

PACS numbers: 28.41.Qb, 28.52.Fa, 68.35.bd, 82.45.Bb, 88.30.Nn

Corrosion Properties Characterization of 06Cr18Ni10Ti, 08Cr18Ni10Ti Steels and 42CrNiMo Alloy under Conditions Simulating Primary Coolant of Pressurized Water Reactor

V. A. Zuyok, R. A. Rud, M. V. Tretyakov, N. V. Rud, Ya. O. Kushtym, and V. V. Shtefan

*National Science Centre “Kharkiv Institute of Physics and Technology”,
N.A.S. of Ukraine,
1, Akademichna Str.,
61108 Kharkiv, Ukraine*

The article presents an analysis of the corrosion properties of structural materials for primary circuit of light-water reactors. Results of autoclave testing of austenitic stainless steels 06Cr18Ni10Ti, 08Cr18Ni10Ti and chromium–nickel alloy 42CrNiMo in a model environment of primary coolant at a temperature of 350°C and a pressure of 16.5 MPa are presented. Corrosion resistance is estimated by the rate of mass change and the appearance of the samples, the microstructure of the oxide films, and the amount of metal that entered into reaction with the corrosion environment. As established, the samples of the 42CrNiMo alloy, in contrast to the Cr18Ni10Ti steel samples, are oxidized with a mass gain of 9 mg/dm² for 10 000 hours of testing. The mass index of stainless-steels' corrosion during the same exposure time almost did not change and is of 0–2 mg/dm². The reflectivity of the surface of the samples is decreased slightly, the oxide film is firmly attached to the metal substrate; there is no local corrosion or deposits that indicates the high corrosion resistance of the studied materials. The study of the morphology of the oxide-films' surface reveals that compact pyramidal-shaped microcrystalline precipitates grow during autoclaving. The corrosion products are chemically removed from the surface of the samples to evaluate the corrosion damage of the studied materials. As shown, after 10 000 hours, the corrosion loss of Cr18Ni10Ti grade steels is of 55 mg/dm², and for 42CrNiMo alloy, it is 5 mg/dm². As established, the dissolution coefficient of oxide films, that is

Corresponding author: Valeriy Anatoliyovich Zuyok
E-mail: valeriyz@kipt.kharkov.ua

Citation: V. A. Zuyok, R. A. Rud, M. V. Tretyakov, N. V. Rud, Ya. O. Kushtym, and V. V. Shtefan, Corrosion Properties Characterization of 06Cr18Ni10Ti, 08Cr18Ni10Ti Steels and 42CrNiMo Alloy under Conditions Simulating Primary Coolant of Pressurized Water Reactor, *Metallofiz. Noveishie Tekhnol.*, **45**, No. 4: 481–501 (2023). DOI:[10.15407/mfint.45.04.0481](https://doi.org/10.15407/mfint.45.04.0481)

the ratio of the mass of the oxide film transferred to the corrosion environment to the total mass of oxide formed during oxidation of the material, is almost zero for the 42CrNiMo alloy, while it is of 30% for stainless steels. This indicates that the application of the 42CrNiMo alloy as a reactor-core structural material will allow eliminating significantly such an undesirable phenomenon as the transfer of corrosion products into the circuit and their further activation. The dependence approximating the corrosion kinetics of stainless steels and Cr–Ni alloy is established. At the initial stages of autoclave exposure (up to 1000 hours), mass loss is described by a power law with an index of power of 0.817 and 0.720 for steels 06Cr18Ni10Ti and 08Cr18Ni10Ti, respectively. Moreover, the indices of power are of 0.347 and 0.352 for longer tests. The experimental results of the mass change of the 42CrNiMo-alloy samples obtained over the entire period of testing are described by one law with an index of power of 0.510. Based on the results of the work, the main conclusion is made that the chrome–nickel alloy 42CrNiMo, in contrast to the stainless steels Cr18Ni10Ti, possess a higher corrosion resistance under model conditions of the light-water reactors' primary coolant. Oxide films growing on 42CrNiMo surface have almost no tendency to dissolve, in contrast to Cr18Ni10Ti steels with the dissolution coefficient of 30%.

Key words: corrosion, water reactor, oxide, autoclave testing, kinetics of corrosion, 42CrNiMo, Cr18Ni10Ti.

У статті проведено аналізу корозійних властивостей конструкційних матеріалів першого контуру легководних реакторів. Наведено результати автоклавних випробувань аустенітних неіржавійних криць 06X18H10T, 08X18H10T та хромонікелевого ступу 42ХНМ в модельному середовищі теплоносія першого контуру за температури у 350°C і тиску у 16,5 МПа. Корозійна стійкість оцінювалася за швидкістю зміни маси та зовнішнім виглядом зразків, мікроструктурою окисних плівок і кількістю металу, який вступив у взаємодію з корозійним середовищем. Встановлено, що зразки зі ступу 42ХНМ, на відміну від криць Х18Н10Т, окиснювалися з приростом маси у 9 мг/дм² за 10 000 годин випробувань. Масовий показник корозії криць за цей самий час майже не змінювався та становив 0–2 мг/дм². Відбивна здатність поверхні металів знизилася незначно, окисна плівка була міцно зчеплена з основою, будь-які прояви локальної корозії та відкладень були відсутні, що свідчить про високу корозійну стійкість досліджуваних матеріалів. Дослідження морфології поверхні окисних плівок показало, що під час автоклавування на їхній поверхні формуються компактні мікрочастинки виділення пірамідальної форми. Для визначення корозійного ураження досліджуваних матеріалів проведено видалення продуктів корозії хемічним способом з поверхні зразків. Показано, що за 10 000 годин корозійні втрати криць Х18Н10Т становлять 55 мг/дм², ступу 42ХНМ — 5 мг/дм². Встановлено, що коефіцієнт розчинення окисних плівок, який показує відношення маси окисної плівки, що перейшла до корозійного середовища, до загальної маси окису, що утворився при окисненні матеріалу, для ступу 42ХНМ дорівнює нулю, в той час як для криць він становить 30%. Це свідчить про те, що застосування ступу 42ХНМ у якості конструкційного матеріалу активної зони

