Composition and morphology of oxide films formed on PT-7M titanium alloy in high temperature water

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Abstract

The structure of the oxide film on PT-7M titanium alloy used in the construction of the first circuit of Russian small nuclear power plants (SNPP) is considered. The experiment was carried out in stainless-steel autoclaves with PPL liners at a temperature of 240°C. Deoxygenated water and solutions containing salts of metals that are components of stainless steel were used as the aqueous phases. Samples of titanium alloy after heating in autoclaves were examined by high-resolution X-ray diffraction and X-ray fluorescence analysis and by scanning electron microscopy. According to the results of the study, the oxide film consists of a crystalline modification of titanium dioxide – anatase – and includes two layers: a dense one consisting of neat titanium dioxide and a loose one, which may include corrosion products of steel. A film with a thickness of about 100–120 nm is formed after 24 hours of the experiment and reduces the rate of titanium influx into the aqueous phase. After 336 hours (14 days) of heating, the thickness of the solid film is about 200 nm, while the sizes of the crystallites that make up the loose layer are 0.5–4 μm.

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Introduction

Currently, the Russian Federation is actively developing projects of small nuclear power plants (SNPP) for the Far North and Far East regions [1, 2]. The high autonomy and difficult operating conditions require the use of high-strength modern materials in the construction of these stations. In this regard, it is worth using titanium alloys in the design of the SNPP.

Titanium alloy PT-7M is also successfully used as a structural material of the first circuit of transport nuclear power plants, including that on the "Akademik Lomonosov" floating power unit [3, 4]. Despite the fairly long experience of the application of this alloy, there are practically no data on the composition and structure of protective oxide films formed on its surface under the conditions of the first circuit of the nuclear power plant. At the same time, it is the availability of data on the structure and properties of oxide films that would largely allow both to manage the service life of equipment made of titanium alloys and to develop effective and environmentally friendly technologies for decontamination of surfaces.

Bignon *et al.* [5] presented the results of model experiments aimed at studying the composition of the oxide films on titanium materials. Neat titanium of T40 grade, alloys TA6V (6% aluminum, 4% vanadium, balance titanium) and Ti10-2-3 (10% vanadium, 2% iron, 3% aluminum, balance titanium) under conditions of the primary circuit of PWR type reactors (temperature – 300°C, lithium-boron water-chemical regime, pH value 7.5 (25°C), hydrogen concentration – 25.0 nml/kg (0.001 mol/kg), pressure – 150 atm.) were studied. After heating for about 400 hours, a dense film of titanium dioxide with a thickness of about 30 μm formed on the surface of all samples. The structure of the oxide film is different for different materials. The dense oxide film consists of rutile on neat titanium, or anatase on the surface of TA6V and Ti10-2-3 alloys. It was shown by Zhang [6] that the modification of titanium dioxide formed on a titanium alloy depends on its chemical composition.

Small anatase crystallites and large ilmenite crystals were found on the surface of a solid oxide film on titanium and its alloys. Bignon [7] explained the presence of iron on the surface of titanium alloys by the deposition of iron hydroxide (together with titanium hydroxide) from the aqueous phase. The depth of iron penetration into the film on the surface of titanium alloys is 0.5–1 μm. Vanadium and aluminum oxides were not detected in the composition of the oxide film of TA6V and Ti10-2-3 alloys [6]. This fact was explained by the higher diffusion rate of the ions of these metals compared to titanium ions, which leads to their penetration through the oxide film and influx into the coolant.

Selva *et al.* [8] analyzed the structure of an oxide film on pure titanium of TA1 ELI brand after exposure to pure water at a temperature of 300°C and a pressure of 86 atm. for 3000 h in steel autoclaves. It was shown that the oxide film mainly consisted of brookite. Crystallites with the composition Ti_8O_{15} were found on top of the film. Also, crystallites containing iron and nickel were found on the surface without specifying the state of the oxygen detected, *i.e.*, O in solution in the intermetallic FeNi phased or in the oxide phase.

Kasahara [9] considered the structure of an oxide film under the conditions of the first circuit of a promising nuclear power plant with supercritical coolant parameters (temperature 550°C, pressure 250 atm). The thickness of the solid titanium dioxide film after exposure under these conditions for 500 hours was 5–20 μm. After exposure for 1670 h under similar conditions, the film thickness was 3 μm [10].

Earlier [11] we studied the composition and structure of the oxide film on the surface of the process pipeline of the first circuit of the transport nuclear power plant made of PT-3V alloy. It was shown that the surface of the alloy in contact with the coolant is covered with a solid light yellow oxide film. Separate crystallites were also detected on the oxide film, which, like the solid oxide film, mainly consists of titanium compounds. In addition, carbon and corrosion products of steel – chromium, nickel, and iron were found in the composition of most of the particles. The size of the crystallites ranged from 0.8 to 3 μm. The appearance of these crystallites can be explained by the formation of joint titanium oxides with other metals as described in [12–14] or by the sorption of metal ions on titanium dioxide from the solution. A similar process is described in [15–17].

The purpose of this work was to perform autoclave simulation of the composition and structure of oxide films on PT-7M alloy with various compositions of the aqueous phase in contact with the sample that models a coolant with an ammonia water-chemical regime. This goal is relevant not only from the point of view of theoretical chemistry of phase boundaries, but is also of practical importance for the development of methods and measures to improve the corrosion resistance of titanium alloys, as well as technologies for decontamination of the first circuit of the SNPP.

Materials and Methods

The study was carried out on the PT-7M titanium alloy. The chemical composition of the alloy according to X-ray fluorescence analysis and its comparison with the standard are presented in Table 1.

Table 1. Elemental composition of PT-7M alloy.

Element	Mass fraction, %	
	This sample	Standard
Ti	93.6±0.4	balance
Al	3.2±0.2	1.8–2.5
Zr	2.76±0.03	<2–3
Si	0.30±0.05	<0.12
Fe	0.12±0.02	<0.25
Cu	0.058±0.012	<0.3

Some increase in the Al and Si content in the sample is not essential and should not lead to any distortion of the experimental results obtained.

The samples of the PT-7M alloy had the shape of tubes with dimensions (length/diameter) 1.5×0.5 cm. The surface of the samples was polished before the study. The first step is leveling the surface of the alloy on silicon carbide paper with P50 grain size, the processing time being 10 minutes. Then the processing was carried out sequentially with P40, P20, and P10 circles for 5–10 minutes. The second step is polishing with abrasive Cr_2O_3 suspensions with particle sizes of 10 μm, 3 μm, and 1 μm for 5 minutes at each stage, until a mirror shine is achieved. As a result, surface class 11–12 according to GOST 2789-73 was achieved. Surface polishing was necessary to obtain diffraction patterns of thin oxide films with high resolution.

