	82	960	1—2	—	189	177	2617
Batumi (southern maritime region)..	15	77	1787	1—2	6	380	1411	3161
Oscillation of meteorological characteristics, number of times...	10	1.2	1.9	5	4	2.2	8.4	2.3

From presented data it is clear that regions of tests differ from each other the sharpest with respect to temperature. Thus, average annual temperature at northern corrosion station is equal to +1.6°C, and at corrosion station in Batumi +15°C, i.e., 10 times higher. With so great a difference in temperature these regions differ comparatively little with respect to relative atmospheric humidity. Minimum average annual relative atmospheric humidity in Moscow is 69%, and maximum in Zvenigorod 82%, i.e., test regions differ from each other with respect to relative atmospheric humidity by only 1.2 times; with respect to number of hours of solar radiance the regions differ by approximately 2.0 times, and with respect to wind velocity by approximately 5 times. Regions of location of stations differ from each other considerably greater with respect to number of days with fog. Maximum number of days with fog is observed in the north — 26 days per year, but in Batumi fog was scarcely observed.

Regions of location of corrosion stations considerably differ with respect to number of days with atmospheric precipitation, i.e., when samples are moistened with liquid films of moisture in drops. Maximum number of days with atmospheric precipitation (rain, dew, and wet snow) is observed in Batumi, minimum — in Moscow.

In the last column of Table 1 there are given data on tentative duration of wetting τ of metals in atmosphere. These data are obtained by summation of duration of rain τ_1, recorded by pluviograph, and duration of drying of rain water and dew τ_2:

$$\tau = \tau_1 + \tau_2.$$

Duration of drying τ_2 of drop-liquid films of water (rain, dew, wet snow) is calculated as a function of temperature T, relative humidity r, and number of cases of wetting n:

$$\tau_2 = \frac{\delta}{v} = \frac{\delta}{v_0 - (75 - r)\frac{dv}{dr} + (20 - T)\frac{dv}{dT}}\, n, \qquad (1)$$

where δ — thickness of film μm; v — rate of evaporation at assigned temperature and humidity, μm/h; v_0 — rate of evaporation at 20°; relative humidity (75%) is determined experimentally and is equal to 35.5 μm/h; dv/dr = -0.38 per 1% relative humidity; dv/dT = +0.85 per 1°C.

Calculation was conducted by proceeding from thickness of water film after 100 μm. Numerical values of all parameters inserted into equation are obtained according to laboratory investigations [9].

For calculation of duration of wetting in natural conditions we took mean values of temperature, relative humidity, and number of days with atmospheric precipitation for a two-month period of testing of samples.

As can be seen from Table 1, maximum duration of wetting is observed in Batumi region — 3161 h/year and minimum in Moscow — 1342 h/year, i.e., with respect to duration of wetting these regions differ from each other by approximately 2 times.

Basic aggressors of atmospheric corrosion, as it is known, are sulfurous gas and chlorides. In Table 2 there are given data on contamination of air by sulfurous gas and chlorides.

From data given in Table 2 it is clear that contamination of air oscillates from 19 to 40 times.

By analyzing these data, it is possible to assume that rate of atmospheric corrosion of metals in examined regions should be different. If however we consider that the basic factor determing rate of atmospheric corrosion is duration of wetting of metal, then the corrosion rate of metals in inspected regions should be changed only approximately 2 times.

Table 2. Contamination of Air in Regions of Location of Corrosion Stations

Station	Concentration	
	SO_2 average annual mg/m^3	Cl for 2 months g/m^2
Moscow............	0.19	0.10
Zvenigorod.........	0.01	0.02
Batumi............	0.02	0.06
Northern maritime region............	0.012	0.80
Oscillations of air contamination, number of times....	19	40

Rate of Atmospheric Corrosion at Open Exposure

Quantitative data on corrosion rate of investigated metals at open exposure in atmosphere, i.e., when metal is moistened by rain, dew, wet snow, and during winter thaw, are given in Table 3.