уможливить в значній мірі нівелювати таке небажане явище, як винесення продуктів корозії в контур і подальша активація їх. Визначено залежність, що апроксимує кінетику корозії криці та стопу. На початкових стадіях корозії (до 1000 годин) втрата маси описується степеневу залежністю з показником степеня 0,817 і 0,720 для криць марок 06X18H10T та 08X18H10T відповідно. За більш тривалих випробувань показники степеня становили 0,347 і 0,352. Експериментальні результати щодо зміни маси зразків стопу 42ХНМ, одержані за весь період дослідження, описуються однією залежністю з показником степеня 0,510. За результатами роботи зроблено основний висновок, що хромоніклевий стоп 42ХНМ на відміну від неіржавійних криць Х18Н10Т в модельних умовах теплоносія першого контуру легководного реактора має більш високу корозійну стійкість. Окисні плівки, які утворюються на його поверхні, майже не мають схильності до розчинення на відміну від криць Х18Н10Т, для яких коефіцієнт розчинення становить 30%.

Ключові слова: корозія, водяний реактор, окис, автоклавне випробування, кінетика корозії, 42ХНМ, Х18Н10Т.

(Received 2 January, 2023; in final version, 15 February, 2023)

1. INTRODUCTION

There are numerous physical and chemical issues related to ensuring equipment reliability and safety under the operation conditions of nuclear power plants (NPPs) with a water coolant: corrosion of structural materials in the coolant flow; mass transfer and deposition of corrosion products; concentration of impurities; accumulation of radioactive corrosion products and their removal from circuits.

Corrosion resistance of structural materials for the nuclear power installations equipment largely depends on the water chemistry regulation. Therefore, even after the commissioning of the first NPP, the problem of establishment and maintaining such physicochemical parameters of the coolant that would prevent damage to circuit equipment remains relevant [1]. Depending on the material, there is always a certain loss of structural material due to general corrosion (from $\cong 0.2$ mm/year to 2 mm/year) [2, 3]. The accumulated experience makes it possible to ascertain that there is no comprehensive description of the mechanism of corrosion products formation, mass transfer and deposition in the nuclear installation circuits.

Austenitic stainless steels are widely applied in nuclear reactor engineering due to satisfactory mechanical characteristics. In the first reactors of the Soviet design at the beginning of nuclear power industry time, the fuel rod claddings were made of Cr18Ni10Ti steel. Austenitic steels and high-nickel alloys were also applied in western-design reactors [4]. However, a significant genetic disadvantage of these ma-

materials is susceptibility to stress corrosion cracking (SCC) due to radiation-induced depletion of grain boundaries by chromium [5, 6].

Chromium-nickel alloy 42CrNiMo, developed at JSC 'VNIIM', contains 42% by mass of chromium, 1.5% by mass of molybdenum, and the rest is nickel. It is widely applied as a material for fuel rod claddings in the nuclear marine propulsion reactors [7–10]. Experience has demonstrated that the application of the 42CrNiMo alloy as a material for fuel rod claddings has never been accompanied by the depressurization, including tests of fuel assemblies with claddings 0.15 mm thick [11]. Recently, the increased interest in this alloy is due to its application as a cladding material for the absorbing rods of the rod cluster control assembly (RCCA) of VVER reactors [7, 10, 12, 13]. This alloy is promising for application as fuel rod cladding material for low-power nuclear reactors and VVERs [14, 15].

The 42CrNiMo alloy possess exceptionally high corrosion resistance in water and water steam with impurities of chlorine ions and other aggressive environments. Unlike steels, it is not susceptible to SCC, and unlike zirconium alloys, in accidents it is almost not susceptible to reaction with water steam accompanied by increased hydrogen release. The alloy is structurally stable at temperatures of 300–350°C and testing exposure time of 60 000 hours, it possesses high strength and plasticity, and high manufacturability. A positive property of the alloy is high plasticity at operating temperatures in the irradiated state [16]. According to the set of characteristics, the alloy even has the prospect of being applied for a fairly large resource as a material for reactor pressure vessel, steam generator vessel and piping systems, as well as systems of the first wall of the water-cooled blanket of the International Experimental Thermonuclear Reactor [7].

After the Fukushima accident, a requirement arose to develop accident tolerant fuel rods. It was necessary to make a choice among the materials that guarantee high performance characteristics, as well as the integrity of fuel rod claddings and fuel assemblies under conditions of maximum design accidents and in some cases of beyond-design-basis accidents [17]. Not a single case of depressurization of the 42CrNiMo alloy as a material for fuel rod claddings of nuclear marine propulsion reactors was detected during the operation, including tests of fuel assemblies with a 0.15 mm fuel rod cladding wall thickness [11, 18].

