

Titanium oxo-hydroxo complexes as precursors of protective oxide films on the surface of titanium alloys in high-temperature water

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Abstract

Method of electro-spray mass spectrometry has been applied to identify titanium chemical species presented in aqueous solution after exposure of PT-3V titanium alloy sample to high-temperature water under hydrothermal conditions (240°C) for different experiment durations. Nickel, iron(II) and chromium(III) sulfates as well as hydrazine hydrate were used to simulate the composition of nuclear reactor first circuit coolant. Upon exposure to high-temperature water the surface of alloy corrodes and titanium passes into solution in the form of ions Ti^{3+} and Ti^{4+} , which are hydrated and hydrolyzed. $[\text{Ti}(\text{OH})_2(\text{N}_2\text{H}_4)\text{H}_2\text{O}]^+$, $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_6]^{2+}$ and $[\text{Ti}(\text{OH})_2(\text{N}_2\text{H}_5)(\text{H}_2\text{O})_5]^+$ are the principal mononuclear hydroxocomplexes formed. Upon increase of experiment duration hydrolytic polymerization takes place resulting in formation of $[\text{Ti}_2\text{O}_3(\text{OH})(\text{H}_2\text{O})_4]^+$ and $[\text{Ti}_2\text{O}(\text{OH})_3(\text{H}_2\text{O})_7\text{Na}]^{2+}$ as principal dinuclear species and $[\text{Ti}_4\text{O}_2(\text{OH})_7(\text{H}_2\text{O})_6]^+$ tetramer as final step. The evidences of heteronuclear titanium-iron hydroxocomplexes $[\text{FeTiO}(\text{OH})_3\text{Na}]^+$, $[\text{FeTiO}(\text{OH})_3\text{Na}]^{2+}$ presence also have been obtained. The comparison of the results obtained with the data of atomic absorption spectroscopy allows to conclude that polymerization of titanium hydroxocomplexes observed is not associated with an increase in its concentration during the experiment but rather is a consequence of an irreversible hydrolysis process at high temperatures. The results obtained allow us to suggest the next sequence of chemical transformations as a result of corrosion of a titanium alloy: dissolution of titanium with the formation of mononuclear aqua-hydroxocomplexes in solution → polymerization of the resulting hydroxoforms up to the formation of tetramers → precipitation of hydroxides → solid-phase metamorphization into anatase. As for the formation of mixed oxides, the first stage is probably the co-precipitation of hydroxides, and then a solid-phase reaction.

Keywords: titanium alloy, titanium oxo-hydroxocomplexes, protective oxide film, primary circuit, pressurized water reactor.

Introduction

Upon operating of pressurized water reactor a temperature of 240 to 320°C and a pressure of over 150 atm is maintained in the primary circuit. Under these extremely corrosive and aggressive conditions, the integrity and preservation of the functional properties of structural materials is largely determined by the protective oxide films formed on their surface.

The formation of oxide films at the solution-alloy interface under the conditions of the primary circuit of the nuclear power plant has been the subject of a number of studies as this protective oxide film inhibits the further corrosion of material and increases the lifetime of construction material.

However, an analysis of the literature data shows that almost all of them relate mainly to steels, chromium–nickel and zirconium alloys. Thus, it was shown in [1, 2] that the aqueous phase provides both transport of the oxidizer to the surface of the material and also back-transportation of the dissolved oxidized metal into the solution, followed by deposition on the surface of the alloy. A similar approach based on the significant contribution of processes occurring in the primary water coolant to the properties and structures of oxide films on the surface of stainless steels and chromium-nickel alloys can be tracked in more modern works [3, 4]. According to these studies, the transport of the oxidizer to the metal surface is carried out both due to the solid-phase diffusion of O^{2-} ions along the crystal faces, and as a result of the penetration of water molecules through the pores of the oxide film. In turn, the removal of the oxidized metal from the structural material/oxide film interface also occurs both by means of solid-phase diffusion along the crystal faces, and also in the dissolved state through the pores. At the same time, it is shown in [4] that the diffusion coefficient of metal cations in the oxides crystal lattice is 10–15 orders of magnitude lower than the diffusion coefficient in water.

To understand in details the mechanism of transformation processes in structural materials used in the first circuit of nuclear power plants it is necessary to know not only the composition of the oxide film on the surface of materials and the dynamics of its formation, but also the state of the oxidation products of alloys in the aqueous phase - both processes have a significant impact on each other. In the doctoral thesis of A.A. Efimov [5], the structure of polynuclear iron oxo-hydroxocomplexes in the coolant of the first circuit of pressurized water reactor was studied. Their role as precursors of protective oxide films and corrosion inhibitors of carbon steel was revealed. It was shown that the polynuclear iron oxo-hydroxocomplexes are sorbed on the active centers of the steel surface, turn into magnetite under hydrothermal conditions and form a dense protective oxide film tightly coupled with steel.

It was shown in papers [6–8] that under the conditions of the first circuit of a pressurized water reactor, at least the outer oxide layer on titanium alloys is also formed due to the deposition process from the coolant. The authors suggested that titanium and iron

present in the coolant in the form of hydrolyzed particles and are deposited on the surface of structural materials in the form of hydroxides, after which an anatase film and individual ilmenite crystals form on the surface of the alloy. At the same time, the existing data on the processes of hydrolysis and complexation of metal ions [9, 10] allow us to suggest the existence of more complex titanium-containing particles in the aqueous phase under hydrothermal conditions.

The purpose of this work was to analyze the composition and dynamics of transformations of precursors of protective oxide film on titanium alloys – oxo-hydroxo complexes of titanium – in high-temperature water under pressure that is essential for further development of new methods of corrosion prevention.