The samples were placed on the bottom of polyphenylene (PPL) liners. The liners were kept in dilute nitric acid and washed with working solutions prior to the experiment. Working solutions were prepared from distilled water. The pH of the medium was adjusted to a value of ~ 9 by addition of 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 potential in accordance with existing technological requirements [18]. During heating, hydrazine passed into ammonia. The volume of the added hydrazine was 0.3 ml per 10 ml of solution.

In experiments simulating the presence of steel corrosion products, the following salts were added to the working solutions: $NiSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 7H_2O$, and $Cr_2(SO_4)_3 \cdot 6H_2O$. The solutions contained 0.33 g/l of each of the metal cations. All the chemicals, including hydrazine hydrate, were supplied by “Neva-Reactive” company and were of “chemically pure” grade.

10 ml of the working solution was poured into the liners. Then the liners were placed in autoclaves and installed in a drying cabinet. The temperature of the experiment was 240°C; the experiment time was 400 hours. For experiments in which the growth dynamics of the oxide film was studied, the exposure time was varied from 24 to 336 hours (from 1 to 14 days) with increments of at least 24 hours. After the exposure time ended, the autoclaves were removed and cooled naturally. The samples were extracted and the remainders of the solution were removed from their surface with filter paper.

The elemental composition of the surface of the samples was determined by X-ray fluorescence spectroscopy using an EDX-8100P energy dispersive X-ray fluorescence spectrometer (Shimadzu, Japan). The crystalline phases were identified using the Bruker “D8 DISCOVER” research complex. The surface morphology was studied using a Zeiss Merlin scanning electron microscope. In parallel, the chemical composition of the surface was analyzed by the EDX method. An optical emission spectrometer with inductively coupled plasma ICPE-9000 was used to determine the titanium concentration in the solution.

Results and Discussion

Initially, the dynamics of the formation of an oxide film on alloy samples was investigated. Figures 1–7 display the images of the surface oxide film after 24, 48, 72, 96, 120, 168, and 336 hours of heating.

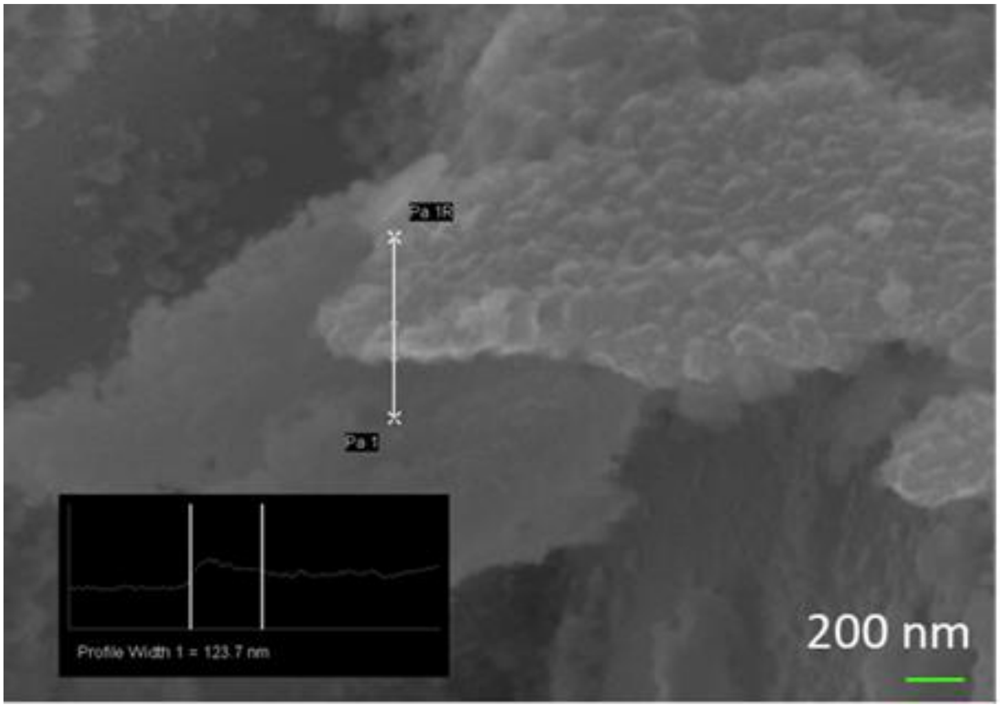

Figure 1. Image of the sample surface after exposure for 24 hours. 60 KX magnification. InLens detection.

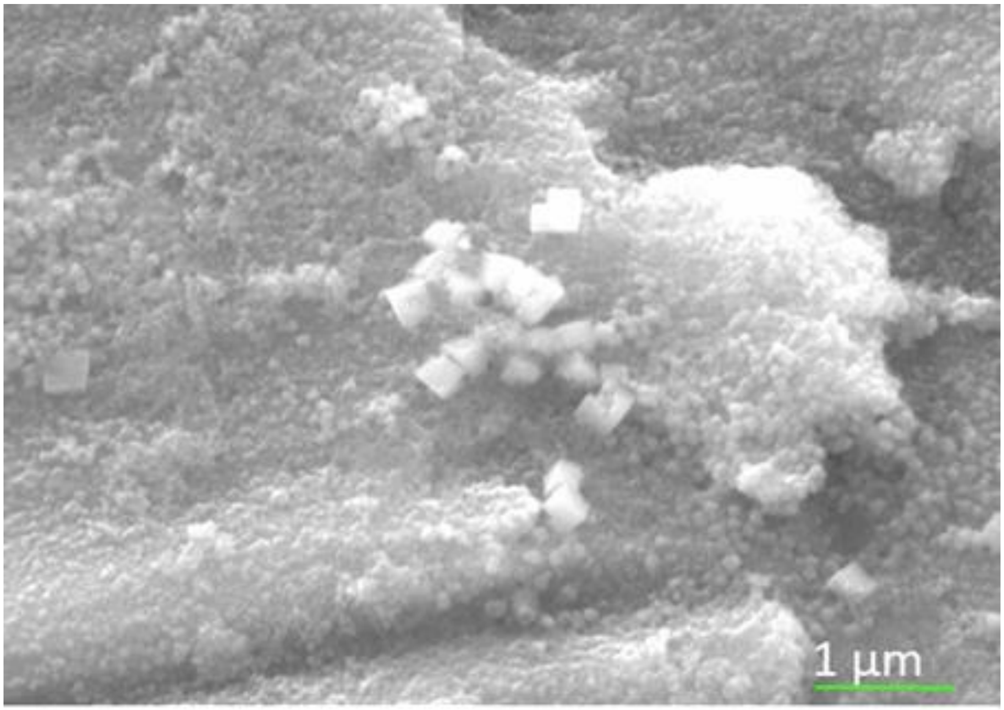

Figure 2. Image of the sample surface after exposure for 48 hours. 30 KX magnification. SE2 detection.