Table 3. Corrosion Rate of Metals for One Year of Continuous Testing in open Atmosphere, g/m^2

Station	St. 3	Zinc	Cadmium	Copper	Aluminum
Moscow (industrial region)	333	17	49.0	9.0	1.0
Zvenigorod (rural region)	217	7	10.0	6.5	0.3
Batumi (maritime region)	204	11	14.0	6.6	0.1
Northern maritime region	250	19	12.0	24.0	7.2
Oscillations of corrosion rate, number of times	~1.6	~3	5.0	4.0	72.0

From data of Table 3 it is clear that with change of climatic conditions and air contamination the corrosion rate of all metals can be changed several times. However, from data given at the end of table it follows that various metals react differently to change of external conditions. Thus, corrosion rate of steel and zinc is changed approximately 2-3 times, wheras corrosion rate of copper, cadmium, and aluminum with the same external conditions is changed considerably greater. Corrosion rate of copper is changed four times, cadmium — five times, and aluminum — 72 times. This indicates that for various metals different external factors are specific aggressors.

Thus, from comparison of corrosion rates of metals tested at corrosion station in Moscow (industrial region) and Zvenigorod (rural region) (see Table 3), it is clear that increase of concentration of sulfurous gas in atmosphere, other things being equal (see Table 2), leads to unequal increase of corrosion rate of all metals.

Corrosion rate of steel and copper is increased approximately 1.5 times; whereas corrosion rate of zinc and aluminum is increased three times, and cadmium — five times. Thus, sulfurous gas is a specific aggressor for nonferrous metals and especially for cadmium.

From comparison of corrosion rates of metals tested at station in Northern maritime region with corrosion rates of the same metals tested in Zvenigorod (rural region), where quantity of chlorides is 40 times less than in the north (Table 2), it follows that chlorides are specific aggressors for such metals as aluminum and copper.

With increase of concentration of chlorides the corrosion rate of steel and cadmium remains practically constant; whereas corrosion rate of copper increases 3.7 times, and aluminum — 22 times.

In given data on predominant effect of sulfurous gas and chlorides on corrosion rate of various metals the influence of temperature was not considered. These data can be used for tentative evaluation of possible changes of corrosion resistance of various metals at different air contamination.

Rate of Atmospheric Corrosion of Metals when Testing in Atmospheric Booths

When testing metal in atmospheric booths, i.e., in conditions when it is moistened only during condensation of moisture, or with accidental hit of separate drops of rain and snow on it with a wind, rate of atmospheric corrosion, as a rule, is noticeably less than on in the open air. In Table 4 there are given quantitiative data on corrosion rate of tested metals in atmospheric booths.

From comparison of results of testing of metals in open atmosphere and in atmospheric booths (see Tables 3 and 4) it is clear that the corrosion rate of steel is decreased in booths approximately 1-4 times. Corrosion rate of zinc, cadmium, and copper is decreased not more than 1.5-3 times, aluminum corrodes in open atmosphere and in booths in all climatic regions with an approximately identical rate.

Table 4. Corrosion rate of Metals for One Year of Continuous Testing in Atmospheric Booths, g/m^2

Station	St. 3	Zinc	Cadmium	Copper	Aluminum
Moscow (industrial region)	44	12.5	17.0	6.5	1.0
Zvenigorod (rural region)	57	6.0	10.0	2.3	0.2
Batumi (maritime region)	66	4.0	6.0	3.5	0.05
Northern maritime region	233	12.0	7.0	14.3	4.3
Oscillations of corrosion rate, number of times . .	4.0	3.0	3.0	7.0	86

As also in open atmosphere, corrosion rate of different metals in booths is changed differently with change of climatic conditions. Corrosion rate of zinc and cadmium is changed least of all — 3 times. Corrosion of copper is changed 7 times, iron 4 times, and aluminum 86 times.