Materials and Methods

The experiments were carried out in steel autoclaves with polyphenylene (PPL) liners. The liners were kept in dilute nitric acid and washed with working solutions prior to experiment. Working solutions were prepared from distilled water. The pH index of the medium was adjusted to ~9 by adding N_2H_4 . A glass electrode was used to control the pH value (ESL 43-07, ZIP, Gomel, Belarus). Hydrazine was added not only to create the pH of the medium, but also to maintain the reducing medium in accordance with existing technological requirements [11]. Under the conditions of the hydrothermal experiment, hydrazine converted into ammonia. The volume of the added hydrazine was 0.3 mL per 10 mL of solution.

To simulate the presence of corrosion products of steel and alloys, salts were added to the working solutions: $NiSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, $CoSO_4 \cdot 7H_2O$. All reagents were supplied by “Neva-reactive” enterprise and were of “chemically pure” grade. Solutions of individual salts containing 1.0 g/L of metal ions and a mixed solution containing 0.33 g/L of each of the ions were used.

Samples of PT-3V titanium alloy used in nuclear industry were placed on the bottom of the inserts. The samples were $1 \times 1 \times 0.2$ cm rectangles, pre-polished to the stripping class 11–12 according to GOST 2789-73.

Next, 10 mL of the working solution was added to the liner and the autoclaves were placed in the drying cabinet. The temperature of the experiment was kept at 240°C, the exposure time varied from 3 to 15 days in increments of at least 1 day. After the expiration of the holding time, the autoclaves were removed and cooled naturally. After cooling, a sample of the aqueous phase was taken from the autoclaves for further studies.

The method of high-resolution mass spectrometry with electrospray ionization was used to identify the principal chemical forms of titanium. The measurements were carried out on the Shimadzu Nexera X2 LCMS-9030 device. This method makes it possible to determine the mass of ions presented in the solution and formed as a result of ionization and is widely used to study the content of various forms of complexes formed as a result of corrosion processes of alloys and pure metals, the effect on the composition of additives or the acidity of the medium [12–16].

The signal registration conditions taken from [17] are listed below in Table 1.

Table 1. Operating conditions of ESI-MS.

Sample volume	5 μL
Mobile phase	Purified water
Q-array RF lens	150 V
Interface voltage	+4.5 kV; –3.5 kV
Heatblock temperature	+250°C
Nebulize gas flow-rate	1.0 L·min ⁻¹
CDL voltage	20 V

Results and Discussion

Taking into account the complexity of the studied systems and the large number of identifiable peaks in the mass spectra, we have chosen the following research strategy. First, the mass spectra of the aqueous phase for the titanium alloy – water–hydrazine system were analyzed at different holding times under hydrothermal conditions, which allowed us to trace the evolution of oxo-hydroxoforms over time. Further, the mass spectra of aqueous solutions containing ions formed upon the corrosion of reactor steels in the form of sulfates were recorded and analyzed after exposure to hydrothermal conditions for 2 weeks, but without contact with titanium alloy. After the oxo-hydroxoforms formed under these conditions were identified, the final stage was the analysis of the composition of aqueous solutions after two weeks of hydrothermal treatment in contact with titanium alloy samples.

Mass spectrometric identification of titanium alloy corrosion products in solutions

Since the formation of a protective film on titanium alloys proceeds over time, it was considered appropriate to consider the dynamics of changes in the forms of existence of titanium in the aqueous phase over time. For this purpose, PT-3V alloy samples were kept under hydrothermal conditions in contact with water with the addition of hydrazine for 3, 5, 7, 10 and 15 days.

Figures 1–3 show the mass spectra of the aqueous phase after holding samples of PT-3V titanium alloy in them under hydrothermal conditions for 3, 10 and 15 days.