A feature of the VVER-1000 reactor core is the significant surface area of the fuel rod claddings, which are in contact with the coolant ($\cong 12500 \text{ m}^2$). In addition, the surface area of steam generator tubes made of stainless steel Cr18Ni10Ti is more than 600 m^2 . The corrosion process of stainless steel in the VVER primary circuit is accompanied by the transfer of corrosion products into the coolant [1].

The potential replacement of zirconium alloys for fuel rod claddings

with 42CrNiMo alloy in the case of even a slight release of corrosion products may result in their activation with a further increase in the radioactivity of the equipment and radiation burden to personnel. However, due to the specifics of the 42CrNiMo alloy application, there is no publicly available information on its oxidation kinetics. At the same time, the kinetics can be approximated by several laws: linear, parabolic, cubic, and logarithmic [19].

The corrosion resistance of a metal is specified by the corrosion rate under certain conditions. Corrosion resistance can be estimated by the mass change of the metal because of corrosion process, related to a unit of surface area and a unit of time. The mass of some metals and alloys can increase or decrease because of corrosion process. It is known that under the conditions of the VVER-1000 primary circuit, the corrosion of austenitic stainless steels of the Cr18Ni10Ti grade is accompanied by a mass loss and, according to [20, 21], after 120000 hours of testing it is $1 \cdot 10^{-4}$ g/m²·h. The amount of corrosion products (CP) transferred to the coolant due to corrosion process of the VVER-440 equipment is more than 12 kg/year [22].

The mass loss of Cr18Ni10Ti steel equipment components under the conditions of the VVER-1000 primary circuit is caused by the partial dissolution of the outer surface layer of the multilayered oxide film under certain conditions. In some cases (significant fluctuations in *pH*, high flow rate of the coolant), the mass loss can result in a negative value of the mass index of corrosion. That is, the mass index of corrosion, which is based on the mass change of samples during the testing, is not informative for such materials, since conditions may arise in the environment when the mass index would be constant (the rate of oxide formation will coincide with the rate of dissolution). Nevertheless, this does not mean that corrosion does not occur.

The research of the above-mentioned structural materials and the assessment of their corrosion resistance are of great importance both for the building of state-of-the-industry nuclear installations and for life extension of existing ones. This issue is relevant against the background of global trends in the designing of SMR reactors with reduced maintenance. It will be possible to design installations and the coolant purification system at a state-of-the-industry level if foreknow such parameters as the rate of metal loss or the rate of wall thinning of the workpiece due to corrosion, as well as the kinetics of the corrosion products transfer to the corrosion environment.

The purpose of the research was to evaluate the corrosion resistance of austenitic stainless steels of the Cr18Ni10Ti grade and the 42CrNiMo chromium-nickel alloy under the conditions of the VVER-1000 primary water chemistry and the corrosion resistance of the 42CrNiMo alloy compared to the results for 06Cr18Ni10Ti and 08Cr18Ni10Ti steels.

TABLE 1. Materials' composition.

Material	Technical Specifications	Mass fraction of elements, %							
		C	Si	Mn	Mo	Cr	Ni	Fe	S
Cr18Ni10Ti	14-3-219-89	0.03– 0.06	<0.8	1.0– 2.0	–	17.0– 19.0	10.0– 11.0	Base	<0.015
42CrNiMo	14-1-5436-2001	<0.03	<0.25	<0.2	1.0– 1.5	41.0– 43.0	Base	<0.6	<0.01

2. PROBLEM STATEMENT AND OBJECTIVE OF THE STUDY

Thin-walled weldless tubes made of stainless steels 06Cr18Ni10Ti, 08Cr18Ni10Ti and chromium-nickel alloy 42CrNiMo with an outer diameter of 8.2 mm and a wall thickness of 0.6 mm, manufactured according to the technical specifications given in Table 1, were selected for the research. The production of these tubes is currently mastered by some Ukrainian enterprises. The selected materials are of high quality, as these enterprises have been supplying products of the 1st and 2nd safety classes for SE 'NNEGC 'Energoatom' for many years. These products are used in the equipment of all 15 nuclear power units of Ukrainian NPPs both directly in the core and in the 2nd and 3rd circuits.

The production and preparation of samples for corrosion tests was carried out in accordance with the requirements of GOST 9.908-85 [23]. The tests were carried out in static autoclaves at a temperature of 350°C under a pressure of 16.5 MPa in accordance with the requirements of the ASTM-G2M standard. The total testing exposure time was 10000 hours. The composition of the corrosion environment was as follows: chemically demineralized water, H₃BO₃—3 g/dm³, NH₃—3 mg/dm³, KOH—12.3 mg/dm³, $pH_{25}=7.2$. The test was divided into stages. The duration of the stages was 75, 150, 300, 500, 1000, 1800, 2500, 6000, 6500, 7000, 8000, 9000 and 10000 hours. At the end of each stage, 3 samples were removed from the autoclave testing for weighing and examination of the appearance.

Corrosion resistance was estimated according to [23]—the ratio of mass change rate of the samples to the surface area (when testing for resistance to general corrosion) and to the exposure time.

3. RESEARCH RESULTS

3.1. Autoclave testing

The generalized results of mass change of 42CrNiMo alloy as well as 06Cr18Ni10Ti and 08Cr18Ni10Ti steels samples after autoclave test-

ing are given in Fig. 1. The obtained results revealed that corrosion of 06Cr18Ni10Ti steel samples is accompanied by a mass loss (Fig. 1. *a*). Based on information in literature sources [24], the main mechanism of mass loss is the dissolution of the oxide film surface layers. The most intensive mass change was observed at the first stages of testing (up to $\cong 1.800$ hours). Further testing resulted in mass loss at almost the same rate. The mass loss of 06Cr18Ni10Ti steel samples was 3 mg/dm^2 after 10 000 hours of testing.

