



# Corrosion resistance of titanium in water solution of hydrochloric acid

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Received 04.04.2007; accepted in revised form 15.05.2007

## ABSTRACT

**Purpose:** Most of conducted research in the area of titanium corrosion are concentrated on determine the corrosion resistance in water solution of hydrochloric acid medium at high temperatures. Recognizing of corrosion mechanisms in liquid mediums can lead to obtain corrosion-proof material e.g. by applying passivation phenomenon. In this paper attention was paid to determine the corrosion resistance of titanium in corrosive medium of liquid hydrochloric acid with concentration of 6 and 10%. Research of material susceptibility to surface activation in the pipeline of corrosion processes are conducted.

**Design/methodology/approach:** In the corrosion tests electrolyser, potentiostat „Solartron 1285” and computer with „CorrWare 2” software were used. Results of the research were worked out with „CorrView” software. The potentials values were determined in relation to normal hydrogen electrode (NHE). The temperature of the solutions was kept at 20°C and 50°C. The recording of potential/density of current - time curve was conducted for 300 s.

**Findings:** The results of research, which were conducted in 6% and 10% HCl solution, show good corrosion resistance of titanium Gr1 in temperature 20°C. Tested samples were characterized by susceptibility to surface self-passivation, with the exception of samples tested at temperature of 50°C in HCl water solution. Damages of titanium passive surface during exploitation can lead to short-lived increase of corrosion rate in higher temperatures.

**Practical implications:** Results of corrosion research allow to determine the durability of titanium in 6% and 10% water solution of hydrochloric acid at temperature 20°C and 50°C.

**Originality/value:** The goal of this work was to on corrosion resistance of titanium in 6% and 10% HCl water solutions.

**Keywords:** Metallic alloy; Corrosion; Titanium

## MATERIALS

### 1. Introduction

Titanium is very interesting structural material, which is applied in many, different fields of technology for very responsible welded constructions. Titanium and titanium alloys are characterized by combination of properties, which distinguished them from other materials – high relative durability and creep-resistance in combination with good corrosion resistance [1,2].

Titanium belongs to group of high-reactive elements, what is indicated by his reduction potential - 1.539 V<sub>NEW</sub> (Ti<sup>2+</sup> + 2e = Ti<sup>0</sup>). But in the presence of oxygen titanium potential is changed significantly and

could reach + 0.4V. This phenomenon can be combined with arising of protective layer of oxides on metal surface [3-8].

Small amount of oxide, which is dissolving in water solution as a result of contact with air, is sufficient for passivation of titanium. Passive layer, which is present on titanium surface, is made up first of all from rutile (TiO<sub>2</sub>) and also from TiO and Ti<sub>2</sub>O<sub>3</sub>, but in much smaller degree [9,10].

Thickness of oxides layer can reach 50-60 Å after longer time of air exposure. On polarization curves of titanium and titanium alloys increase of current density at values of potential ca. 700-1000 mV<sub>NEW</sub> can be observed. This phenomenon can be combined from

analysis of potential-pH chart with transition of titanium from +4 oxidation state ( $\text{TiO}_2$ ) to +6 oxidation state ( $\text{TiO}_3$ ) [11,12].

Corrosion resistance of titanium in mediums, which contains chlorine is good. Titanium is showing total corrosion resistance for: moist chlorine,  $\text{ClO}_2$ , hypochlorous acid, chloridessolutions: aCl, KCl,  $\text{MgCl}_2$ ,  $\text{BaCl}_2$ , NaCl, KCl,  $\text{MgCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{CuCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ .

Non-favourable effect on titanium have e.g. acids: sulphuric acid (VI), hydrochloric acid, and ortophosphoric acid [13].

Titanium corrosion resistance on effect of hydrochloric acid, phosphoric acid and sulphuric acid depends from concentration as well as temperature of acid and decreases with increase of this parameters.

The only factor, which is limiting the application of titanium and titanium alloys in medium of chlorides, is possibility of crevice corrosion appearance [13-14]. This threat concerns especially  $\alpha$  titanium [13].

One of problems, which must be explained, is determining of corrosion resistance of titanium in water solution of hydrochloric acid, which contains chlorine ions. In this connection research were took in order to determine corrosion resistance of welding joints from titanium Gr1 in water solution of hydrochloric acid (6% and 10%) at temperature 20° and 50°C.

## 2. Material and methodology

The goal of this work was on  $\alpha$  titanium corrosion resistance (SB265Ti Gr1 symbol) in water solution of hydrochloric acid. Chemical composition of titanium GR1 (by using a norm ASTM B265-99 G1) is presented in table 1.

Table 1.

Chemical composition of titanium GR1

Maximum permissible concentration [%]					
H	O	N	Fe	C	Ti
0.015	0.018	0.003	0.02	0.008	rest

The research programme included:

1. Potentiostatic examinations.
2. Galvanostatic examinations.
3. Potentiodynamic examinations.
4. Evaluation of surface condition after corrosion tests.

To eliminate influence of surface state on corrosion resistance of tested samples welded joints were polished by using abrasive paper (up to granularity of 600).

