

AD 768473

PTD-HT-23-153-74

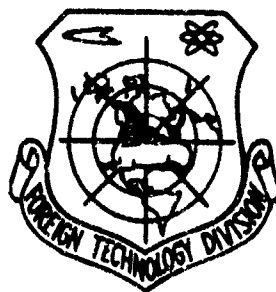
## FOREIGN TECHNOLOGY DIVISION



### MECHANISM OF TITANIUM CORROSION IN MINERAL ACIDS AND THEIR MIXTURES

by

A. P. Brynza, L. I. Gerasyutina,  
E. A. Zhivotovskiy



Approved for public release;  
distribution unlimited.

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE

U.S. Government Printing Office  
Stock No. 22151

FTD-HT- 23-153-74

## EDITED TRANSLATION

FTD-HT-23-153-74

MECHANISM OF TITANIUM CORROSION IN MINERAL ACIDS  
AND THEIR MIXTURES

By: A. P. Brynza, L. I. Gerasyutina,  
E. A. Zhivotovskiy

English pages: 8

Source: Novyy Konstruktsionny Material - Titan,  
1972, pp. 174-179

Country of Origin: USSR

Translated by: Sgt Paul J. Reiff

Requester: FTD/PDTI/R. F. Frontani

Approved for public release;  
distribution unlimited.

THIS TRANSLATION IS A RENDITION OF THE ORIGINAL FOREIGN TEXT WITHOUT ANY ANALYTICAL OR EDITORIAL COMMENT. STATEMENTS OR THEORIES ADVOCATED OR IMPLIED ARE THOSE OF THE SOURCE AND DO NOT NECESSARILY REFLECT THE POSITION OR OPINION OF THE FOREIGN TECHNOLOGY DIVISION.

PREPARED BY:

TRANSLATION DIVISION  
FOREIGN TECHNOLOGY DIVISION  
WP-AFB, OHIO.

FTD-HT- 23-153-74

Date 10 Oct 1973

# U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

| Block | Italic     | Transliteration | Block | Italic     | Transliteration |
|-------|------------|-----------------|-------|------------|-----------------|
| А а   | <i>А а</i> | A, a            | Р р   | <i>Р р</i> | R, r            |
| Б б   | <i>Б б</i> | B, b            | С с   | <i>С с</i> | S, s            |
| В в   | <i>В в</i> | V, v            | Т т   | <i>Т т</i> | T, t            |
| Г г   | <i>Г г</i> | G, g            | У у   | <i>У у</i> | U, u            |
| Д д   | <i>Д д</i> | D, d            | Ф ф   | <i>Ф ф</i> | F, f            |
| Е е   | <i>Е е</i> | Ye, ye; E, e*   | Х х   | <i>Х х</i> | Kh, kh          |
| Ж ж   | <i>Ж ж</i> | Zh, zh          | Ц ц   | <i>Ц ц</i> | Ts, ts          |
| З з   | <i>З з</i> | Z, z            | Ч ч   | <i>Ч ч</i> | Ch, ch          |
| И и   | <i>И и</i> | I, i            | Ш ш   | <i>Ш ш</i> | Sh, sh          |
| Й й   | <i>Й й</i> | Y, y            | Щ щ   | <i>Щ щ</i> | Shch, shch      |
| К к   | <i>К к</i> | K, k            | Ъ ъ   | <i>Ъ ъ</i> | "               |
| Л л   | <i>Л л</i> | L, l            | Ы ы   | <i>Ы ы</i> | Y, y            |
| М м   | <i>М м</i> | M, m            | Ь ь   | <i>Ь ь</i> | '               |
| Н н   | <i>Н н</i> | N, n            | Э э   | <i>Э э</i> | E, e            |
| О о   | <i>О о</i> | O, o            | Ю ю   | <i>Ю ю</i> | Yu, yu          |
| П п   | <i>П п</i> | P, p            | Я я   | <i>Я я</i> | Ya, ya          |