Thus, as when testing in open air, increase of concentration of sulfurous gas affects corrosion rate of iron least of all. However, in distinction from open atmosphere the effect of sulfurous gas on corrosion of zinc and cadmium in booth is reduced. This, apparently, is explained by decrease of diffusion rate of sulfurous gas at surface of metal through layers of dust and dense corrosion products.

The difference in degree of effect of chlorides on corrosion rate of metals during tests in atmospheric booths is not as great as the effect of sulfurous gas (compare the corrosion rate of metals in atmosphere and in booth in Northern maritime region with corrosion rate of the same metals in rural region of Zvenigorod). This is probably connected with the fact that quantity of chlorides on surface of metals, exposed in atmosphere and booth, is approximately equal. This position is confirmed by results of conducted analysis of corrosion products in atmosphere and booth on their content of chlorine ion.

Atmospheric Corrosion on Differently Positioned Surfaces of Metal Samples

Corrosion on differently positioned surfaces of metal samples flows at an unequal rate. This is explained by the fact that differently oriented surfaces of the same article can be under a film of moisture for unequal length of time. In Table 5 there are given relationships of corrosion rate on face of samples $K_{\text{лиц}}$, turned to the sky, to corrosion rate on the opposite side of samples $K_{\text{обор}}$, turned to the ground, in open atmosphere and in atmospheric booths.

Table 5. Relationship of Corrosion Rate on Differently Positioned Surfaces of Metal Samples During Tests in Open Atmosphere (a) and Atmospheric Booths (b) ($K_{\text{лиц}}:K_{\text{обор}}$)

Station	St. 3		Zinc		Cadmium		Copper		Aluminum	
	a	b	a	b	a	b	a	b	a	b
Moscow	0.6	1.1	1.0	1.8	0.7	1.4	1.4	1.1	0.2	0.7
Zvenigorod	0.8	1.4	0.8	1.8	0.8	0.7	0.7	1.4	0.9	3.1
Batumi	0.6	1.4	1.2	1.0	1.7	1.0	2.6	1.4	0.5	3.0
Northern maritime regions	0.6	1.0	0.5	2.0	1.0	1.4	0.7	1.0	0.5	1.2

From consideration of data of table it is clear that with open exposure in an overwhelming majority of cases steel corrodes on the face slower than on the turned side of samples, whereas during exposure in atmospheric booths the inverse relation is clearly revealed.

For nonferrous metals the difference of corrosion rates on face and reverse side of samples is revealed less clearly. Relationship of corrosion rates $K_{\text{лиц}}/K_{\text{обор}}$ for them depends not only on conditions of exposure (open atmosphere, booth), but also on climatic conditions and air contamination. In Zvenigorode and the Northern region corrosion of all nonferrous metals, just as steel, in open atmosphere is greater on back side of samples, but in atmospheric booths — on the face.

In industrial region of Moscow there is observed such regularity, as in Zvenigorod, for all nonferrous metals, except copper.

In Batumi (maritime region) with joint action of aerosols of sea water and sulfurous gas on metals the corrosion on face of samples at open exposure for all nonferrous metals, except aluminum, is greater than on the back. With exposure in atmospheric booths corrosion on the face and back sides of sample is approximately commensurable.

Effect of Corrosion Products

Formation of phase layers of corrosion products on surface of metals, corroding in atmospheric conditions, leads to noticeable inhibition of process of corrosion. Table 6 contains data on value of protective effect of corrosion products on various metals, forming for one year of continuous testing in open air. Protective effect of corrosion products was determined by us from relationship:

$$\frac{\text{Corrosion for one year of continuous testing}}{\text{Corrosion for six two-month periods of testing}}$$

From data given in Table 6 it is clear that the corrosion rate of all investigated metals in nonindustrial regions is decreased during formation of

Table 6. Protective Effect of Corrosion Products, Formed on Metals in Open Air

Station	Fe	Zn	Cd	Cu
Moscow . .	1.0	0.7	1.1	1.1
Zvenigorod . .	1.4	0.9	0.6	1.7
Batumi.	0.6	0.6	0.5	0.8
North . .	0.7	0.8	0.7	0.7

corrosion products 1.5-2 times and only in the industrial region of Moscow and in Zvenigorod the products of corrosion do not inhibit, but, conversely, somewhat accelerate the process of corrosion of such metals as steel, cadmium, and copper. At more prolonged tests the effect of corrosion products is expressed still more distinctly.