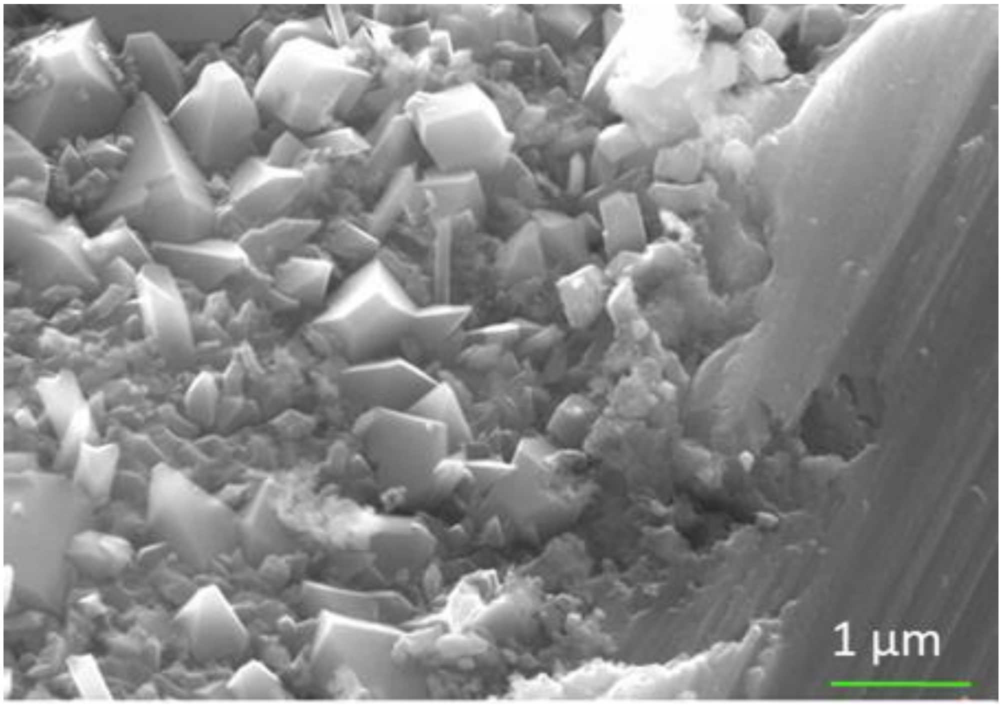

Figure 3. Image of the sample surface after exposure for 72 hours. 30 KX magnification. SE2 detection.

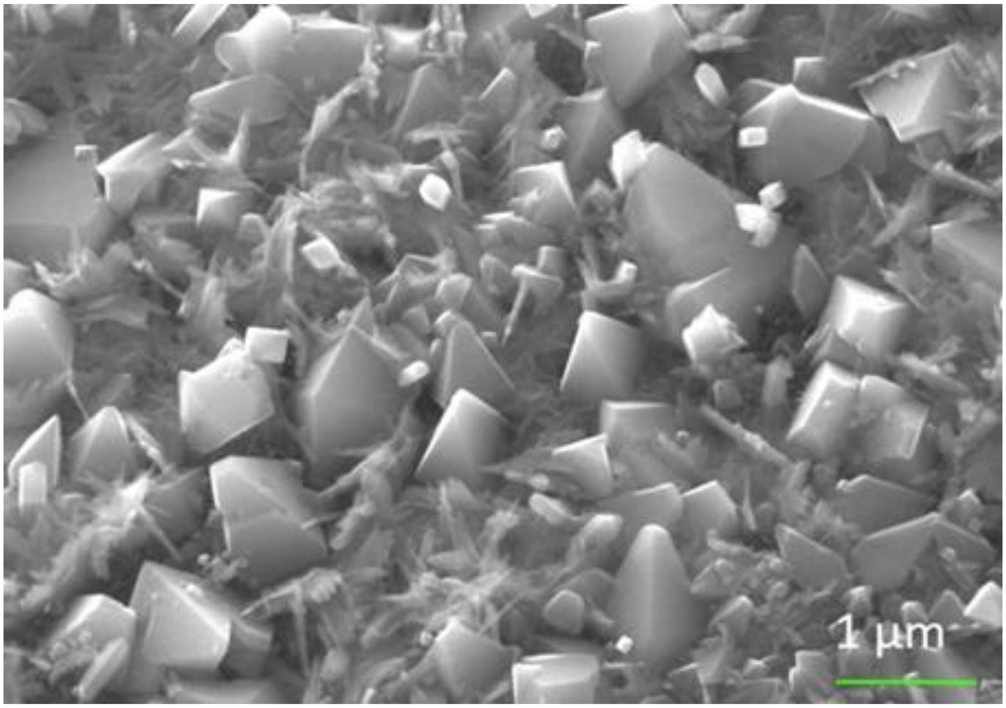

Figure 4. Image of the sample surface after exposure for 96 hours. 30 KX magnification. SE2 detection.

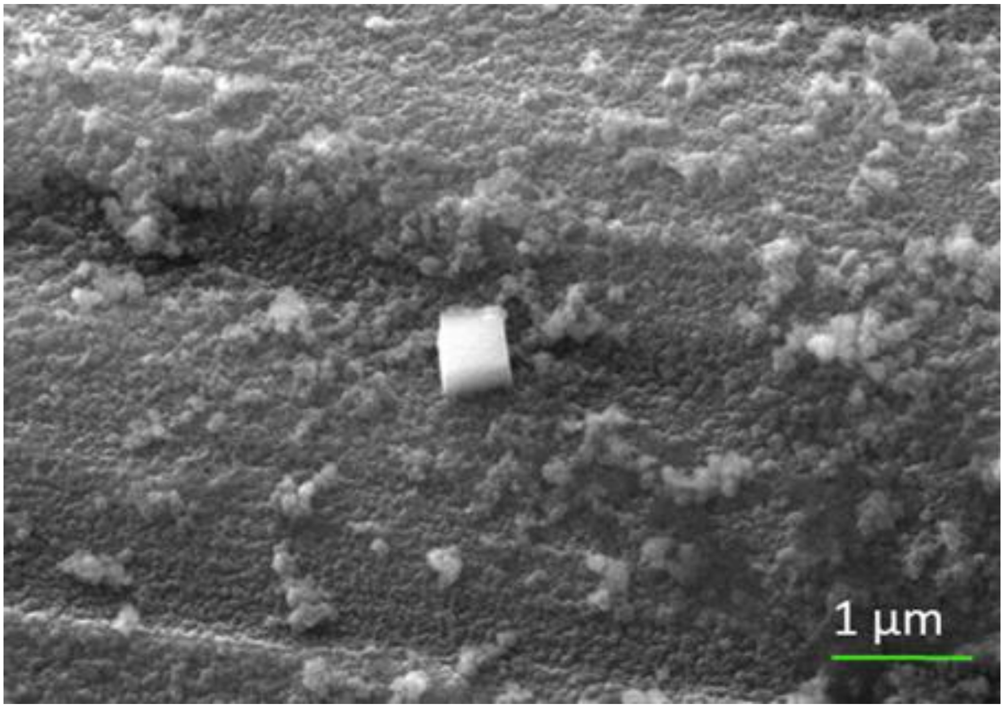

Figure 5. Image of the sample surface after exposure for 120 hours. 30 KX magnification. SE2 detection.