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

FOLLOWING ARE THE CORRESPONDING RUSSIAN AND ENGLISH  
DESIGNATIONS OF THE TRIGONOMETRIC FUNCTIONS

| Russian   | English            |
|-----------|--------------------|
| sin       | sin                |
| cos       | cos                |
| tg        | tan                |
| ctg       | cot                |
| sec       | sec                |
| cosec     | csc                |
| sh        | sinh               |
| ch        | cosh               |
| th        | tanh               |
| cth       | coth               |
| sch       | sech               |
| csch      | csch               |
| arc sin   | sin <sup>-1</sup>  |
| arc cos   | cos <sup>-1</sup>  |
| arc tg    | tan <sup>-1</sup>  |
| arc ctg   | cot <sup>-1</sup>  |
| arc sec   | sec <sup>-1</sup>  |
| arc cosec | csc <sup>-1</sup>  |
| arc sh    | sinh <sup>-1</sup> |
| arc ch    | cosh <sup>-1</sup> |
| arc th    | tanh <sup>-1</sup> |
| arc cth   | coth <sup>-1</sup> |
| arc sch   | sech <sup>-1</sup> |
| arc csch  | csch <sup>-1</sup> |
| <hr/>     |                    |
| rot       | curl               |
| lg        | log                |

## MECHANISM OF TITANIUM CORROSION IN MINERAL ACIDS AND THEIR MIXTURES

A. P. Brynza, L. I. Gerasyutina and  
E. A. Zhivotovskiy

Acid etching of titanium in mineral acid solutions is used for removing scale and removing the alpha-deposited layer from the surface [1-3]. Mixtures of mineral acids are also used for depositing anodic oxide films on the surface of titanium. These films serve as sorbents in vacuum technology [4]. The hydrides which form in the mineral acid mixtures insure good adhesion of galvanized coatings to the titanium [5]. Undoubtedly, the mechanism of the indicated processes is determined not only by the acidity of the medium but by its anion composition.

This article examines several of the laws governing the corrosion and electromechanical behavior of titanium (VTI-1 brand) in sulfuric, hydrochloric, and phosphoric acids and their mixtures, as well as in solutions of the indicated acids having additives of from 0.001 to 0.1 mole/l of sodium chloride, and acid and normal sulphates and phosphates of sodium at 20-80°. The methodology of corrosion testing and electromechanical measurements is described in work [6]. The resultant data show (Table 1) that the most aggressive medium with respect to titanium is sulphuric acid. This apparently is associated to a considerable degree with the

stimulating effect of the acid's anions, since with one and the same Hammett function the rate of titanium corrosion in sulphuric acid is greater than in hydrochloric or phosphoric acid (Fig. 1). In order to activate the metal with chloride or phosphate ions a certain acidity is necessary; this is found in accordance with the data of N. D. Tomashov et al. [7], studying the effect of chloride ions on the corrosion of titanium in sulphuric acid. Introducing the chloride and sulphate of sodium into a solution of 5.5 molar phosphoric acid increases the dissolution rate of titanium (Table 2). Sodium sulphate, as can be expected, was more aggressive than sodium chloride.

Table 1. Corrosion rate ( $v$ ) of titanium in solutions of sulphuric, hydrochloric, and phosphoric acid at different temperatures.

| C,<br>moles/l     | $v, \text{g/m}^2 \cdot \text{h}$ |     |      |      |      |
|-------------------|----------------------------------|-----|------|------|------|
|                   | 20°                              | 40° | 60°  | 80°  | 100° |
| Sulphuric acid    |                                  |     |      |      |      |
| 0,5               | —                                | 1,2 | 3,6  | 8    |      |
| 1,1               | —                                | 1,6 | 4,5  | 11   |      |
| 1,7               | —                                | 2,0 | 5,8  | 13,6 |      |
| 2,3               | 0,9                              | 2,5 | 8,0  | 20   |      |
| 3                 | 1,1                              | 3,2 | 11   | 31   |      |
| 5,3               | 1,6                              | 6,3 | 23   | 80   |      |
| Hydrochloric acid |                                  |     |      |      |      |
| 0,5               | —                                | —   | 1,25 | 2,8  |      |
| 1,1               | —                                | 0,1 | 1,4  | 3,2  |      |
| 2,0               | —                                | 0,4 | 1,6  | 4    |      |
| 2,0               | —                                | 0,9 | 2,8  | 6,8  |      |
| 4,4               | 0,65                             | 2   | 5,1  | 15,3 |      |
| 6,2               | 1,1                              | 3,5 | 9,2  | 28   |      |
| Phosphoric acid   |                                  |     |      |      |      |
| 1,7               | —                                | —   | 1,2  | 4,7  | 8    |
| 3,5               | —                                | 0,2 | 1,6  | 5,1  | 15   |
| 5,5               | —                                | 0,4 | 2,1  | 6,5  | 24   |
| 8,7               | —                                | 0,7 | 3,0  | 12,5 | 35   |
| 14,7              | —                                | 1,2 | 4,4  | 20   | 60   |