Discussion of Results

Scientifically substantiated prediction of rate of atmospheric corrosion is a very complecated question. This is explained by the circumstance that rate of atmospheric corrosion depends on a very great number of factors. We consider that these factors can be divided into four basic groups:

1. External meteorological factors and air contamination:

a) duration of wetting of metal in atmospheric conditions, which is a function: number of days with atmospheric precipitation, temperature, relative atmospheric humidity, duration of rain, wind velocity, and number of solar days;

b) concentration of industrial gases and aerosols of sea water.

2. Conditions of exposure:

a) free access of corrosional medium to surface of metal, exposed in open atmosphere. Wetting of metal by rain, dew, during thaw of snow or ice cap;

b) limited access of corrosional medium — exposure in booths. simulating conditions of unheated storehouses. Wetting of metal only with formation of dew or with accidental hit of separate drops of rain or snow.

3. Constructive factors:

a) position of corroding surfaces, possibility of runoff of moisture or, on the contrary, its accumulation on separate sections of surface;

b) mass of metallic article affecting speed of achievement of dew point by article.

4. Internal factors:

a) nature of metal, its electrochemical properties;

b) nature and physical-chemical properties of corrosion products.

Initial Stage of Corrosion of Metal

In order to mathematically express the dependence of rate of atmospheric corrosion upon all the above-indicated factors, let us first investigate corrosion on clean metal surface. To begin with, let us examine corrosion for small intervals of time, i.e., intervals in which corrosion products do not noticeably affect corrosion rate. In this case corrosion rate K is constant. Corrosion increases linearly in time: $Q = K\tau$, where τ – time of wetting.

Time, during which the surface remains dry, we do not consider, since it is known that process of corrosion is practically not observed on dry surface. Corrosion rate on a moist surface depends on temperature T and concentration C of gas SO_2 in film of moisture.

In the first approximation dependence of K on the above-indicated parameters of T and C can be represented in the form of Taylor series:

$$K(T,C) = K(T_0C_0) + \frac{dK}{dT}\Big|_{T_0C_0}(T - T_0) + \frac{dK}{dC}\Big|_{T_0C_0}(C - C_0) + \\ + \frac{d^2K}{dTdC}\Big|_{T_0C_0}(T - T_0)(C - C_0), \tag{2}$$

where $K(T_0, C_0)$ – corrosion rate at $T = T_0$ and $C = C_0$; it is convenient to take $T_0 = 20^\circ C$ and $C_0 = 0$; $\frac{dK}{dT}\Big|_{T_0C_0}$ – first derivative from corrosion rate with respect to temperature at $T = T_0$, $C = C_0$.

Let us introduce the following designations:

$$K(T_0C_0) = K_0;\ \frac{dK}{dT}\Big|_{T_0C_0} = \left(\frac{dK}{dT}\right)_0; \\ \frac{dK}{dC}\Big|_{T_0C_0} = \left(\frac{dK}{dC}\right)_0;\ \frac{d^2K}{dTdC}\Big|_{T_0C_0} = \left(\frac{d^2K}{dTdC}\right)_0 \text{ and } T - T_0 = \Delta T.$$

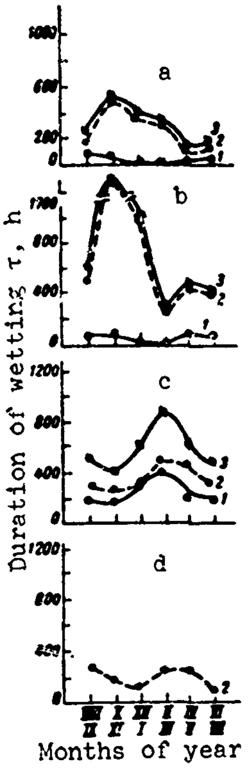
Then the formula can be written so:

$$K(T,C) = K_0 + \left(\frac{dK}{dT}\right)_0\Delta T + \left(\frac{dK}{dC}\right)_0 C + \left(\frac{d^2K}{dTdC}\right)_0\Delta TC. \tag{3}$$

Numerical values of coefficients in approximate formula (3) were found from experimentally derived data for corrosion rates of [St. 3] (Ст. 3), Zn, and Cd, and are cited in Table 7.