At the initial stages of testing (up to 500 hours), a small mass gain ($\cong 1\text{--}2 \text{ mg/dm}^2$) was detected for 08Cr18Ni10Ti steel samples (Fig. 1. *b*). Further testing resulted in a mass loss. The rate of mass loss of the 06Cr18Ni10Ti and 08Cr18Ni10Ti steel samples was almost the same after exposure for more than 2000 hours, as evidenced by the slope of the curves in Fig. 1. *a* and Fig. 1. *b*. It can be assumed that the most likely reason for the temporary mass gain of the 08Cr18Ni10Ti steel samples at the initial stages of testing (up to 500 hours) is the difference in the surface treatment from the 06Cr18Ni10Ti samples.

Corrosion of 42CrNiMo alloy samples is characterized by a constant mass gain, in contrast to 06Cr18Ni10Ti and 08Cr18Ni10Ti samples.

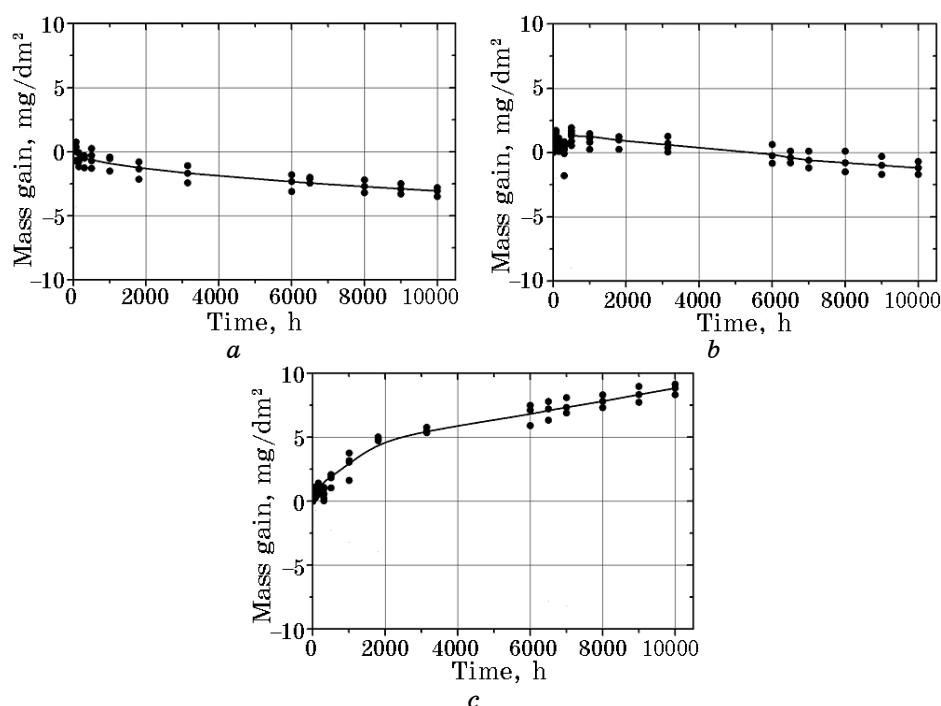


Fig. 1. Mass change of samples during autoclave tests at 350°C and 16.5 MPa: *a*—06Cr18Ni10Ti, *b*—08Cr18Ni10Ti, *c*—42CrNiMo.

The rate of mass gain of 42CrNiMo samples was not constant, and at the initial stages of testing (up to 1.800–2.500 hours) it was higher than at the final stages (from 2 500 to 10 000 hours). The dependence that describes the mass change of the samples on the test time (Fig. 1. *c*) is damping, which indicates the protective properties of the oxide films. The mass gain of 42CrNiMo samples was almost 9 mg/dm² after 10 000 hours of testing.

3.2. Appearance of samples

The surface of the 42CrNiMo samples became a solid dark yellow (straw) colour without cracks and defects, with high reflectivity after autoclave tests. The surface of 06Cr18Ni10Ti and 08Cr18Ni10Ti samples had the same dark grey colour. Based on the general concept of corrosion, the high reflectivity of the samples surface and the absence of loose deposits on the surface indicate the high corrosion resistance of the researched materials.

The surface morphology of the oxide films was studied at a magnification of up to 25 000 times by means of SEM. On the SEM micrograph of surfaces of the oxide films both 42CrNiMo alloy and Cr18Ni10Ti steels samples, it is noticeable that, compact pyramidal-shaped microcrystalline precipitates formed during autoclaving (Fig. 2). The most likely mechanism of their formation is the dissolution of the surface layers of the oxide film and the subsequent formation of pyramidal precipitates. It can be noted that on the 42CrNiMo samples, most of the pyramidal precipitates have a quadrangular base (Fig. 2, *a*), and on the Cr18Ni10Ti samples they have a pentagonal base (Fig. 2, *b*). The surface morphology of the samples was studied at all stages of testing and