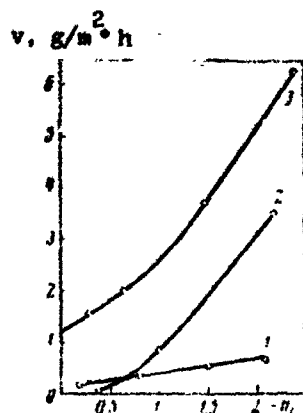


Fig. 1. Corrosion rate of titanium in phosphoric (1), hydrochloric (2) and sulphuric (3) acid as a function of acidity  $H_0$ .

Table 2. Corrosion rate of titanium  $v$  in  $g/m^2 \cdot h$ .

| Additive                        | Concentration of additives, mole/l |      |      |      |      |      |      |
|---------------------------------|------------------------------------|------|------|------|------|------|------|
|                                 | 0                                  | 0,5  | 1    | 5    | 10   | 50   | 100  |
| NaCl                            | 0,40                               | 0,44 | 0,47 | 0,49 | 0,51 | 0,56 | 0,58 |
| Na <sub>2</sub> SO <sub>4</sub> | 0,40                               | 0,64 | 0,65 | 0,68 | 0,69 | 0,71 | 0,78 |

The dependence of the titanium passivation current at the passivation potential ( $\phi = -0.20$  V) on salt concentration is described by the exponential function

$$i = aC^b \exp\left(\frac{\beta n \phi F}{RT}\right),$$

where  $a$  and  $b$  are constants;  $\beta$  is the apparent transfer coefficient;  $n$  is the number of electrons participating in the electrode reaction, which takes the form of straight lines in the coordinates  $\lg i$  vs.  $\lg C$  (Fig. 2).

The results obtained make it possible to propose that chloride and sulphate ions, by absorbing on the surface,<sup>1</sup> play an indirect

<sup>1</sup>The positive charge of the titanium surface ( $\phi_{CT} = 0.2$  V while the potential of its negative charge, according to the data of various authors, is  $-0.76$  [8] or  $-1.04$  V [9] facilitates anion absorption.

part in accelerating the electrochemical stage of the anion dissolution process [10]. Apparently, as a result of specific absorption a surface complex forms, which hydrates and easily loses connection with the main mass of metal and transfers into solution. This leads to the ionization of an atom entering into the complex which, in turn, removes the overvoltage of the process of metal dissolution.

Acid and normal sodium phosphates slightly decrease the titanium corrosion rate (Fig. 3). The inhibiting effect of phosphates increases in isoacidic (i.e., those having identical Hammett acidity functions) solutions of sulphuric and hydrochloric acids in proportion to their increased concentration. The effectiveness

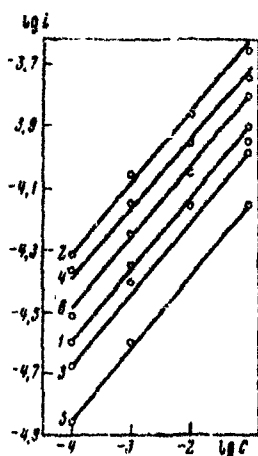


Fig. 2.

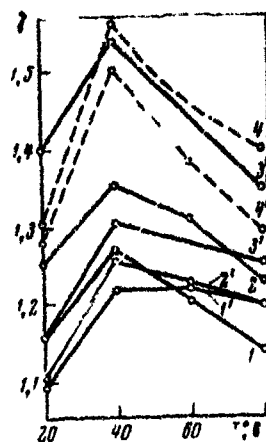


Fig. 3.