In the corrosion research electrolyser, potentiostat "Solartron 1285" and computer with "CorrWare 2" software were used. Results of the research were worked out with "CorrView" software. The potentials values were determined in relation to normal hydrogen electrode (NEW). The temperature of the solutions was kept on 20°C and 50°C. The recording of potential/density of current - time curve was conducted for 300 s. Samples polarization was conducted in range from potential smaller by 200 mV from normal potential up to 4000 mV. Rate of changing the potential amounted 10 mV/min in each case. Observations of the surface were conducted using scanning electron microscope HITACHI S4200 with magnifications from 30 to 4000.

## 3. Results

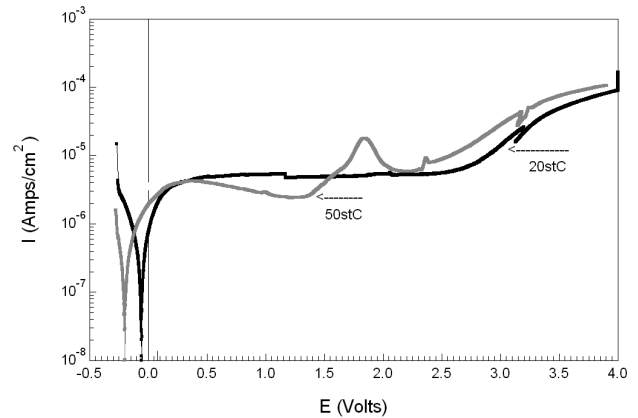


Fig. 1. Matching of potentiodynamic curves for titanium in 6% water solution of HCl

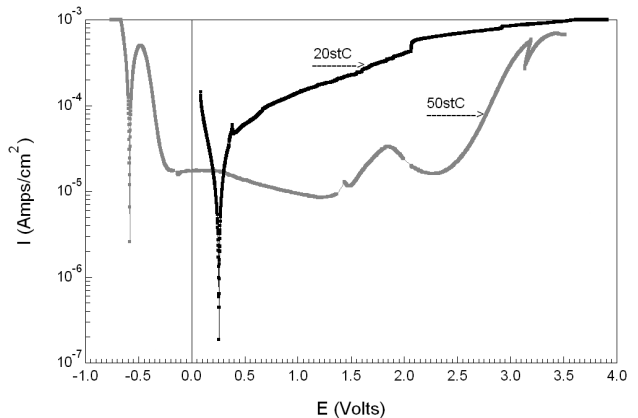


Fig. 2. Matching of potentiodynamic curves for titanium in 10% water solution of HCl



Fig. 3. Evaluation of joint surface condition after corrosion tests in 6% HCl water solution at temperature of 50°C, SEM

Table 2.

Results of potentiodynamic research of titanium T=20°C; 6% and 10% HCl

Temp./concentration solution	$E_{kor}$ [mV]	$i_{kor}$ [ $\mu\text{A}/\text{cm}^2$ ]	$E_p$ [mV]	$i_p$ [ $\mu\text{A}/\text{cm}^2$ ]	$E_{np}$ [mV]
T=20°C/6%	-57.7	0.21	417.51	4.61	2621.7
T=20°C/10%	-23.95	0.31	545.1	22.67	2900.0

Table 3.

Results of potentiodynamic research of titanium T=50°C; 6% and 10% HCl

Temp./concentration solution	$E_{kor}$ [mV]	$i_{kor}$ [ $\mu\text{A}/\text{cm}^2$ ]	prepassive		peak 1		passive			
			$E_1$ [mV]	$E_2$ [mV]	$i_{p1}$ [ $\mu\text{A}/\text{cm}^2$ ]	$E_{kp1}$ [mV]	$i_{kp1}$ [ $\mu\text{A}/\text{cm}^2$ ]	$E_1$ [mV]	$E_2$ [mV]	$i_{p2}$ [ $\mu\text{A}/\text{cm}^2$ ]
T=50°C/6%	-198.4	0.11	345.3	1310.7	2.46	1848.6	17.87	2140.0	2330.0	6.0
T=50°C/10%	-344.35	1.72	168.2	1407.5	2.26	-278.4	3.00	2064.1	2422.8	5.00

where:  $E_{cor}$  - corrosion potential;  $i_{cor}$  - density of corrosion current;  $E_p$  - passivation potential;  $i_p$  - density of passivation current;  $E_{np}$  - perforation potential;  $E_1$ ,  $E_2$  - beginning and the end of prepassive and passive range,  $i_{p1}$  - density of current in prepassive range,  $i_{p2}$  - density of current in passive range,  $E_{kp1}$  - critical potential of passivation for first peak,  $i_{kp1}$  - critical current density of passivation for first peak,  $E_{kp2}$  - critical potential of passivation for second peak,  $i_{kp2}$  - critical current density of passivation for second peak

The potentiodynamic research results of titanium tested in 6% and 10% water solution of hydrochloric acid at temperature of 20°C are presented in table 2, and 50°C in table 3. At figures 1 and 2 presented matching of potentiodynamic curves, at fig. 3 surface state of the samples after corrosion research, which were observed using the scanning electron microscope.