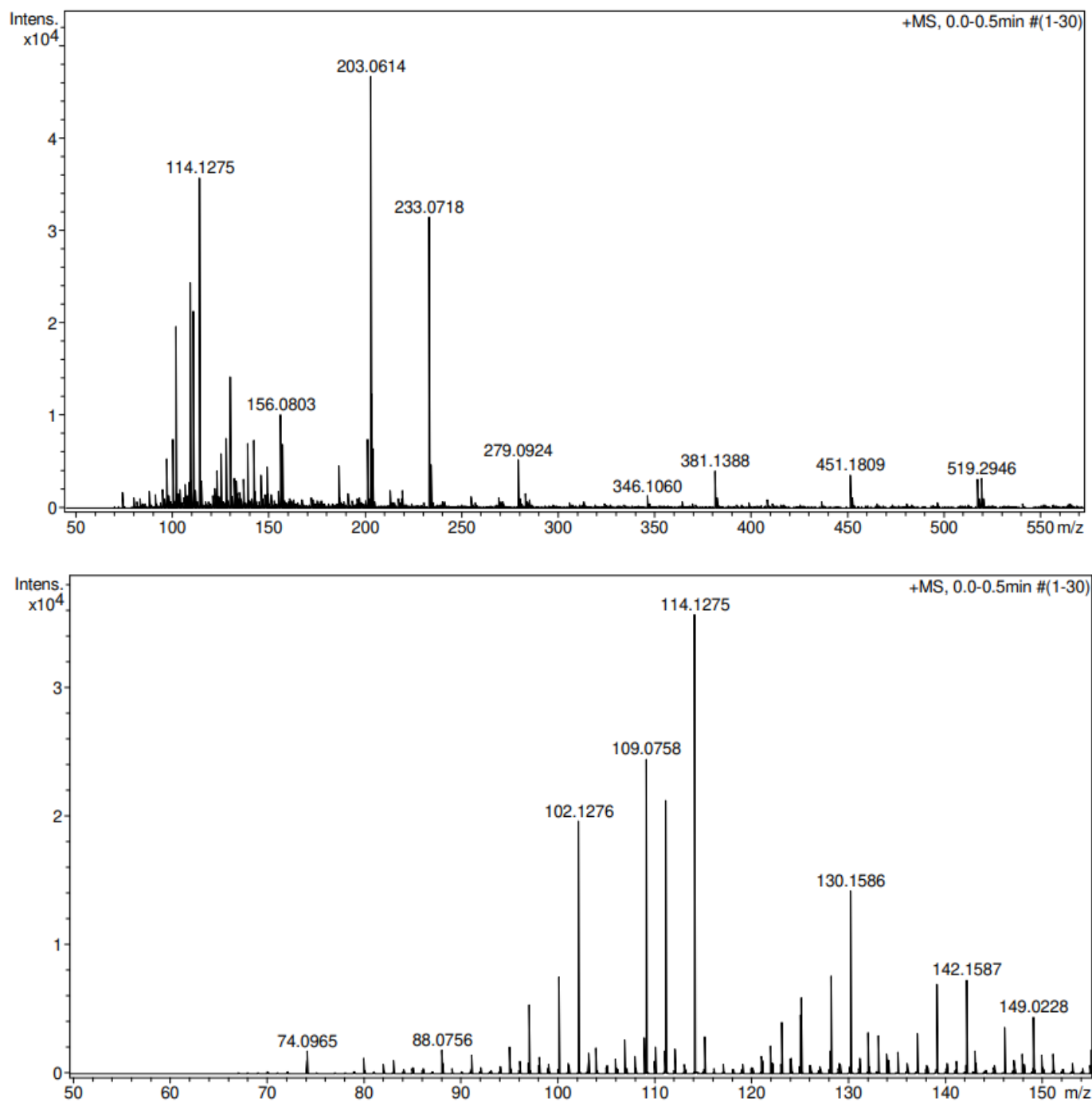


Figure 1. Mass spectrum of the aqueous phase of the PT-3V titanium alloy – water–hydrazine system after hydrothermal treatment for 3 days.

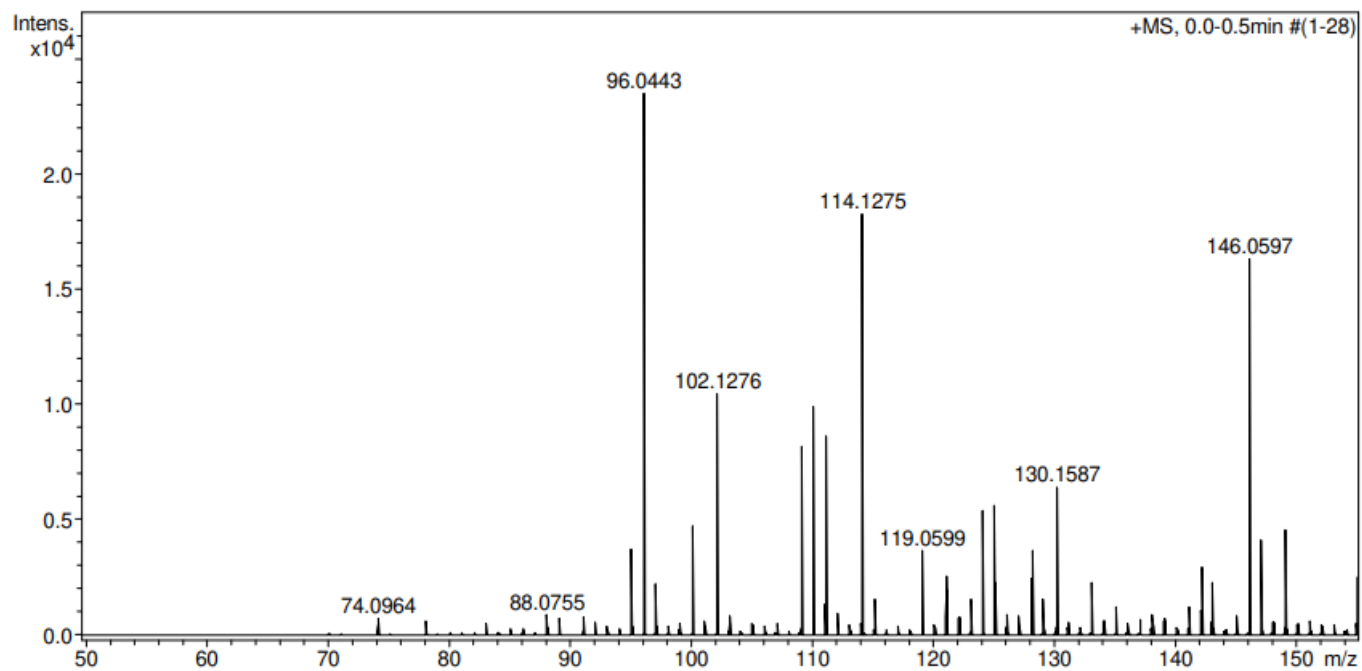
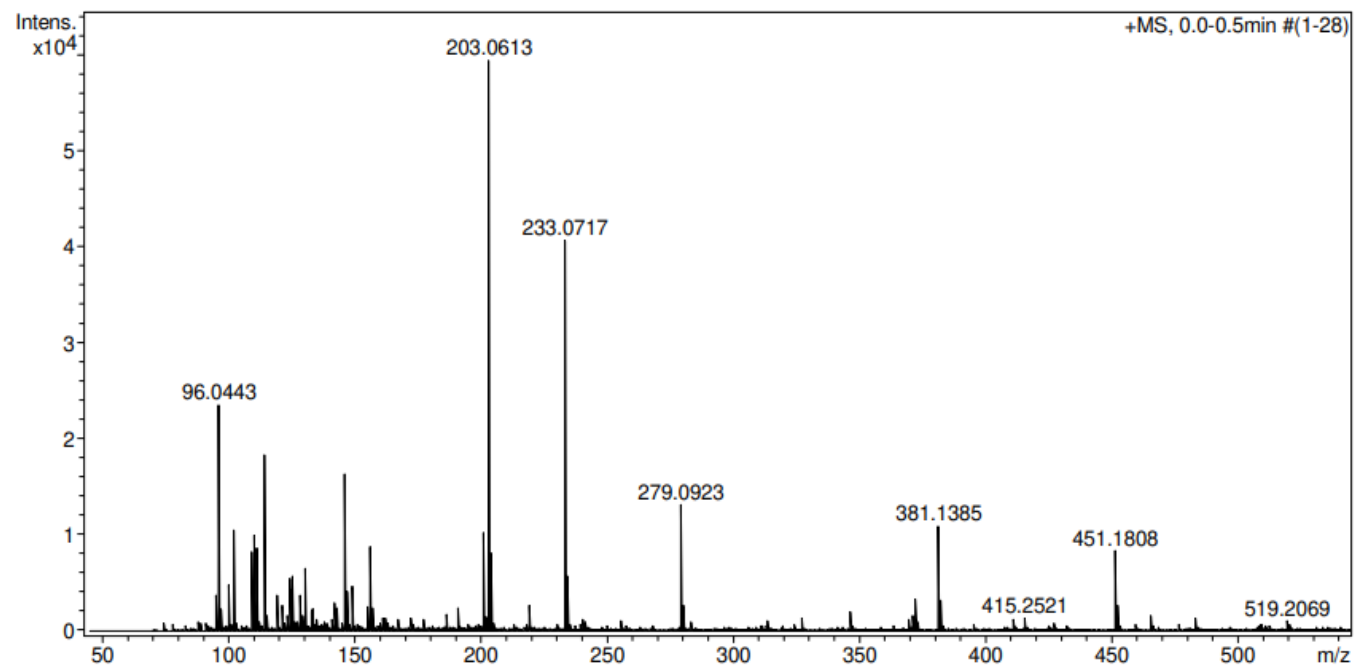