Fig. 2. Dependence of titanium passivation currents ( $\phi = -0.2'$ ) in 5.5 molar phosphoric acid on sodium sulphate (1, 2), hydro-sulphate (3, 4), and chloride (5, 6) concentration at  $40^\circ$ .

Rate of potential change, V/s: 1, 3, 5 -  $0.55 \cdot 10^{-3}$ ; 2, 4, 6 -  $9 \cdot 10^{-3}$ .

Fig. 3. Dependence of inhibiting effects of primary (1, 1'), secondary (2, 2'), and tertiary (3, 3') sodium phosphates on temperature in 6.2 molar hydrochloric (1-4) and 5.3 molar sulphuric (1'-4') acids.

4, 4' - addition of 1.4 mole/l phosphoric acid.



of phosphates as corrosion inhibitors for titanium increases in the series  $\text{NaH}_2\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{Na}_3\text{PO}_4$ . As inhibitors the phosphates are more effective in hydrochloric acid. Their inhibiting effect increases with temperature, achieving a maximum at  $40^\circ$  (see Table 3). This provides the basis on which to assume that the phosphates are chemisorbed on the surface of titanium. Chemical absorption is possible only for particles with great energy reserves. Therefore, chemisorption occurs at a noticeable rate only at increased temperature. However, with an inordinate temperature increase increased particle desorption is possible; this reduces the inhibiting effect. Indicative of this absorption mechanism is the fact that the data regarding the dependence of corrosion rate and currents of anode diffusion of titanium on phosphate concentration agree with the equation of the Langmuir isotherm of adsorption, modified as applied to corrosion [11], and graphically represent straight lines in the coordinates  $\lg[(v_0/v) - 1] - \lg C$  Fig. 4.

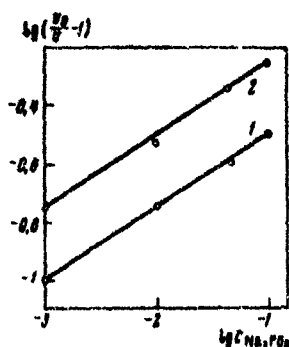


Fig. 4. Dependence of the quantity  $\lg\left(\frac{v_0}{v} - 1\right)$  on concentration of tertiary sodium phosphate in 5.3 M sulphuric (1) and 6.2 M hydrochloric (2) acid at  $40^\circ$ .

The special features and laws governing the corrosion resistance and electrochemical behavior of titanium in mineral acids having anion additives and previously published data [12] on the corrosion and electrochemical behavior of titanium in mixtures of acids were used as the basis for selecting a solution in which the chemical removal of oxides from the titanium surface would be possible. Oxidation of titanium leads to the formation of an outer layer of  $\text{TiO}_2$  oxide and a  $\text{TiO}$  layer securely fastened

to the metallic base [13]. According to published data,  $TiO$  dissolves better in sulphuric than in hydrochloric acid [14]. Accordingly, and also because lifting of the scale must be insured during etching, sulphuric acid was introduced into the solution. However, during etching poorly soluble phosphates can form in it; by screening the metal surface these can facilitate nonuniform etching. Uniform etching is possible with chloride ions, since the easily soluble product of the  $TiCl_3$  reaction is drawn away from the metal/solution interface. To insure uniform etching sodium chloride was added to the etching solution.

The work tested the possibility of using mixtures of sulphuric and phosphoric acid with sodium chloride additives for the chemical removal of scale from titanium. The most important technical characteristic of the metal etching process is its rate, which is associated with the change of potential. This work studied the time dependence of the amount of etched metal and scale during parallel measurement of the potential of samples in acid solutions. It also determined the hydrogen content in the samples after etching. The effectiveness and quality of the etching were determined by its duration, overall weight losses, external appearance of specimens, and hydrogen content after etching. Alloy samples heat treated at temperatures of  $780-820^\circ$  were used for the study. The time dependences of potential  $\phi$  ( $\phi$  vs  $\tau$  curves) and weight loss with respect to a unit area of the visible surface of scale-covered VT1-1 alloy samples (curves  $(\Delta P/S) - \tau$ ) were studied. It was found that the process of scale removal consists of the following periods: 1) induction when the scale is impregnated by the solution; in this period there is no noticeable weight change; 2) main period - rapid deterioration of potential and considerable sample losses; 3) the period of etching of scale residues and dissolution of the metal itself; the standard potential approaches that for the metal stripped of oxides.