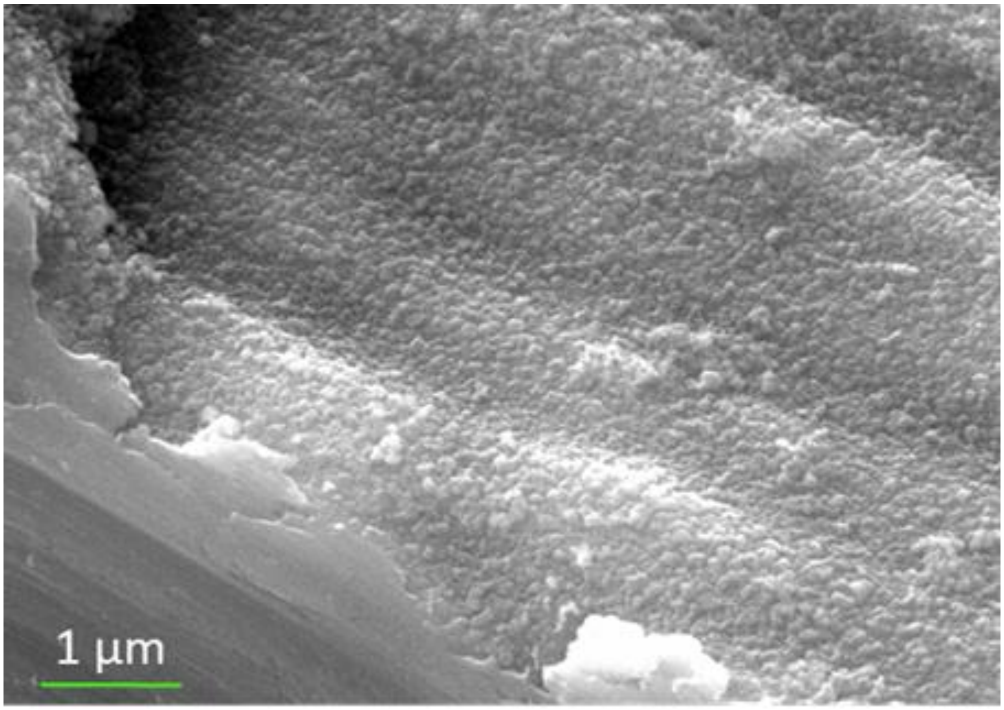

Figure 6. Image of the sample surface after exposure for 168 hours. 30 KX magnification. SE2 detection.

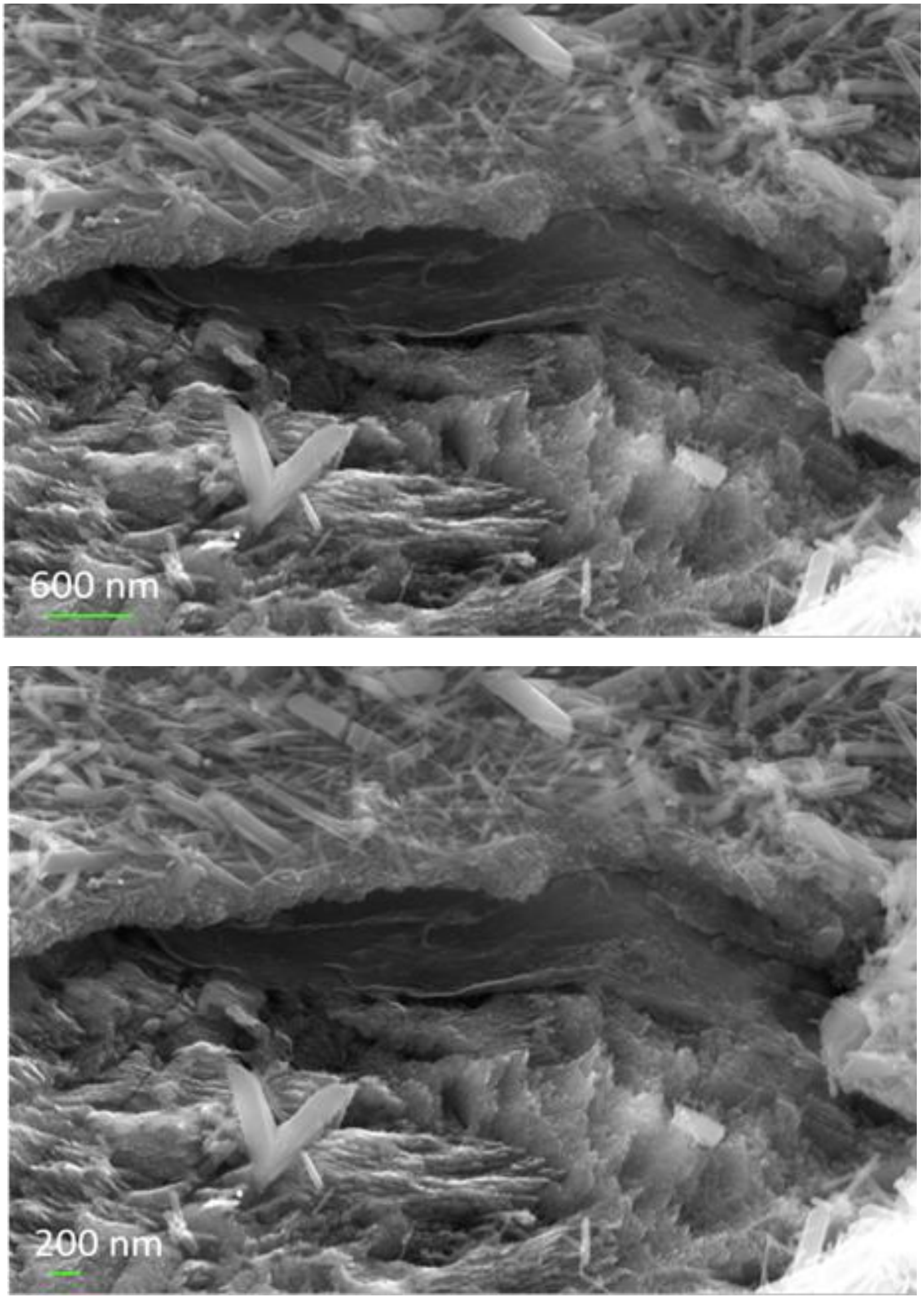

Figure 7. Images of the sample surface after exposure for 336 hours. 32.85 KX magnification. SE2 detection.