Figure 2. Mass spectrum of the aqueous phase of the PT-3V titanium alloy – water–hydrazine system after hydrothermal treatment for 10 days.

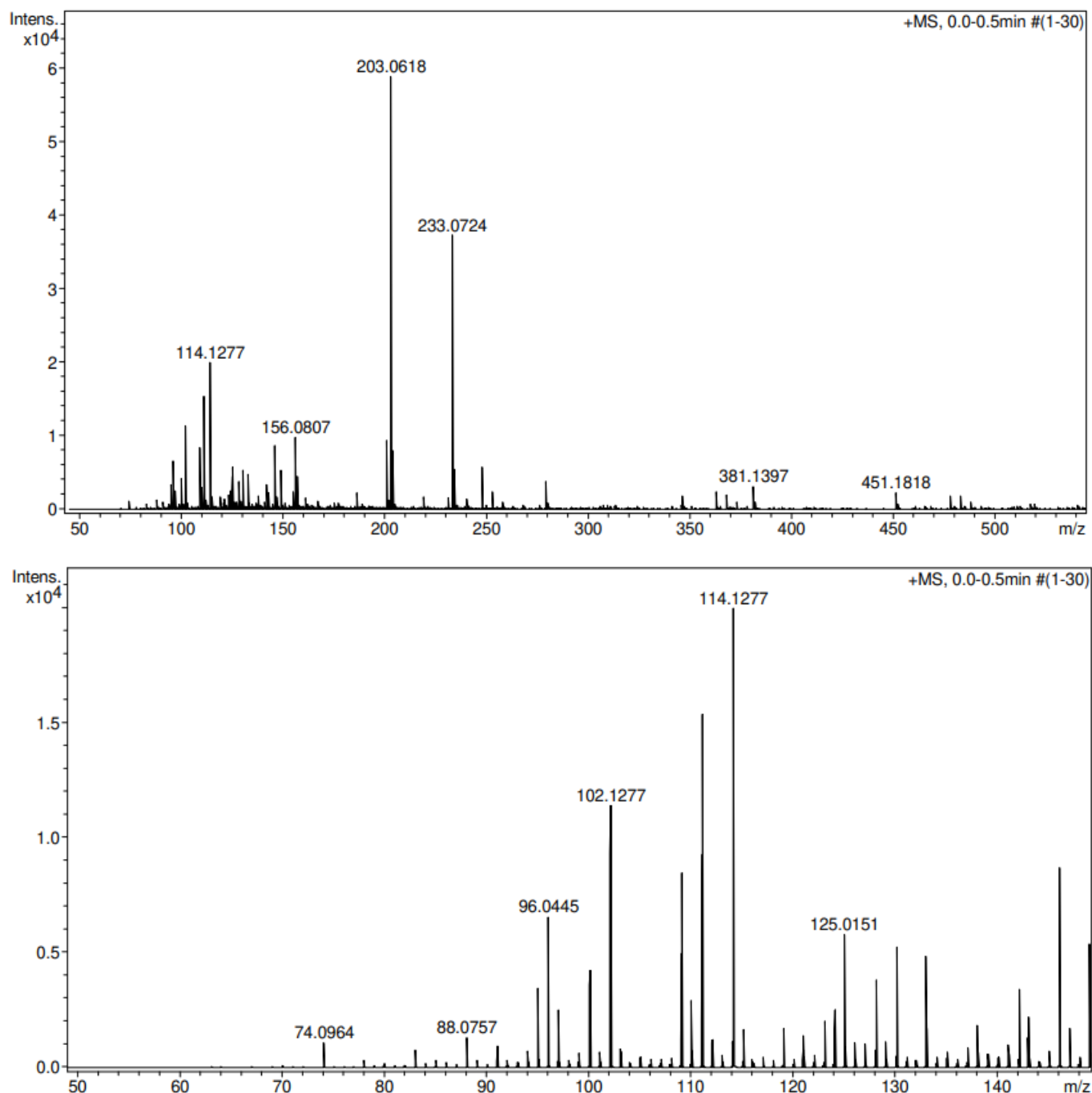


Figure 3. Mass spectrum of the aqueous phase of the PT-3V titanium alloy – water–hydrazine system after hydrothermal treatment for 15 days.