Table 7. Values of Coefficients in Formula (3)

Metal	K_0 g/(m^2·h)	$\left(\frac{dK}{dT}\right)_0$ $\frac{\varepsilon}{m^2\cdot h\cdot deg}$	$\left(\frac{dK}{dC}\right)_0$ $\frac{\delta}{m^2\cdot h\cdot 10^{-3}\ mg/l}$	$\left(\frac{d^2K}{dTdC}\right)_0$ $\frac{\delta}{m^2\cdot r\cdot deg\cdot 10^{-3}\ mg/l}$
St. 3 . . .	0.1200	$5\cdot10^{-3}$	$2.8\cdot10^{-2}$	$+1\cdot10^{-3}$
Zinc . . .	0.0065	$3\cdot10^{-4}$	$2.5\cdot10^{-4}$	$-5\cdot10^{-5}$
Cadmium . .	0.0078	$3\cdot10^{-4}$	$1\cdot10^{-2}$	$-5\cdot10^{-5}$



·Fig. 1. Duration of wetting by rain τ_1 (1), duration of drying of rain water and dew τ_2 (2), and overall duration of wetting $\tau_1 + \tau_2$ (3) in different months of the year in investigated climatic regions: a – Moscow (industrial region): b – Zvenigorod (rural region: c – Batumi (Maritime region): d – North (maritime region).

In order to determine numerical values of all parameters, introduced into equation (3), it was necessary first of all to determine numerical values of corrosion of tested metals for one hour of wetting at various external conditions, or, in other words, corrosivity of atmosphere in regions of location of corrosion stations. For this purpose there were used data on corrosion rate of metals for six two-month periods of testing and data on duration of wetting were determined on a model of microcorrosion element and by formula (1). Correctness of calculation formula was determined from comparison of calculated and experimental data, shown in Fig. 2. Curves in Fig. 2 show that experimental and calculated data adequately coincide.

Obtained data on corrosion rate of St. 3, zinc, and cadmium for onw hour of wetting were used by us for determination of numerical values of K_0 and $\frac{Kd}{dT}$.

In Fig. 3 there is given dependence of corrosion of St. 3, zinc, and cadmium for one hour of wetting upon average temperature of two-month period of testing. Value of corrosion for 1 hour of wetting is satisfactorily packed into linear dependence with temperature.

In order to exclude the effect of sulfurous gas, during determination of K_0 and $\frac{dK}{dT}$ for calculation we took data on small-industrial region (Batumi).

Numerical values of $K_0(T = 20^\circ C,\ C = 0)$ were determined from straight lines, shown in Fig. 3. By angle of inclination of straight lines to axis of abscissas in temperature range 10-20°C there were determined numerical values of $\frac{dK}{dT}$.

Numerical values of $\frac{dK}{dC}$ at different temperatures for St. 3, zinc, and cadmium are shown in Fig. 4.