As a result of the study, it was found that a dense part of the oxide film was formed within a day after the start of the experiment (Figure 1). It consists of crystallites about 30 nm in size. The resulting crystallites have the shape of “scales” and are arranged evenly over the entire surface. The thickness of such a film is about 100–120 nm. In the following days, an increase in the crystallite sizes was observed: up to 60–80 nm by day 4 (Figure 4) and up to 100–120 nm by day 7 (Figure 6). The thickness of the dense oxide layer after 14 days of the experiment was about 200 nm (Figure 7). At the same time, the morphology of the loose film layer was not constant. Both polyhedral and needle-like forms of TiO_2 growth were observed. The size of these crystallites was 0.5–4.0 μm. Enlarged images of these shapes and a solid scaly film are shown in Figures 8–10.

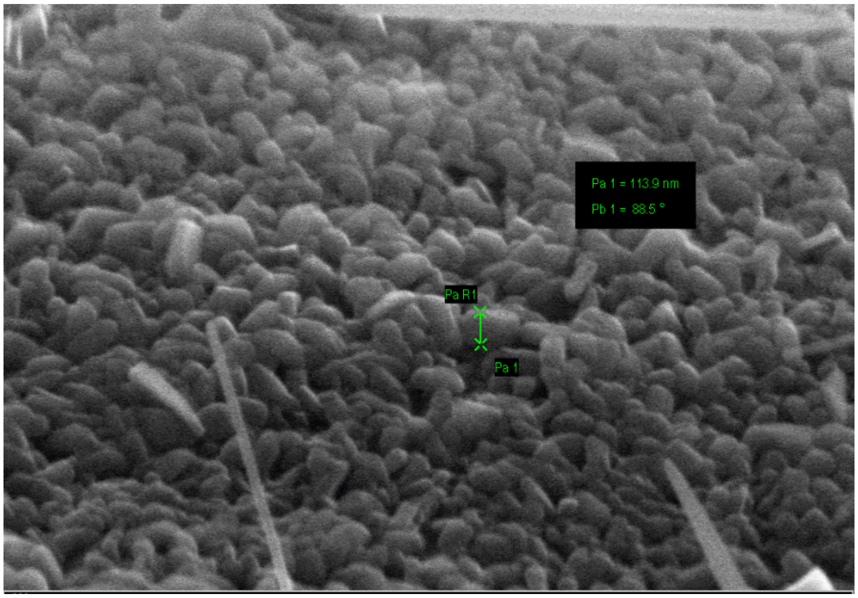

Figure 8. Dense oxide film in the form of "scales".

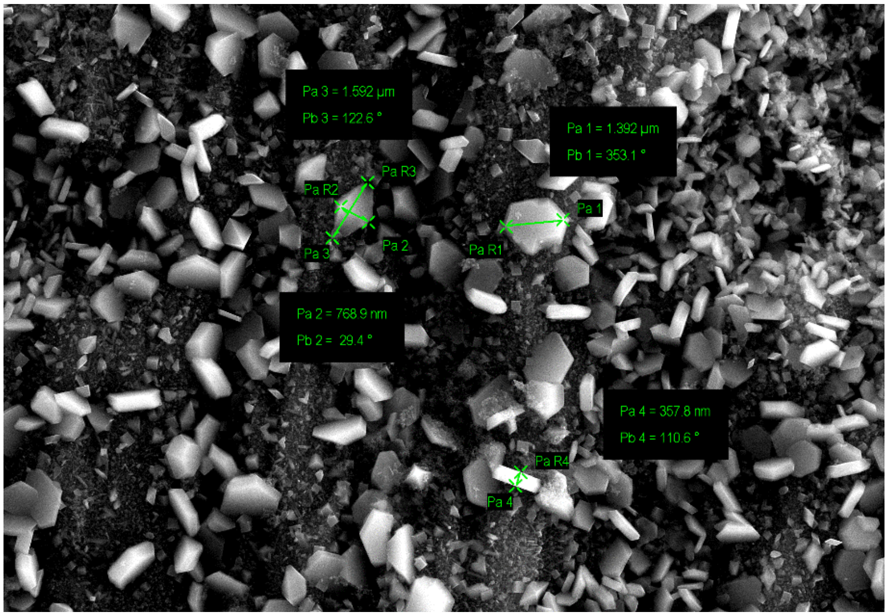

Figure 9. Polyhedral titanium dioxide forms of growth.

Figure 10. Needle-like titanium dioxide forms of growth.

The titanium content in the aqueous phase after heating was also analyzed during the experiments. The data obtained are presented in Table 2.

Table 2. Titanium content in the aqueous phase.

Heating duration, h	Titanium concentration, μg/kg
72	7±1
168	3±1
336	<1

As it can be seen from the data presented in Table 2, initially there is an influx of titanium from the sample into the aqueous phase. Then the titanium content in the aqueous phase decreases with increasing duration of the experiment.

The composition of the surface oxide film aged in distilled water

The results of the study of the oxide film formed on PT-7M alloy after heating in distilled water for 400 hours are presented at Figure 11 and in Table 3. To compare the composition of the oxide film and the alloy, furrows were made in the oxide films using a sharp hard blade (Spectrum 3 region).