All the obtained mass spectra can be divided into 3 regions according to the mass numbers: up to m/z 150, from 150 to 300, after 300. In the first region, peaks are observed, the mass numbers of which correspond to aluminum oxo-cations (this metal is part of the alloy – its content is 3.5–5% [18]) and titanium hydroxocomplexes with different amounts of water molecules: $[\text{AlO}(\text{H}_2\text{O})_4]^+\text{N}_2\text{H}_5^+$ ($m/z=74$), $[\text{AlO}(\text{H}_2\text{O})_6]^+\text{Na}^+$ ($m/z=88$), $[\text{Al}(\text{OH})_2(\text{H}_2\text{O})_8]^+\text{Na}^+$ ($m/z=114$), $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_6]^{2+}$ ($m/z=95$), $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})]^+$

($m/z = 100$); $[\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_{5,6}]^+\text{N}_2\text{H}_5^+$ ($m/z = 102, 111$); dimers $[\text{Ti}_2\text{O}_2\text{OH}(\text{H}_2\text{O})_{3,4}]^+$ ($m/z = 100, 109$), $[\text{Ti}_2\text{O}_2\text{OH}(\text{H}_2\text{O})_{1,2,3}]^+\text{Na}^+$ ($m/z = 93, 102, 111$), $[\text{Ti}_2\text{O}(\text{OH})_3(\text{H}_2\text{O})_3]^+\text{N}_2\text{H}_5^+$ ($m/z = 125$). Also, after 3 days of exposure, peak with $m/z = 146$ was observed in the spectrum, which relative intensity increases with increasing exposure time. It can be tentatively assigned to a dimeric hydroxocomplex of titanium in different oxidation states (+3, +4): $[\text{Ti}(\text{III})\text{Ti}(\text{IV})\text{O}(\text{OH})_4(\text{H}_2\text{O})_5\text{Na}]^{2+}$.

In addition to the above mentioned, the spectrum exhibit peaks with $m/z = 97, 102, 115, 124$ and 142 , which can be attributed to heteronuclear hydroxocomplexes $[\text{FeTiO}(\text{OH})_3\text{Na}]^{2+}$ ($m/z = 97$); $[\text{FeTiO}(\text{OH})_3(\text{N}_2\text{H}_4)]^{2+}$ ($m/z = 102$); $[\text{FeTiO}(\text{OH})_3(\text{H}_2\text{O})_n\text{Na}]^{2+}$ ($n = 2, 3, 5$; $m/z = 115, 124, 142$). Probably, the simultaneous influx of iron and titanium from the alloy surface into solution contributes to the formation of such heteronuclear particles.

In the middle region of the mass spectra there are intense signals with mass numbers $m/z = 156, 203, 233$ and 279 , which can be attributed as follows: $[\text{Ti}_2\text{O}(\text{OH})_3(\text{H}_2\text{O})_7]^+\text{Na}^+$ ($m/z = 156$), $[\text{FeTiO}(\text{OH})_3(\text{N}_2\text{H}_4)]^+$ ($m/z = 203$), $[\text{Ti}_2\text{O}_2(\text{OH})_3(\text{H}_2\text{O})_2]^+$, $[\text{Ti}_2\text{O}(\text{OH})_5(\text{H}_2\text{O})_2]^+$, $[\text{Ti}_2\text{O}_3(\text{OH})(\text{H}_2\text{O})_4]^+$ ($m/z = 233$), $[\text{FeTiO}(\text{OH})_3(\text{H}_2\text{O})_6]^+$ ($m/z = 279$).

In the region of large mass numbers, there are peaks with $m/z = 381, 451, 519$, which are absent in the samples with a holding time of more than 10 days. They correspond to various polynuclear hydroxocomplexes (for example, $m/z = 451$ corresponds to a tetramer of the composition $[\text{Ti}_4\text{O}_2(\text{OH})_7(\text{H}_2\text{O})_6]^+$), which are products of hydrolytic polymerization of titanium ions.

Analysis of changes in the relative intensity of the peaks of individual complexes over time allowed us to draw conclusions about the processes occurring in the system in this time interval. So, after 3 days of contact with the titanium alloy, oxo- and hydroxo forms of titanium appear in the aqueous phase in the form of monomers and dimers; also, aluminum in oxo-form passes into the solution; partial oxidation of titanium (+3) to titanium (+4) occurs.

With an increase in the hydrothermal treatment time to 5–7 days, the relative intensity of peaks corresponding to dimeric particles increases and new dimeric forms $[\text{NaTi}_2\text{O}(\text{OH})_5]^{2+}$, $[\text{NaTi}_2\text{O}_2(\text{OH})_3(\text{H}_2\text{O})]^{2+}$ ($m/z = 110$) appear. The relative intensity of peaks of monomeric forms, on the contrary, decreases, that indicates dimerization of hydroxocomplexes as dominating process upon this period of experiment. It should be noted that the peaks in the region of mass numbers 90–142, attributed to mixed binuclear titanium-iron hydroxoforms, have much lower relative intensity, and some are not identified at all in these spectra. This fact may indicate a decrease in their content due to polymerization and subsequent deposition on the surface of the alloy.

In addition, after seven days of holding titanium plates in hydrothermal conditions, a peak with a mass number of 248 appears. This value of the mass number corresponds to the dimer of titanium (III, IV) of the composition $[\text{Ti}(\text{OH})_2\text{Ti}(\text{OH})_4(\text{H}_2\text{O})\text{N}_2\text{H}_4]^+$ ($m/z = 248$). It can be assumed that the precursors of titanium (III, IV) hydroxides namely complex ions $[\text{Ti}(\text{OH})_2(\text{N}_2\text{H}_4)(\text{H}_2\text{O})_n]^+$ ($n = 0, 1$; 114, 132) and $\text{Ti}(\text{OH})_4$ ($m/z = 116$) are gradually formed in the solution and their further association occurs with subsequent deposition of titanium hydroxide on the surface of the plates.

Increasing the experiment duration time to 10 days leads to a noticeable change in mass spectra of the samples in the region of large mass numbers. The observed new peaks can be attributed both to the emerging polynuclear iron oxo-hydroxo complexes and to mixed titanium-iron complexes, since the m/z signals 248, 363, 478, 593, 708, 823, 938 all have a difference in mass of 115 units, which corresponds to the particles $[\text{Ti}(\text{OH})_2(\text{N}_2\text{H}_4)]^+$ ($m/z = 114$), $[\text{Ti}(\text{OH})_4]$ ($m/z = 116$), $[\text{FeTiO}(\text{OH})_3(\text{H}_2\text{O})_2\text{Na}]^{2+}$ ($m/z = 115$).