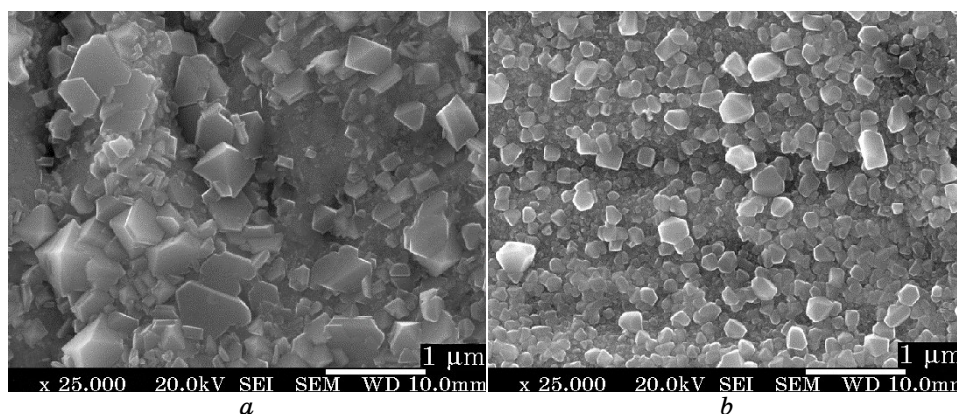


Fig. 2. SEM micrographs of surface morphology of oxide films on 42CrNiMo samples (*a*) and Cr18Ni10Ti samples (*b*) after 500 hours of autoclave testing.

it almost does not differ from the micrographs given in Fig. 2.

3.3. Estimation of the amount of metal transformed into oxide after long-term autoclave tests by chemical removing corrosion products from the surface of the samples

The results of autoclave tests revealed that mass gain of 42CrNiMo samples was 9 mg/dm^2 after 10 000 hours of testing, and Cr18Ni10Ti samples— $2\text{--}3 \text{ mg/dm}^2$. A greater mass gain of 42CrNiMo samples does not mean lower corrosion resistance. Two mutually competing processes occur during oxidizing of similar materials: the formation of oxide film results in a mass gain; dissolution/spalling of the outer layers of the oxide film—a mass loss. To establish the valid corrosion rate is possible only after establishing the actual amount of metal lost during corrosion process. It becomes possible only after removing the oxide film, which has a strong adhesion to the metal surface.

According to GOST 9.908-85 [23], it is advisable to implement the mass index of corrosion for materials that oxidize with formation of loose or soluble corrosion products on the surface. The mass index of corrosion reflects the mass loss per unit of surface area. It is necessary to remove the oxide film from the surface of the sample to determine the mass of the material that transformed into oxide during testing. The removal of the oxide film is regulated by ISO 8407:1991 [25]. The methods specified in this standard are designed to remove corrosion products without significant dissolution of the base metal. This allows estimating accurately the corrosion losses of samples after exposure in a corrosion environment.

Based on the experience of performing similar works on the removal of corrosion products formed on samples during autoclave tests at 350°C and 16.5 MPa [26], a method was chosen that consists in the oxidation of the constituent oxide films in a KMnO_4 solution and subsequent two-stage etching in the solution of EDTA (ethylenediaminetetraacetic acid) and H_3Cit (citric acid) at temperatures in the range of $90\text{--}160^\circ\text{C}$. The micrograph of the 08Cr18Ni10Ti stainless-steel sample surface after autoclave testing for 3500 hours and after different stages of the oxide film removal process is given in Fig. 3. The appearance of the oxide films indicates that one cycle of surface etching after KMnO_4 treatment is sufficient.

Evaluation of the effect of the studied solutions for removing the oxide film revealed that the etching stages do not result in significant dissolution of the base metal by the method described above. The mass change of the samples after one stage (cycle) of removal did not exceed 0.25 mg/dm^2 . Mainly the components of the oxide film undergo oxidation in the KMnO_4 solution. Therefore, it can be assumed with some certainty that, because of sequential treatment of the samples with the