Curves are obtained on Fig. 3 for Moscow and Batumi, where concentration of sulfurous gas differed by approximately one order. For plotting of curves there are taken data on corrosion rate for one hour of wetting after those two-month periods of testing, during which average temperatures in Moscow and Batumi were

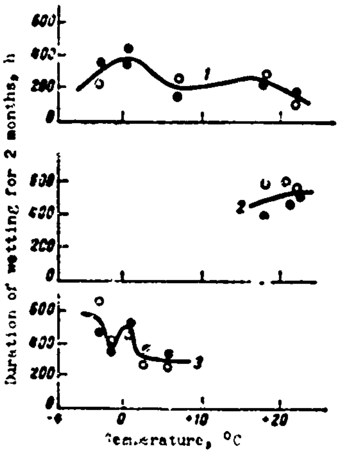


Fig. 2. Comparison of calculated (○-○) and experimental observed (●-●) values of duration of wetting of metal in atmospheric conditions at different temperatures: 1 — in Moscow; 2 — in Batumi; 3 — in the North

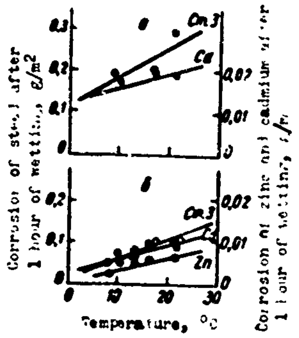


Fig. 3. Dependence of corrosion of steel, zinc, and cadmium after one hour of wetting upon average temperature of two-month period of testing in various climatic regions of USSR: a — Moscow; b — Batumi.

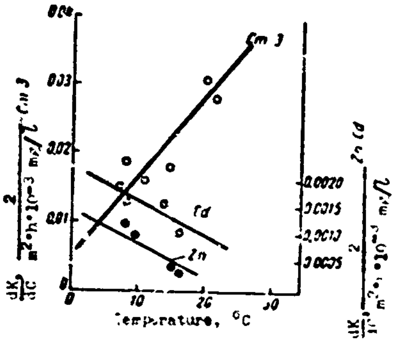


Fig. 4. Temperature dependence of coefficient $\frac{dK}{dC}$ for St. 3, zinc, and cadmium. Curves are obtained from Fig. 3 at identical average temperatures for Moscow and Batumi.

approximately identical. From Fig. 4 it is clear that value of $\frac{dK}{dC}$ increases with temperature for steel and, on the contrary, decreases for zinc and cadmium.

Numerical values of $\frac{d^2K}{dT\,dC}$, characterizing the effect of temperature on value of $\frac{dK}{dC}$, are determined from the same Fig. 4 by slope of corresponding curves.

Thus, there were determined all parameters of equation necessary for determination of value of corrosion for one hour of wetting, i.e., for those conditions when corrosion products do not yet have a significant effect on the rate of process of corrosion. Correctness of given formula (3) was checked by comparison of calculated and experimental values of corrosion rate of St. 3, zinc, and cadmium after one hour of wetting, obtained for two-month periods of testing. Obtained results are shown in Figs. 5 and 6.

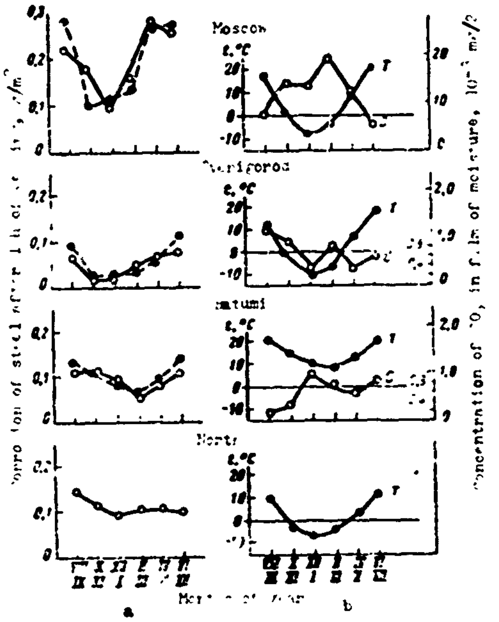


Fig. 5. Corrosion rate of steel after one hour of wetting in different months of the year in investigated climatic regions of USSR (a); average temperature T and average concentration C of sulfur dioxide in film of moisture (b): -○-○ — experimentally observed values; -●-● — values, calculated by formula (3).