It can be assumed that one of the designated particles attaches to the existing ions in the solution, contributing to their growth. Interestingly, after 15 days, the signals at $m/z = 363$, 478, 593, 708, 823, 938 disappear. This may indicate a noticeable decrease in the content of heavy hydroxo-forms in the solution. Indeed, the presence of such large polymer complexes in the aqueous phase leads to their deposition on the surface of titanium plates and the growth of a protective film. The decrease in their content agrees fairly well with our previous results obtained during study of protective oxide films [19].

The results of study of titanium chemical species are summarized in Table 2 below.

Table 2. Cationic forms of titanium as function of experiment duration according to the ESI-MS method.

Duration of experiment, days	Titanium chemical species	m/z theor	m/z exp
≥ 3	$[\text{Ti}_2\text{O}_2\text{OH}(\text{Na})(\text{H}_2\text{O})_n]^{2+}$, $n = 1, 2, 3$	93, 102, 111	93, 102, 111
≥ 3	$\text{H}^+ - [\text{Ti}(\text{OH})_2(\text{H}_2\text{O})_6]^+$	96	96
≥ 3	$[\text{Ti}(\text{OH})_2\text{H}_2\text{O}]^+$	100	100
3–10	$\text{H}^+ - [\text{Ti}(\text{OH})_2(\text{N}_2\text{H}_5)(\text{H}_2\text{O})_5]^+$, $[\text{Ti}(\text{OH})_2(\text{N}_2\text{H}_5)(\text{H}_2\text{O})_6]^+$	102, 111	102.12, 111.12
3–10	$[\text{Ti}(\text{OH})_2(\text{N}_2\text{H}_4)\text{H}_2\text{O}]^+$	114	114.12
3–10	$[\text{Ti}_2\text{O}(\text{OH})_3(\text{N}_2\text{H}_5)(\text{H}_2\text{O})_3]^{2+}$	125	125.01
≥ 5	$[\text{NaTi}_2\text{O}(\text{OH})_5]^{2+}$, $[\text{NaTi}_2\text{O}_2(\text{OH})_3(\text{H}_2\text{O})]^{2+}$	110	110.02
≥ 3	$[\text{Ti}(\text{III})\text{Ti}(\text{IV})\text{O}(\text{OH})_4(\text{H}_2\text{O})_5\text{Na}]^{2+}$	146	146.06
3–10	$[\text{FeTiO}(\text{OH})_3\text{Na}]^{2+}$	97	97
≥ 3	$[\text{FeTiO}(\text{OH})_3(\text{N}_2\text{H}_4)]^{2+}$	102	102.12
≥ 3	$[\text{FeTiO}(\text{OH})_3\text{Na}(\text{H}_2\text{O})_n]^{2+}$, $n = 2, 3, 5$	115, 124, 142	115, 124, 142.15
≥ 3	$[\text{Ti}_2\text{O}(\text{OH})_3(\text{H}_2\text{O})_7\text{Na}]^{2+}$	156	156.08
≥ 3	$[\text{FeTiO}(\text{OH})_3(\text{N}_2\text{H}_4)]^+$	203	203.06
≥ 3	$[\text{Ti}_2\text{O}_3(\text{OH})(\text{H}_2\text{O})_4]^+$	233	233.07
≥ 3	$[\text{FeTiO}(\text{OH})_3(\text{H}_2\text{O})_6]^+$	279	279.09
≥ 7	$[\text{Ti}(\text{OH})_2\text{Ti}(\text{OH})_4(\text{H}_2\text{O})\text{N}_2\text{H}_4]^+$	248	248.02
3–7	$[\text{Ti}_4\text{O}_2(\text{OH})_7(\text{H}_2\text{O})_6]^+$	451	451.18

The analysis of data allow us to conclude that hydrated oxo- and hydroxo-forms of titanium (IV) dominate in the aqueous phase, which corresponds to the literature data on the composition and structure of complexes of multicharged metal ions in aqueous solutions [10]. Single-charge aqua-cations are mainly observed, also due to the presence of H_3O^+ , Na^+ and N_2H_5^+ ions in solutions, there are also two-charge cations. The identified forms correlate with the results of the study of the forms of titanium salts (+4) in aqueous media by the ESI-MS method available in the literature [18].

After 3 days of experiment, the principal chemical species of titanium are hydrolysis products – oxo- and hydroxo-forms of titanium (+3, +4) in the form of monomers and dimers shown in Table 2. A number of peaks can be attributed to mixed titanium (+3, +4) – iron (+3) cationic complexes.

Upon an increase in the holding time, an increase in the intensity of peaks corresponding to dimeric forms is observed that reflects appearance of polymers. However, after 15 days of exposure, the presence of polymers with mass numbers greater than 450 is practically not detected (Figure 7). This may indicate the deposition of these forms from the solution onto the surface of titanium plates and the formation of a protective film as the result of practically irreversible hydrolysis at high temperatures.

Analysis of mass spectra of comparison solutions – model solutions containing corrosion products of reactor steels

At Figures 4 and 5 ESI-MS spectra of aqueous solutions containing metal ions representing corrosion products of reactor steels are presented.