#### 4. Analysis of research results

Titanium are characterized by tendency to self-passivation of surface in 6% HCl water solution. This is favourable property of the material, because possible damages of surface during installation assembly (first of all protective passive layer damages), could not lead to acceleration of corrosion process. In place where passive layer is damaged, new layer will arise spontaneous. In a result of temperature increase from 20°C to 50°C this tendency didn't change, surface of titanium yielded to faster and larger self-passivation. Increase of Cl<sup>-</sup> ions concentration at temperature of 50°C causes that surface yielded to activation, followed by stable state. Damages of surface during exploitation in higher temperatures are dangerous, because can lead to short-lived increase of corrosion rate.

Low values of corrosive current density for tested samples show high corrosive resistance of them. Corrosive current density of tested samples at temperature of 20°C was significantly lower than density of corrosive current of samples at temperature of 50°C, for both research in 6% and 10% water solution of HCl. Increase of temperature has crucial effect on increasing (by two orders of magnitude) of corrosive current density and also of corrosion rate. Higher concentration of Cl<sup>-</sup> ions causes decrease of registered values of corrosive current density, both at temperature of 20°C and 50°C.

On potentiodynamic curve of tested titanium in 6% and 10% HCl water solution at temperature of 20°C prepassive range, peak and passive range were observed, however at temperature of 50°C first peak, prepassive range, second peak and passive range were observed. The width of prepassive range is significantly larger

than for passive range. Also payed attention on lower values of current density in prepassive range in comparison with passive range it can be supposed that layer, which is present on the surface, is more tight and stable in prepassive range, corresponding to lower values of potential. On basis of current density values comparison in prepassive range it can be affirmed, that temperature increase, both in 6% and 10% HCl water solution, causes increase of current density values as well as corrosion rate. This increase is higher for higher concentration of Cl<sup>-</sup> ions. Similarly increase of Cl<sup>-</sup> ions concentration at temperature of 50°C causes increase of registered current density values in prepassive range. But at temperature of 20°C this tendency is reverse, increase of concentration causes decrease of current density values. In passive range both increase of solution concentration and increase of temperature causes registered current values density increase.

Characteristic property of titanium in 6% and 10% HCl water solution at temperature of 20°C is significant increase of current density from value of corrosive current density to value of current density in prepassive range by above one order of magnitude.

In temperature of 20°C not significant increase of current density was registered for samples after research in 10% HCl water solution and decrease for samples after research in 6% HCl water solution. Titanium is characterized by high resistance for pitting corrosion, which is showed by high value of puncture potential. Pitting corrosion resistance was higher for samples after research in 10% HCl water solution. The lowest pitting corrosion resistance was showed by samples after research in 6% HCl water solution at temperature of 20°C. It must be marked, that pitting corrosion resistance was so high, that differences appeared between samples were very low.

Analysis of samples state surface after corrosion research in 6% and 10% HCl water solution at temperature of 20°C wasn't showed appearance of pits on surface. Occurred scratches on surface, arise as a result of polishing, were mild. Thus main mechanism of corrosion was uniform corrosion. After crossing of puncture potential uniform corrosion rate increase significantly, but pits weren't arisen. Considering low values of current density and also low corrosion rate, this property is favourable especially. However on surface of

samples after research in HCl water solutions at temperature of 50°C few pits were observed. Appearance of narrow pits, which probably proceed along grain boundaries, was observed in 6% HCl water solution. However groups of shallow and sparse pits were observed in 10% HCl water solution. In this case corrosion products were also grouped in range of places, where pits appeared. So after crossing of puncture potential dominant corrosion mechanism was local pits corrosion in 10% HCl water solution at temperature of 50°C. However corrosion products were evenly spread after research in 6% HCl water solution at temperature of 50°C. Considering the shape of pits it can be the beginning of pulping. But explanation of this phenomenon requires further research. Considering very high value of puncture potential in both cases, possibility of pits corrosion appearance is very slight.

## 5. Conclusions

1. Tested samples are characterized by susceptibility to self-passivation of surface. Exception were samples after research in 10% HCl water solution at temperature of 50°C. Thus damages of titanium passivation surface, which can arise during exploitation, in higher temperatures can be dangerous, because can lead to short-lived increase of corrosion rate.
2. Increase of temperature has significant influence on increasing of corrosive current density and also of corrosion rate. Higher Cl<sup>-</sup> ions concentration caused decrease of registered values of corrosive current density both at 20°C and 50°C temperature.
3. Increase of Cl<sup>-</sup> ions concentration and increase of temperature causes increase of current density values in prepassive and passive range, thus also increase of corrosion rate. But higher Cl<sup>-</sup> ions concentration at temperature of 20°C caused decrease of registered current density values.
4. Corrosion main mechanism of tested samples was uniform corrosion.
5. In tested potential range samples subjected to effect of 6% and 10% HCl water solution at temperature of 20°C weren't yield to pits corrosion. After crossing the potential corrosion rate is increased significantly, but on the surface pits weren't arise.
6. In tested potential range samples subjected to effect of 6% and 10% HCl water solution at temperature of 50°C weren't yield to pits corrosion. But value of puncture potential is so high, that possibility of pits appearing is very slight.

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