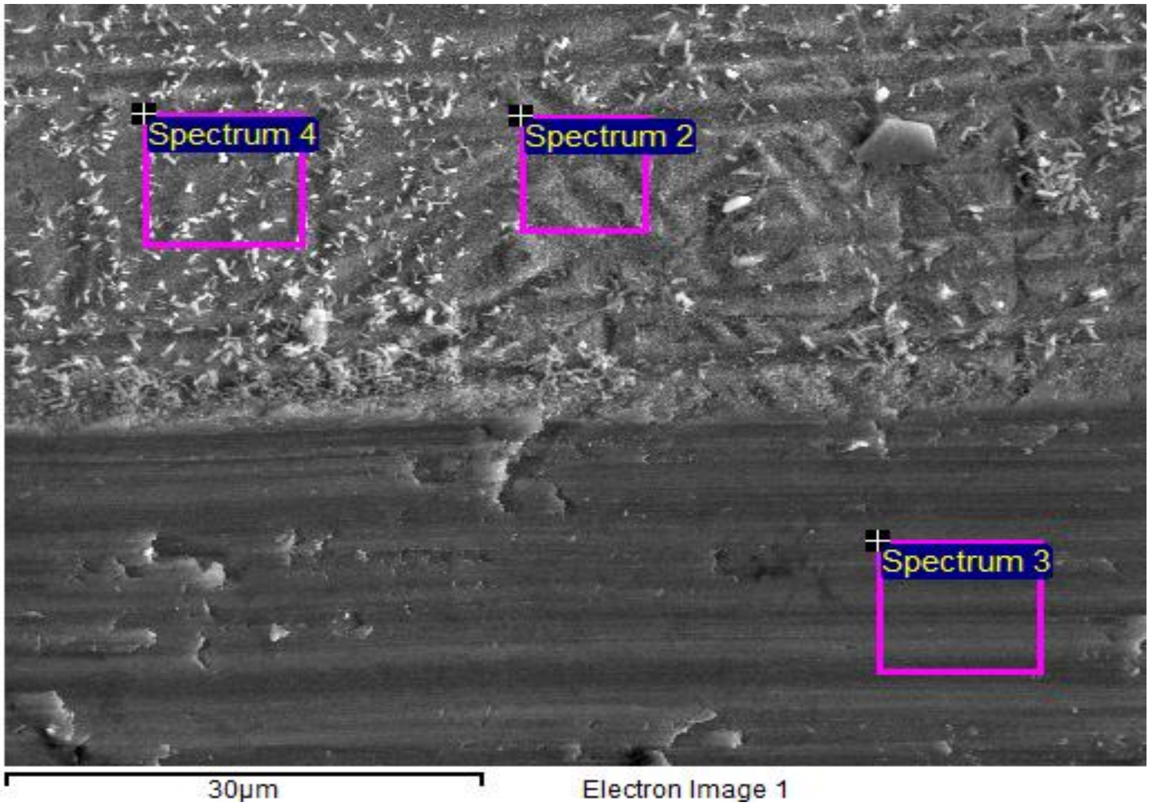

Figure 11. Image of the sample surface after aging in distilled water with hydrazine. 1 KX magnification. SE2 detection.

Table 3. Composition of the selected areas in Figure 11 (results in atomic percentage).

Area	O	Al	Si	Ti	Zr
Spectrum 2	55.43	1.58	0.16	41.51	0.51
Spectrum 3	0	4.07	0.20	94.29	1.36
Spectrum 4	56.47	1.50	0.10	40.66	0.59

The formation of a "scaly" oxide film is observed, the main component of which is TiO_2. It is worthy of note that alloying impurities – zirconium, silicon, and aluminum – are present in the oxide film. Both octahedral and needle-like forms of titanium dioxide growth are observed on the surface.

High-resolution X-ray diffraction was used to determine the phase composition of the surface film. The diffraction pattern of the alloy surface is shown in Figure 12.

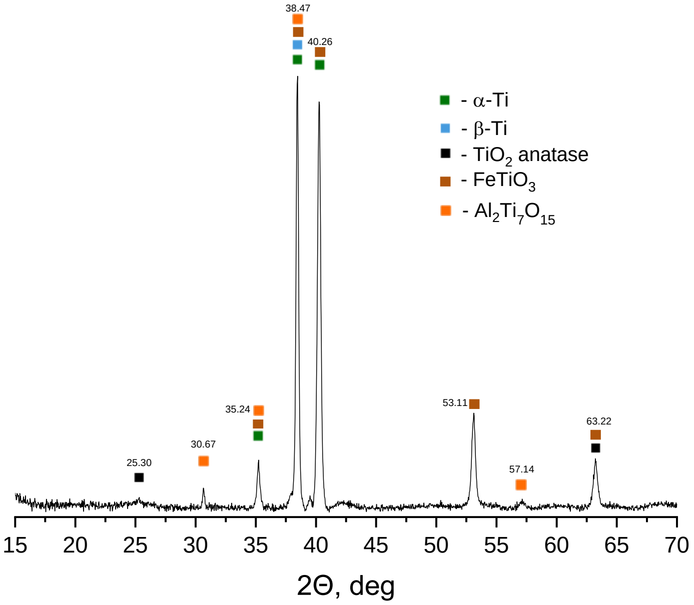

Figure 12. Diffraction pattern of PT-7M alloy surface after exposure in water.

The α-Ti and β-Ti peaks are clearly visible in the diffraction pattern. The presence of anatase, one of the crystalline modifications of TiO_2, was also detected. In addition, evidence of the presence of aluminum/titanium $Al_2Ti_7O_{15}$ [12] and iron/titanium $FeTiO_3$ mixed oxides [14] is observed.

Composition of the oxide film on the surface aged in a solution of salts

Figure 13 and Table 4 show the results of studying the surface morphology and elemental composition of the oxide film formed on PT-7M alloy after heating in a solution of metal salts for 400 hours.

Table 4. Composition of the selected areas in Figure 13 (results in atomic percentage).

Area	O	Al	Ti	Cr	Fe	Ni	Zr
Spectrum 1	44.46	1.19	43.57	1.80	4.18	3.88	0.93
Spectrum 2	50.58	1.32	39.72	1.51	1.62	4.26	0.99
Spectrum 3	47.21	1.12	49.42	0.53	0.36	0.42	0.93
Spectrum 4	22.43	1.74	73.75	0.00	0.00	0.40	1.68

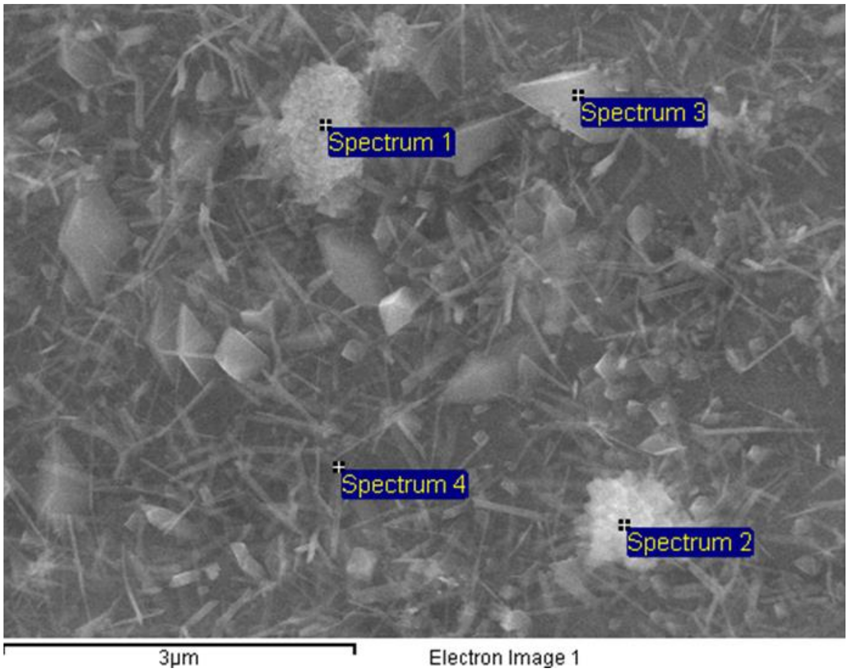

Figure 13. Image of the surface of a sample of PT-7M alloy aged in a solution of metal salts. 30 KX magnification. SE2 detection.