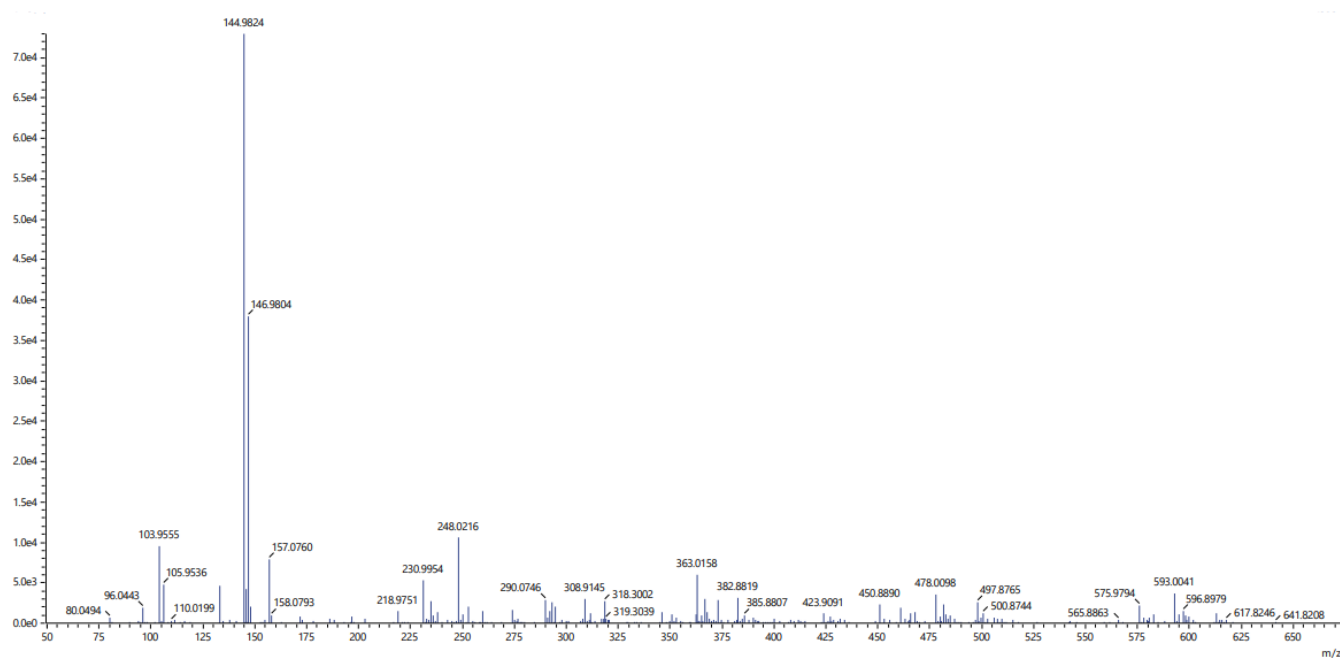


Figure 4. Mass spectrum of iron sulfate solution (2) with the addition of hydrazine.

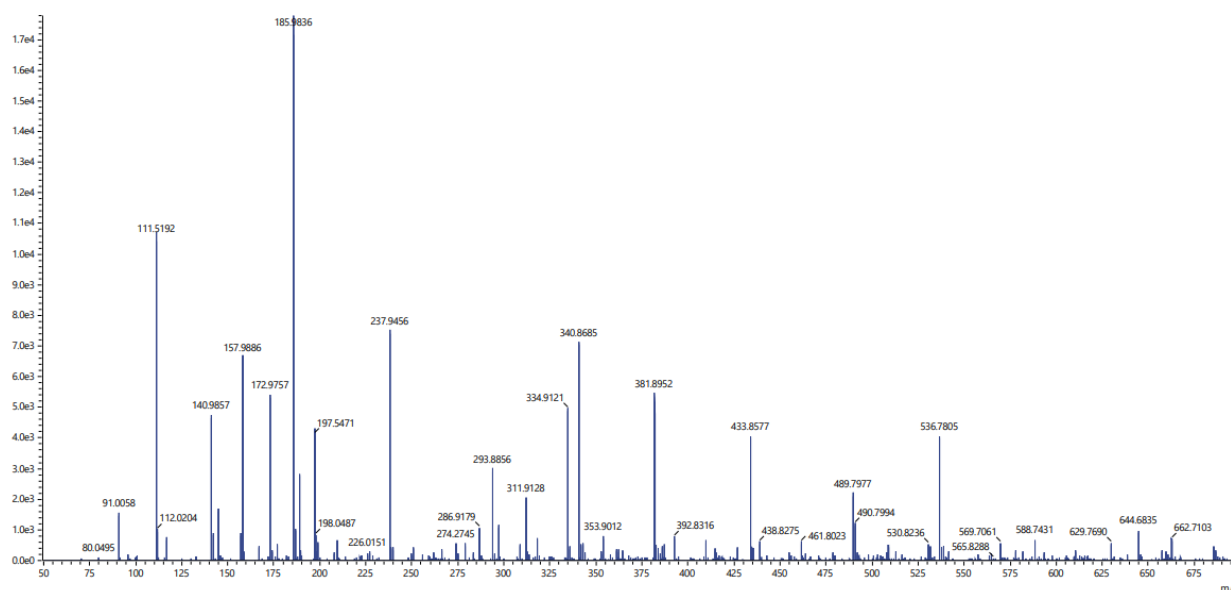


Figure 5. Mass spectrum of mixed (iron, cobalt, nickel) sulfate solution with the addition of hydrazine.

Analysis of the spectra of solutions of individual salts after exposure to hydrothermal conditions for 15 days showed that the principal cationic forms in these solutions are: for iron – ions $[\text{FeOH}(\text{H}_2\text{O})_n]^+$, $[\text{Fe}_2\text{O}(\text{OH})(\text{H}_2\text{O})_n]^+$, $[\text{Fe}_2(\text{OH})_5(\text{H}_2\text{O})(\text{N}_2\text{H}_4)]^+$ (m/z : 145, 231, 247, 318, 363); for nickel – ions $[\text{NiOH}(\text{H}_2\text{O})_n]^+$, $[\text{H}\text{Ni}_2\text{O}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$, $[\text{NaNi}_2\text{O}(\text{OH})(\text{H}_2\text{O})_n]^{2+}$ (m/z : 111, 122, 140), and for cobalt – $[\text{CoOH}(\text{H}_2\text{O})_n]^+$, $[\text{NaCo}_2(\text{OH})_3(\text{H}_2\text{O})_n]^{2+}$ (m/z : 112, 141).