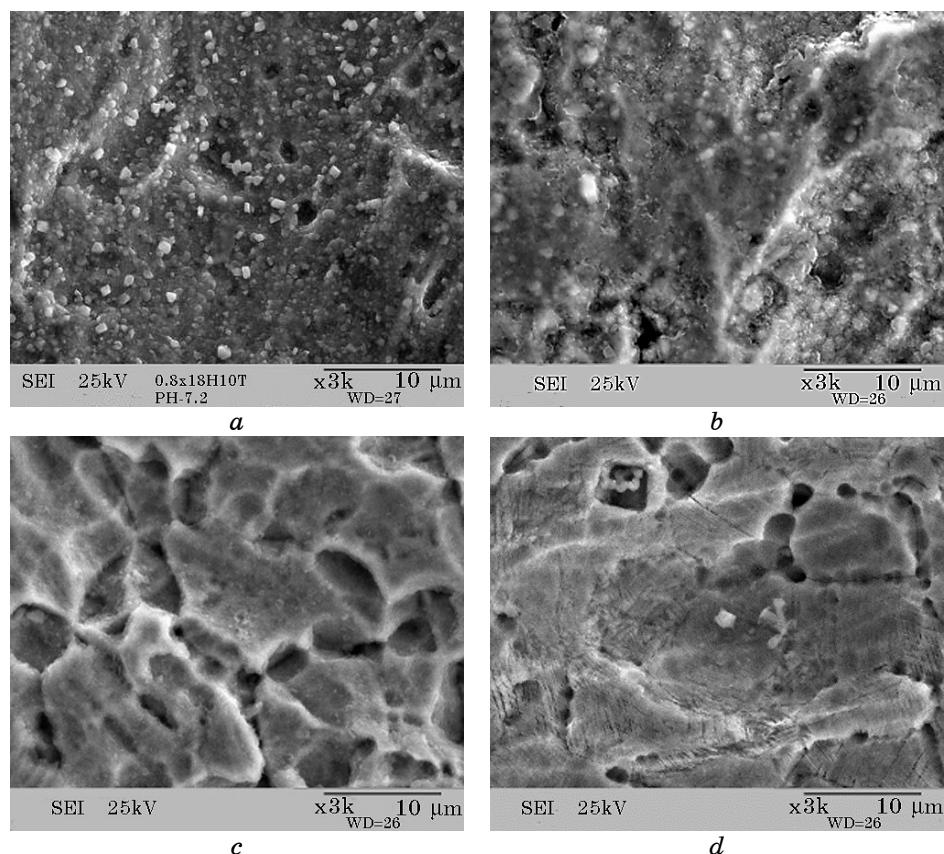


Fig. 3. SEM micrographs of surface morphology of 08Cr18Ni10Ti samples after autoclave testing and after different stages of oxide film removal: *a*—after autoclave testing, 3500 hours; *b*—oxidation in KMnO_4 solution; *c*—etching for 4 hours in EDTA and H_3Cit ; *d*—etching for 4 hours in EDTA and H_3Cit .

specified solutions, only the oxide layer is removed, without significant dissolution of the base metal.

When removing the oxide film from the surface of the samples of each batch, control samples of the same alloys, but with an unoxidized surface, were used to confirm significant etching of the base by solutions. After three surface treatments of 06Cr18Ni10Ti and 08Cr18Ni10Ti samples, it was established that the mass change before and after testing did not exceed 1 mg/dm^2 for the first treatment cycle, and 0.25 mg/dm^2 for subsequent treatment cycles, which, according to [25], makes this recipe acceptable for chemical removal of the oxide film without significant effect on the base metal.

It should be noted that the specified recipe had a significant effect on the metallic base of the 42CrNiMo alloy samples. The weight loss of the samples during processing reached 3 mg/dm^2 in one cycle. It was decided to reduce the processing temperature from 160°C to 95°C to reduce the effect on the base metal. This resulted in lower losses of the base metal (2 mg/dm^2), but the surface of the samples after processing remained dark and without a characteristic metallic lustre. Since this method of removing oxide films formed during autoclave tests proved to be the most optimal, its composition and processing parameters were optimized for the 42CrNiMo alloy.

The dependence of the mass change of austenitic stainless steels samples and chromium-nickel alloy, pre-oxidized in an aqueous environment at a temperature of 350°C and a pressure of 16.5 MPa after removal of oxide films, on the testing exposure time is shown in Fig. 4. According to the obtained results, not all the oxide film transfers into the aqueous environment during autoclave tests. The amount of metal that has turned into oxides increases with the exposure time of the autoclave testing.

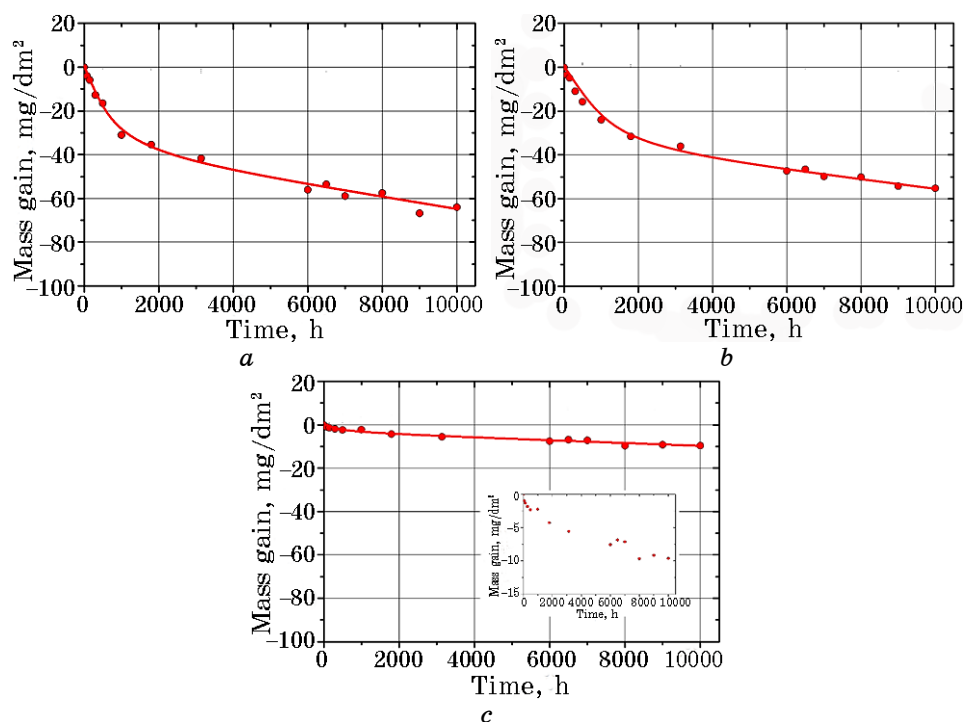


Fig. 4. Mass change of samples after autoclave tests at 350°C and 16.5 MPa and chemical removal of oxide films: *a*—06Cr18Ni10Ti; *b*—08Cr18Ni10Ti; *c*—42CrNiMo.