The data presented enables us to conclude that iron, chromium, and nickel are included in the composition of the loose layer of the oxide film. These metals are distributed in small amounts in the film, which may indicate the formation of an intermetallic phase similar to that described in [6].

A diffraction pattern of the surface of a sample exposed to a solution of metal salts is shown in Figure 14.

The diffraction pattern makes it possible to uniquely identify the following phases: α-Ti and β-Ti, anatase, $Al_2Ti_7O_{15}$, $FeTiO_3$, Fe_3O_4, Fe_2TiO_5. Moreover, the presence of $NiTiO_3$ and Al_2TiO_5 phases is likely. The latter mixed oxide is isomorphic to the Fe_2TiO_5 phase.

Discussion

The experiments that we carried out allow us to suggest the following structure of the oxide film formed on PT-7M alloy under the conditions of the first circuit of a nuclear power plant. Directly adjacent to the alloy is an internal “scaly” layer of an oxide film consisting of anatase with a thickness of about 200 nm tightly coupled with the structural material after 14 days of exposure. In addition to titanium, the dense layer was also found to comprise aluminum, which is part of the PT-7M alloy.

The outer layer of the oxide film consists of individual polyhedral and needle-shaped crystallites 0.5–4 μm large. The crystallites and the inner layer of the oxide film mainly consist of titanium dioxide. Also, if present in the coolant, the corrosion products of steel can be part of the crystallites forming mixed oxides and mixed intermetallic solutions. The resulting structure of the oxide film on PT-7M alloy is schematically shown in Figure 15.

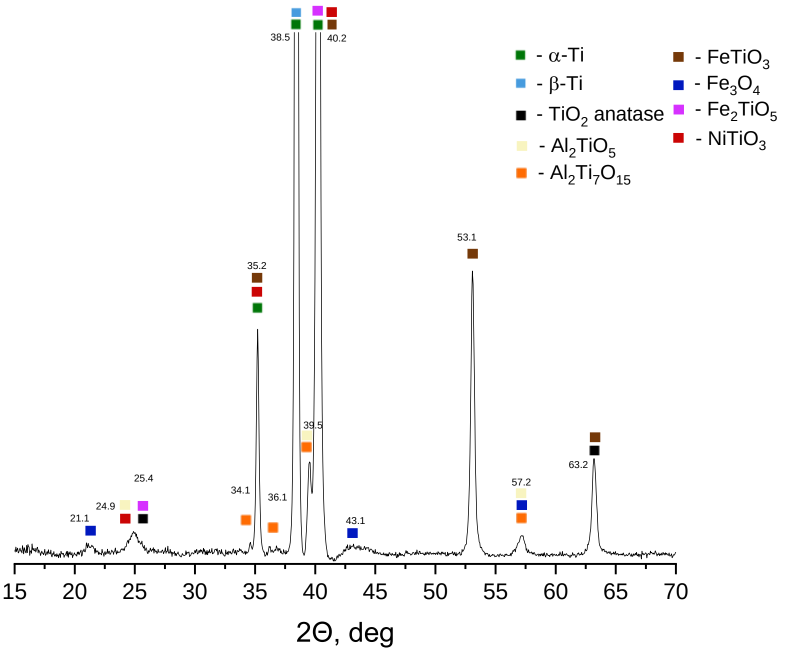

Figure 14. Diffraction pattern of PT-7M alloy surface after treatment in a solution of salts.

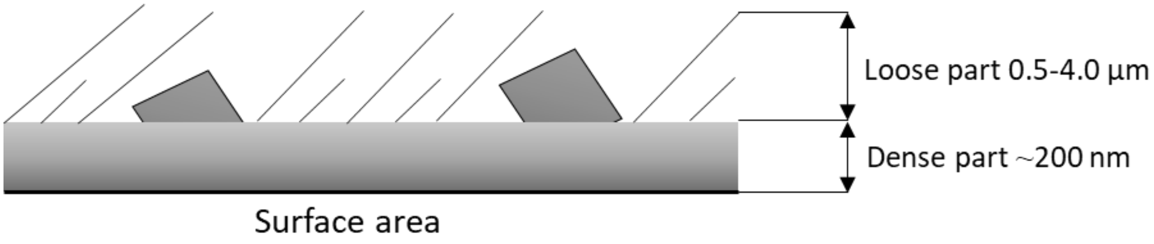

Figure 15. Schematic representation of the oxide film on the surface of PT-7M alloy after hydrothermal surface treatment.

It can be noted that the presented data are consistent with the results obtained by us during the examination of a sample of titanium alloy PT-3V [10] extracted from the primary circuit of a nuclear power plant during repair work. The general structure of the oxide film coincides with the size of the crystallites and the presence of a mixed intermetallic phase of titanium with corrosion products of steel in their composition. The obtained coincidence confirms the adequacy of the conditions chosen for the model experiments.

A significant difference between the samples obtained in the model experiments and the samples extracted from the first circuit is the presence of needle-like titanium dioxide growth forms on the former. This difference can be explained by the mechanism of oxide film growth. It is indicated in [6–8] that the outer layer of the oxide film is formed due to the deposition of compounds of titanium and other metals from the aqueous phase. The data obtained in this work, in particular the dynamics of titanium content variation in the aqueous phase – an increase at the beginning of the experiment and a subsequent gradual decrease – confirms this assumption. With this in mind, it can be assumed that needle-like growth forms can precipitate from solution on the surface of the oxide film during autoclave cooling, which is much faster than the cooling of the nuclear power plant during the shutdown period.

With regard to the mechanism of oxide film formation, the formation of new phases-mixed oxides of titanium and of steel corrosion products and the results of their substitution for aluminum-detected by X-ray diffraction is also worthy of note. This fact indicates that the processes occurring both in the aqueous and solid phases seem to have a more complex nature than those described in [6–8]. Analysis of the forms of existence of titanium in the aqueous phase, including heteropolynuclear complexes with ions of other metals, and their transformations after the transition to the solid phase will be the subject of further research.