The mass spectrum of a mixture of salts of these metals (Figure 5) demonstrates the diversity of particles and their isotopologues in the aqueous phase containing the main corrosion products of steels. At the same time, almost all peaks correspond to those identified in the analysis of individual salt solutions, which indicates the absence of heteronuclear hydroxocomplexes and other new hydroxoforms.

Analysis of mass spectra of solutions after exposure to hydrothermal conditions with samples of titanium alloy

Identification of peaks corresponding to the hydrated/hydrolyzed forms of metal ions presented in the coolant as a result of corrosion of steels allowed us to proceed to the solution of the following problem – determination of the forms of existence of titanium in these solutions. At figure 6 ESI-MS spectrum of solution of iron(II) sulfate after 15 days of exposure under hydrothermal conditions in contact with PT-3V titanium alloy is presented as the example.

The mass spectra of samples aged for 15 days in solutions of the above-mentioned metal salts in contact with the alloy sample were to a large extent a superposition of the mass spectra of salt solutions and the aqueous phase of the titanium alloy–water–hydrazine system, moreover, significant differences in the relative intensity of peaks of oxo-

hydroxoforms of titanium, allowing to judge the effect of corrosion products on the ratio of forms in solution were not observed. The only exception are peaks corresponding to the possible formation of heteronuclear hydroxocomplexes – they were observed only in the presence of iron salts, moreover, they are characterized by a higher relative intensity than in the alloy–water–hydrazine system. As a result, it can be concluded that the joint oxides of titanium and iron found in the outer layer of the oxide film of titanium alloys [7, 8] are formed in an aqueous medium.

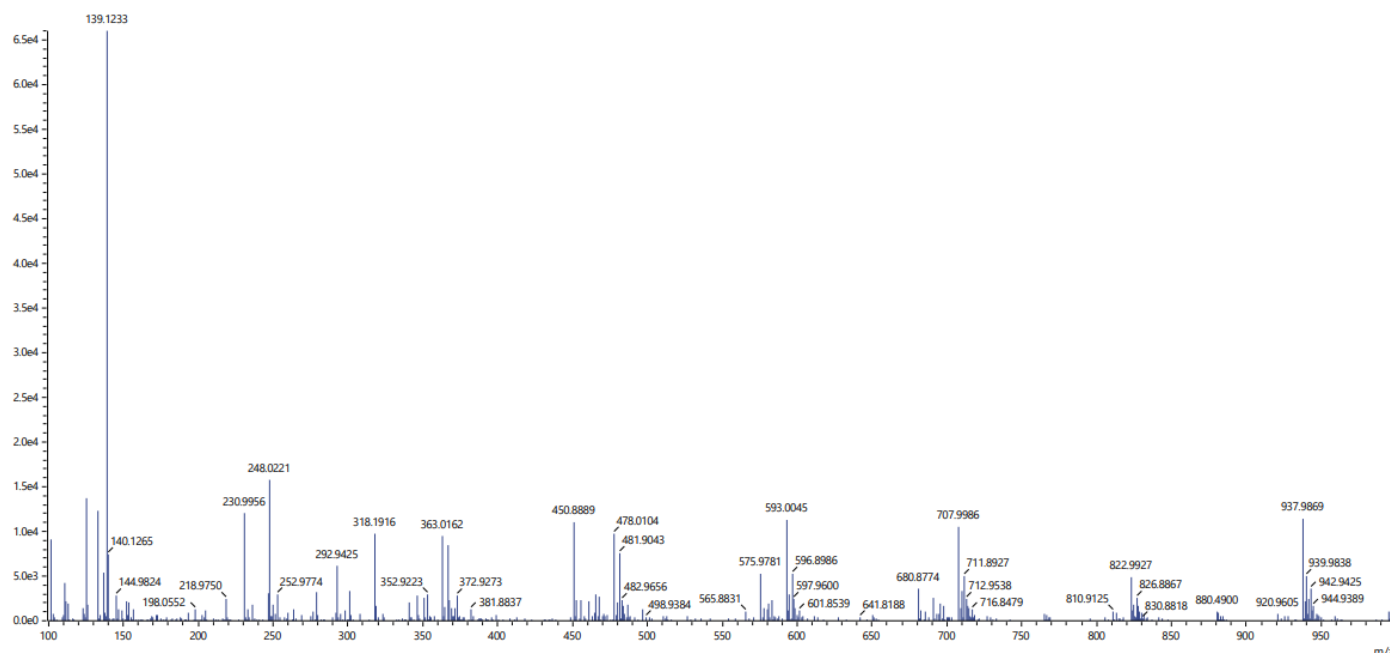


Figure 6. Mass spectrum of the aqueous phase after holding the PT-3V alloy with the addition of iron (II) sulfate and hydrazine.

Conclusions

Based on the research undertaken, the following conclusions can be drawn:

1. Under hydrothermal conditions, the surface of titanium alloys corrodes. As a result, titanium passes into the solution in the form of ions Ti^{3+} and Ti^{4+} , which are hydrated and hydrolyzed.
2. Upon increasing heating duration titanium hydroxocomplexes polymerization takes place. As a result, dimers and trimers become the predominant chemical species.
3. Polymerization of titanium hydroxocomplexes is not associated with an increase in its concentration during the experiment but rather is a consequence of an irreversible hydrolysis process at high temperatures.
4. During the experiments, evidence of the formation of heteronuclear hydroxocomplexes of titanium and iron was obtained.

The results obtained allow us to suggest the next sequence of chemical transformations as a result of corrosion of a titanium alloy: dissolution of titanium with the formation of

mononuclear aqua-hydroxocomplexes in solution → polymerization of the resulting hydroxofoms up to the formation of tetramers → precipitation of hydroxides → solid-phase metamorphization into anatase. As for the formation of mixed oxides, the first stage is probably the co-precipitation of hydroxides, and then a solid-phase reaction.

The further research will be the study of the processes of transition of titanium hydroxocomplexes to the alloy surface and their effect on the inhibition of corrosion of the material surface.

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