As the content of sodium chloride in the solution during the induction period increases, consequently, the descaling time

decreases. Thus, the descaling time without sodium chloride in 5.3 M sulphuric acid is 145 min. and with the addition of 50 g/l, 120 min. Additions of phosphoric acid slow down the etching process of titanium alloys slightly, from 120 to 145 min with the addition of 3 M phosphoric acid. Introducing phosphoric acid reduces the amount of hydrogen in the samples from 0.08 to 0.04%, while the hydrogen content after clarification of the surface is reduced to 0.024% (the hydrogen content in the original titanium samples). Consequently, during the indicated etching regime all the hydrogen concentrates in the surface layer, forming hydrides which protect the titanium surface from corroding. It is an advantage that the proposed mixture of mineral acids, as opposed to those used [1-3], does not contain fluorides and silicon fluorides.

#### CONCLUSIONS

1. The corrosion resistance and electromechanical behavior of titanium in solutions of sulphuric, hydrochloric, and phosphoric acid in the 20-80° temperature interval were studied. It was shown that given identical solution acidity, the most aggressive with respect to titanium is sulphuric acid.
2. The addition of sodium chloride and sulphate to phosphoric acid stimulates titanium dissolution; the stimulating effect of the sulphate ions is expressed to a greater degree than those of the chloride. Sodium phosphates slow down titanium corrosion in sulphuric and hydrochloric acid slightly. The most effect in this respect is tertiary sodium phosphate.
3. A foundation was developed for selecting a solution for the chemical removal from the titanium surface of scale which forms on its surface at 780-820°.

# BIBLIOGRAPHY

1. С. А. Кушакевич, Э. К. Ханина. Сб. «Травление и обезжиривание труб из сталей и сплавов». «Металлургия», 1967, с. 250.
2. Н. В. Боговаденская, Л. Н. Эхрамович. Сб. «Травление и обезжиривание труб из сталей и сплавов». «Металлургия», 1967, с. 226.
3. А. П. Брынаа, Л. П. Власова, Ю. П. Коробочкин и др. Сб. «Травление и обезжиривание труб из сталей и сплавов». «Металлургия», 1967, с. 246.
4. Г. Г. Черненко. Исследование и разработка процесса толстостенного анодирования титана. Автореф. канд. дисс. Харьковский политехнич. ин-т, 1968.
5. Р. М. Сагисва. Адсорбция водорода на титане и ее роль при нанесении гальванических покрытий. Автореф. канд. дисс. Казанский ун-т, 1967.
6. А. П. Брынаа, Л. И. Герасютина. Ж. прикл. хим., 1962, 35, 58.
7. И. Д. Томашов, Р. М. Альтовский. Ж. физ. хим., 1959, 33, 610.
8. Л. И. Антропов. Укр. хим. журн., 1963, 29, 555.
9. И. Е. Хомутов. Журн. физ. химии, 1962, 36, 2721.
10. Я. М. Колотыркин. Защита металлов, 1967, 3, 131.
11. Л. А. Маркоевич, Н. П. Жук. Сб. «Коррозия и защита конструкционных металлических материалов». Мачигиз, 1961, с. 93.
12. А. П. Брынаа, Л. П. Герасютина, Э. А. Животовский. Защита металлов, 1968, 4, 488.
13. Г. А. Смоляков, Г. Н. Кругер. Методы очистки поверхности титана Цетиние металлы, 1956, № 5.
14. M. Chene, C. Deischberg, O. Martin--Borret. Ann. chim. analyt., 1946, 28, 197.
15. И. С. Ашотов, С. А. Горбунов. Ж. прикл. хим., 1961, 34, 4.