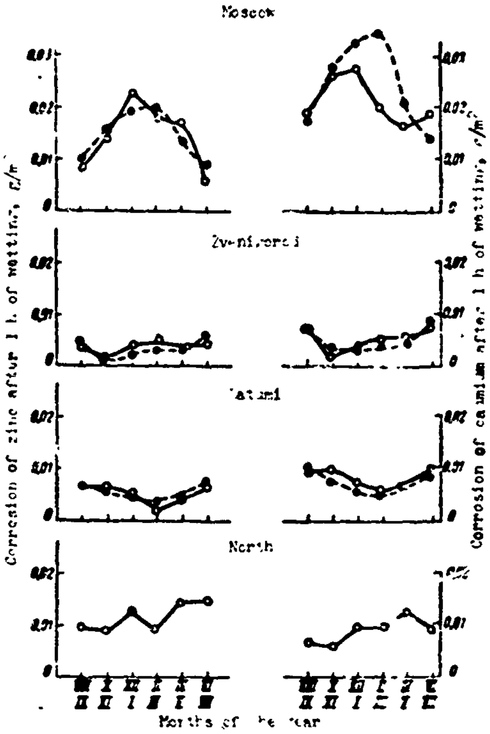


Fig. 6. Corrosion rate of zinc and cadmium after one hour of wetting in different months of the year in various climatic regions: -○-○ — experimentally found values; -●-● — values calculated by formula (3).

Corrosion at Prolonged Exposure

Let us examine corrosion of metals in large intervals of time, i.e., when corrosion rate can essentially depend on quantity and protective properties of corrosion products.

In this case corrosion rate K(T, C, τ) can be expressed by the following formula:

$$K(T, C, \tau) = P(\tau) K(TC), \qquad (4)$$

where K(T, C) — corrosion rate on clear surface, as was examined above; P(τ) — certain numerical coefficient, depending upon time τ.

Physical value of coefficient P — this is relationship of corrosion rate in given moment of time to corrosion rate in initial moment of time. Numerical value of coefficient P for various periods and metals is presented graphically in Fig. 7.

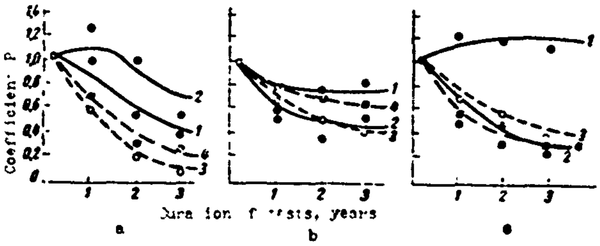


Fig. 7. Protective effect of corrosion products of steel (a), zinc (b), and cadmium (c) in various climatic regions: 1 — Moscow; 2 — Zvenigorod; 3 — Batumi; 4 — North.

We calculated value of coefficient P for various periods in the following way: we determined values of corrosion after first, second, and third year of test. Obtained values were related to sum of corrosional losses for six two-month periods of the first year of teste, i.e., to value of corrosion after a year for a case when corrosion products apparently do not essentially affect corrosion rate.

Correctness of formula was checked by comparison of calculated and experimental values of corrosion rates of steel, zinc, and cadmium according to data of one year of continuous testing. Calculation was conducted with respect to average annual temperature, average annual concentration of sulfurous gas, and total duration of wetting of metal for a year. In this case there also was obtained satisfactory coincidence of experimental and calculated data.

Complicating Factors

With limited influence of atmospheric precipitation on metal, i.e., when testing metal in atmospheric booths (unheated storehouses, under a canopy) and on differently positioned surfaces (back side of sample turned to the ground), corrosion rate of metal $\bar{K}$ is not equal to corrosion rate K, which is observed in open atmosphere for face of samples. This difference can be considered by introduction of additional co-factors into formula in the form of coefficients a and b, then corrosion rate $\bar{K}$ will be expressed so:

$$\bar{K} = K(T, C)P(\tau)ab. \quad (5)$$

In this work we did not conduct detailed investigations of the effect of different positions of sample on value of coefficient a, characterizing change of corrosion rate on differently positioned surfaces. For tentative evaluation of this effect we found the value of coefficient a for one position of sample — at 45° angle. Value of a for this position we designated by $\bar{a}$. Tentatively we determined value of $\bar{a}$ from relationship: $\bar{a} = \frac{K_{\text{об.р}}}{K_{\text{лиц}}}$ for one year of continuous testing and by two-month periods of testing. At $\bar{a} > 1$ the corrosion rate on back side of sample is greater than on the face. Numerical value of coefficient $\bar{a}$ in the majority of regions for steel, zinc, and cadmium approaches 1 and practically does not depend on temperature. At more prolonged tests (according to data of one year of continuous testing) there is quite clearly revealed the tendency toward increase of numerical value of coefficient $\bar{a}$ in regions with low average annual temperature.

In atmospheric booths the corrosion rate on back side of samples of steel, zinc, and cadmium is practically always smaller or is commensurable with corrosion rate on face of samples.

Values of coefficient $\bar{a}$ are changed in open atmosphere for steel approximately from 0.8 to 2, for zinc from 0.6 to 1.8, and for cadmium from 0.6 to 1.4.

In atmospheric booths values of coefficient $\bar{a}$ lie within limits of 0.2-1 for steel, 0.4-1 for zinc, and 0.2-1.2 for cadmium.

Value of coefficient $\bar{b}$, characterizing effect of conditions of tests of metal (in atmospheric booths), was determined by us from relationship

$$\bar{b} = \frac{K_{\text{атмосферная будка}}}{K_{\text{открытая атмосфера}}}.$$

Values of K were calculated according to data of one year of continuous testing and according to two-month tests, conducted in different seasons of the year. Numerical values of coefficient $\bar{b}$, according to data of one year of continuous testing, are changed within limits of 0.25-0.5; this means that corrosion in atmospheric booths is approximately 2-4 times less than in open atmosphere. Oscillations of values of δ are explained, apparently, not so much by meteorological conditions, as constructive features of atmospheric booths themselves, causing unequal possibility of atmospheric precipitation hitting them during a wind.

Conclusions

1. There is investigated the effect of meteorological conditions, contamination of air, and also the effect of forming corrosion products on rate of atmospheric corrosion of metals in industrial, rural, and maritime regions of USSR.

2. Inspected climatic regions noticeably differ from each other with respect to basic meteorological characteristics. Average annual temperature is changed from 1.6°C in Northern maritime region to 15°C in region of Batumi, i.e., 10 times. Average annual relative humidity is changed considerably less — from 69% in Moscow to 82% in Zvenigorod, i.e., 1.2 times. Duration of wetting of metal by atmospheric precipitation is changed from 1342 h/year in region of Moscow to 3161 h/year in Batumi, i.e., 2 times. With respect to number of hours of solar radiation the inspected regions differ from each other by approximately 2 times, with respect to wind velocity 5 times, and with respect to contamination of air by sulfurous gas and sea water salts -- approximately 20-40 times.

3. Results of corrosion tests show that depending upon change of climatic conditions the corrosion rate of steel and zinc in inspected regions is changed 2-3 times, copper — 4 times, cadmium — 5 times, and aluminum — 72 times.

4. Corrosion rate of metals in atmospheric booths is less than in open atmosphere. Steel corrodes approximately 1-4 times less in booths than in open atmosphere; zinc, copper, and cadmium — approximately 115-3 times less. Corrosion rate of aluminum in open atmosphere and in booths is identical in all climatic regions.

5. There is shown the possibility in principle of scientific and founded calculation of corrosion rate of metals during tests in open atmosphere with respect to meteorological factors and contamination of atmosphere taking into account testing conditions, nature of metals, and physical-chemical properties of corrosion products.

6. Obtained data can be used by designers during assignment of protective coatings of parts of instruments and equipment. Results of this investigation will be used by us during development of methods of accelerated corrosion tests for production of conversion factors from accelerated tests for conditions of exploitation.

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