At the initial stages of testing (up to 1000–1800 hours), all steel samples were characterized by a high rate of oxidation, that was evidenced by a more intense mass change after removing the remains of the oxide film. The rate of mass loss decreases with increasing testing exposure time. The first 1000 hours of testing resulted in a metal mass loss of $\cong 30 \text{ mg/dm}^2$ for 06Cr18Ni10Ti samples (Fig. 4, *a*) and $\cong 25 \text{ mg/dm}^2$ for 08Cr18Ni10Ti (Fig. 4, *b*), which corresponds to an average mass loss rate of $0.030 \text{ mg}/(\text{dm}^2 \cdot \text{h})$ and $0.025 \text{ mg}/(\text{dm}^2 \cdot \text{h})$, respectively. The average rate of mass loss over 10 000 hours was $\cong 0.0064 \text{ mg}/(\text{dm}^2 \cdot \text{h})$ for the 06Cr18Ni10Ti steel samples and $\cong 0.0055 \text{ mg}/(\text{dm}^2 \cdot \text{h})$ for the 08Cr18Ni10Ti. In accordance with the existing ideas about corrosion, such damping curve of the dependence of the mass change on the testing exposure time confirms the protective properties of the oxide films formed on the samples.

Based on the results of measuring the mass change of the 42CrNiMo alloy samples after removing the oxide films (Fig. 4, *c*), the rate of transformation of the metal into the oxide for this alloy is much lower and is $0.0022 \text{ mg}/(\text{dm}^2 \cdot \text{h})$ in the first 1 000 hours, in contrast to the average rate for Cr18Ni10Ti steels, which is about $0.0255 \text{ mg}/(\text{dm}^2 \cdot \text{h})$ for the same period. During longer tests (more than 1 000 hours), the rate of mass loss of 42CrNiMo alloy samples decreases by almost 2 times and is $0.0010 \text{ mg}/(\text{dm}^2 \cdot \text{h})$, while for Cr18Ni10Ti steels, a decrease of almost 4.5 times was registered. The change in corrosion rate over time can be estimated by the slope of the mass loss curve shown in Fig. 4, *c*.

Summarizing the given results, it can be concluded that the 06Cr18Ni10Ti and 08Cr18Ni10Ti steels are oxidized at almost the same rates, which was shown by the results of the mass change after autoclave tests and after removing the oxide films. The results of estimation the mass of lost metal during oxidation revealed that the corrosion resistance of the 42CrNiMo alloy is almost 5–6 times higher than that of austenitic stainless steels of the Cr18Ni10Ti grade. The obtained experimental results, with appropriate reduction, allow estimating the following:

- dissolution coefficient of outer surface layers of oxide films during corrosion of steels 06Cr18Ni10Ti, 08Cr18Ni10Ti and 42CrNiMo alloy;
- the kinetics of the corrosion products transfer to the corrosion environment at the initial stage (up to 1000 hours) and during long-term (more than 2000 hours) testing/operation.

4. TEST RESULTS REDUCTION

4.1 Dissolution coefficient of outer surface layers of oxide film

Based on gravimetric data of the mass change (Fig. 1), one can draw a

false conclusion that the 42CrNiMo alloys possess the lowest corrosion resistance due to the fact that it has the greatest mass gain. Removing the remains of oxide films made it possible to estimate the amount of metal that reacted with the corrosion environment and transformed into oxide (Fig. 4), which, in turn, allows calculating the amount of oxygen necessary for the formation of oxides Fe_2O_3 , Fe_3O_4 , Cr_2O_3 , NiO . The amount of oxygen spent on the formation of oxides corresponds to the mass change in the case if the surface layers of the oxide film do not dissolve.

The method of chemical removal of oxide films was implemented because the etching stage would not result in a significant dissolution of the alloy material that was not preliminary oxidized. Only the oxide film formed during the autoclave tests undergoes oxidation in the KMnO_4 solution. At the additional treatment of samples from which the oxide film was completely removed in the above-mentioned solutions, the mass loss after chemical removal did not exceed 0.25 mg/dm^2 . Therefore, with a certain probability, it can be assumed that, because of sequential treatment of samples with the proposed solutions, only the oxide layer is removed, without significant dissolution of the metal base.

Figure 5 shows the summarized results of measuring the mass change of 06Cr18Ni10Ti (Fig. 5, *a*) and 08Cr18Ni10Ti (Fig. 5, *b*) steel samples at different stages of autoclave testing, mass changes after removing oxide films, and a calculated curve showing the amount of oxygen required for corrosion process. The generalized results reveal that if the dissolution of the surface layers of the oxide film did not occur, then during 10000 hours of testing in the aqueous environment of the composition of the VVER-1000 primary coolant at a temperature of

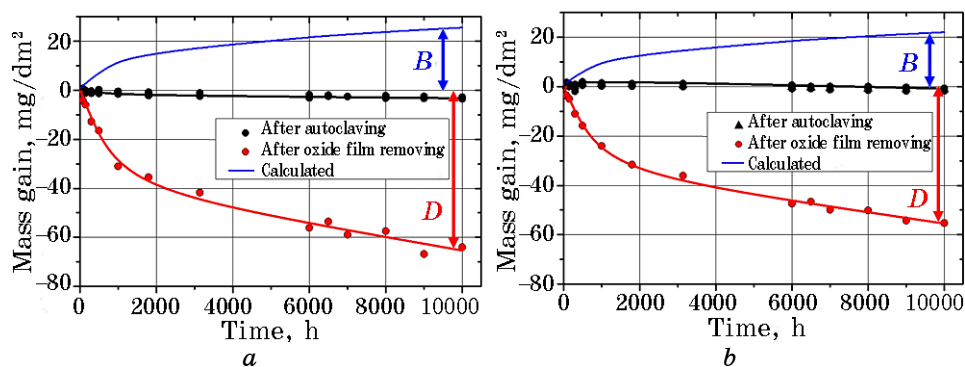


Fig. 5. Mass change of 06Cr18Ni10Ti (*a*) and 08Cr18Ni10Ti (*b*) samples at different stages of testing: — calculated mass change in the of the sample taken into account absorbed oxygen, ■—mass change of studied sample, ●—mass change of sample without taking into account the oxide film (after oxide removal).