Conclusion

The study on the composition and structure of the oxide film formed on the surface of PT-7M titanium alloy under hydrothermal conditions corresponding to the conditions in low-power nuclear power plant steam generators has shown that:

- The oxide film consists of an inner “scaly” layer tightly coupled with the alloy surface and an outer “loose” layer consisting of individual crystallites. The solid inner layer consists of anatase and reaches a thickness of 0.1–0.12 μm after 24 hours of the experiment. After 336 hours of the experiment, the thickness of the inner layer reaches 0.2 μm.
- The formation of a solid oxide layer reduces the rate of titanium escape from the alloy surface into the aqueous phase, which leads to a gradual decrease in its concentration.
- The crystallites that make up the loose layer mainly consist of titanium dioxide. Both needle-like and octahedral growth forms with a size of 0.5–4.0 μm are observed.
- Metal ions that are components of stainless steel can be embedded in the loose film layer, both as mixed oxides with titanium and within intermetallic solutions.
- The results obtained are consistent with the results of studying the surface of PT-3V alloy samples extracted from the primary circuit of a nuclear power plant. The difference is that needle crystallites are present on autoclave samples; their formation can be explained by the relatively rapid cooling of autoclaves.

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Studies", "Chemical Analysis and Materials Research Centre", "Centre for Optical and Laser Materials Research", "Thermogravimetric and Calorimetric Research Centre".

References

1. A.O. Pimenov, D.G. Kulikov, A.P. Vasilyev and N.A. Molokanov, Small Nuclear Power Plants in the Arctic Regions: Issues of Economic Feasibility and Environmental Safety, *Arctic: Ecology and Economy*, 2019, **2**, 120–128. doi: 10.25283/2223-4594-2019-2-120-128 (In Russian).
2. L.A. Andreeva, E.N. Gol'tsov, A.V. Kaplienko, V.V. Kudinov, D.G. Kulikov, N.A. Molokanov and A.O. Pimenov, Actual Developmental Problems of Small Energy Installations: SNPP Based on the SHELF-M Reactor Installation, *At. Energy*, 2021, **129**, 201–207. doi: 10.1007/s10512-021-00734-7
3. D.L. Zverev, S.M. Neevin, D.L. Doronkov and L.B. Sokolova, Nuclear Ship Reactor Installations: From Gen 1 to 5, *At. Energy*, 2020, **129**, 1–7. doi: 10.1007/s10512-021-00704-z
4. V.M. Belyaev, M.A. Bol'shukhin, A.N. Pakhomov, A.M. Khizbullin, A.N. Lepekhin, V.I. Polunichev, K.B. Veshnyakov, A.N. Sokolov and A.Yu. Trusov, The World's First Floating NPP: Origination and Direction of Future Development, *At. Energy*, 2020, **129**, 27–34. doi: 10.1007/s10512-021-00707-w
5. Q. Bignon, F. Martin, Q. Auzoux, F. Miserque, M. Tabarant, L. Latu-Romain and Y. Wouters, Oxide formation on titanium alloys in primary water of nuclear pressurised water reactor, *Corros. Sci.*, 2019, **150**, 32–41. doi: 10.1016/j.corsci.2019.01.020
6. L. Zhang, D. Sun and R. Xiong, Study of corrosion kinetics and microstructure of α-phase pure titanium tube in environment 300°C and 8.6 MPa water, *Corros. Sci.*, 2020, **162**, 108217. doi: 10.1016/j.corsci.2019.108217.
7. Q. Bignon, Q. Auzoux, F. Martin, A. Raynal, F. Miserque, M. Tabarant, L. Latu-Romain and Y. Wouters, Corrosion of titanium alloys in pressurized water at 300°C and 15 MPa, MATEC Web of Conferences 321, 2020, The 14th World Conference on Titanium. doi: 10.1051/matecconf/202032106006
8. S. Selva, Q. Bignon, A. Raynal, F. Martin, Q. Auzoux, G. Renou, M. Tabarant, F. Miserque, L. Latu-Romain and Y. Wouters, Corrosion of titanium alloys in pressurised water at 300°C: Kinetics and modeling, *Corros. Sci.*, 2021, **190**, 109646. doi: 10.1016/j.corsci.2021.109646
9. S. Kasahara, J. Kuniya, K. Moriy, N. Saito and S. Shiga, General corrosion of iron, nickel and titanium alloys as candidate materials for the fuel cladding for the supercritical water-cooled power reactor, GENES4/ANP2003, Kyoto, 2003.
10. A. Horváth, A.R. Imre and G. Jákli, Investigation of Corrosion Resistance of Alloys with Potential Application in Supercritical Water-cooled Nuclear Reactors, *Period. Polytech. Chem. Eng.*, 2019, **63**, 328–332. doi: 10.3311/PPch.12923

11. N.A. Glukhoedov, V.N. Epimakhov, A.A. Tsapko, A.N. Orlov, A.A. Zmitrodan, G.A. Zmitrodan and M.Yu. Skripkin, Sorption of ^{137}Cs and ^{60}Co on Titanium Oxide Films in Light Water Reactor Primary Circuit Environment, *Materials*, 2022, **15**, 4261–4670. doi: 10.3390/ma15124261
12. Y. Ohya, Y. Kawauchi and T. Ban, Cation distribution of pseudobrookite-type titanates and their phase stability, *J. Ceram. Soc. Jpn.*, 2017, **125**, 695–700. doi: 10.2109/jcersj2.17086
13. F. Remy, O. Monnereau, A. Casalot, F. Dahan and J. Galy, Titane à valence mixte, un nouvel oxyde ternaire: $Al_2Ti_7O_{15}$, *J. Solid State Chem.*, 1988, **76**, 167–177. doi: 10.1016/0022-4596(88)90204-6.
14. A.F. Buddington and D.H. Lindsley, Iron-Titanium Oxide Minerals and Synthetic Equivalents, *J. Petrol.*, 1964, **5**, 310–357. doi: 10.1093/petrology/5.2.310
15. G. Zhao, X. Wu, X. Tan and X. Wang, Sorption of heavy metal ions from aqueous solutions: a review, *Open Colloid Sci. J.*, 2011, **4**, 19–31. doi: 10.2174/1876530001104010019
16. M.V. Maslova and L.G. Gerasimova, Sorption of non-ferrous metal cations on hydrated titanium dioxide, *Non-ferrous Metals*, 2017, **2**, 27–32. doi: 10.17580/nfm.2017.02.05
17. G.R. Doshi and V.N. Sastry, Hydrous titanium oxide as a concentrator for trace nuclides in seawater, *Indian J. Chem.*, 1977, **15**, 904–906. doi: 10.1002/CHIN.197813023
18. Industry standard 95 10002-95, *Water quality standards of the first and third circuits of the reactor unit of vessels of the Maritime Department of the Russian Federation with water-water reactors of the KLT-40 type*, Moscow, Russia, 1995 (in Russian).

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