TABLE 2. Total calculated mass gain (B), amount of lost metal (D) and dissolution coefficient (a) of oxide films of the studied alloys samples after 10 000 hours of autoclave tests.

Material	Mass gain (B), mg/dm ²	Metal loss (D), mg/dm ²	Dissolution coefficient (a), %
42CrNiMo	9.15	-9.6	≅ 0
06Cr18Ni10Ti	25	-64	31
08Cr18Ni10Ti	22	-55	30

350°C and a pressure of 16.5 MPa, the mass gain of the samples would be almost the same ≅ 25.6 mg/dm² and 22.0 mg/dm² for 06Cr18Ni10Ti and 08Cr18Ni10Ti steels, respectively (Table 2).

The obtained results made it possible to calculate the dissolution coefficient (a) of oxide films formed during autoclave tests. This coefficient is the ratio of the mass of the oxide film that has transferred to the corrosion environment to the total mass of the oxide film that was formed during oxidation of the sample. For the above-specified parameters of the autoclave tests, the dissolution coefficient was almost the same and was 31% and 30% for steels 06Cr18Ni10Ti and 08Cr18Ni10Ti, respectively (Table 2).

When removing oxide films from 42CrNiMo samples, it was established that the amount of lost material (-9.6 mg/dm²) almost coincides with the mass gain of the samples during the test (9.15 mg/dm²). However, this is not valid, because the amount of lost metal should be ≅ 22 mg/dm² (additional curve in Fig. 6). Therefore, it can be assumed that the recipes developed and tested for austenitic stainless steels do not allow removing completely the oxide film from the surface of the

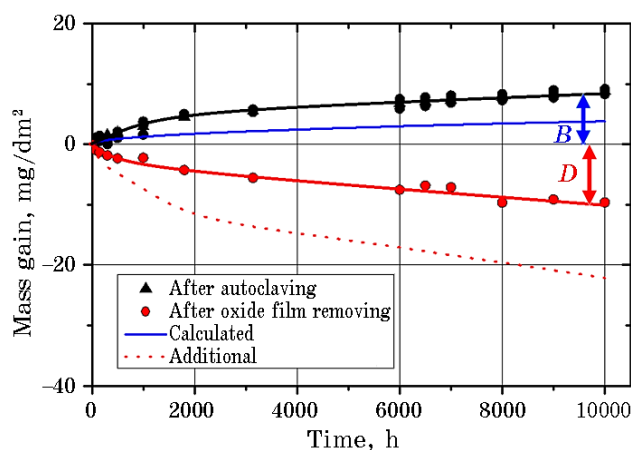


Fig. 6. Mass change of 42CrNiMo samples at different stages of testing.

42CrNiMo sample. That is, it is likely that the recipes need to be adapted for processing 42CrNiMo alloy. Nevertheless, the obtained results allowed concluding confidently that the dissolution coefficient of oxide films on 42CrNiMo samples is insignificant or even equal to zero.

4.2. Kinetics of corrosion and transfer of corrosion products to the corrosion environment

Formulas that describe the corrosion process are of great practical importance. They are part of majority of computer codes for the thermo-mechanical analysis of both core structural materials and nuclear fuel assemblies. Since the corrosion process affects, at least, the thermal conductivity of the workpiece surface (the thermal conductivity of the oxide is lower than the thermal conductivity of the base metal) and the mechanical characteristics (due to a decrease in the thickness of the workpiece or cladding). Calculations of corrosion processes are important in predicting the amount of corrosion products that can transfer to the corrosion environment (the primary coolant), which purity requires severe limitations.

The corrosion kinetics of metals and alloys can be approximated by several laws: linear, parabolic, cubic, and logarithmic [19]. The choice of one or another approximation law should be established by experimental results, which may have statistical scatter. For most metals, the corrosion kinetics is described by a formula of the following type:

$$\frac{\Delta m}{S} = A \cdot t^n, \quad (1)$$

where: Δm —mass change of sample, mg; S —surface area of sample, dm^2 ; t —exposure time, hours; A —proportionality factor; n —the degree of reaction, which depends on the type of material and oxidation conditions, for reactor conditions it is in the range from 0.33 to 1.0. The degree of reaction (n) defines the approximation law.

The experimental results of measuring the mass change of samples during autoclave tests at 350°C and 16.5 MPa and after chemical removal of oxide films are presented in logarithmic coordinates in Fig. 7. The obtained results for steels of the Cr18Ni10Ti grade are superimposed on two segments. On the first segment, the results of tests with exposure time up to 1000 hours are given and are characterized by an index of power (n) equal to 0.817 and 0.720 for steels 06Cr18Ni10Ti and 08Cr18Ni10Ti, respectively (Table 3). On the second segment, the test results of testing for more than 1000 hours are given, and the n value is 0.347 and 0.352 for steels 06Cr18Ni10Ti and 08Cr18Ni10Ti, respectively.

The experimental results of measuring the mass change of

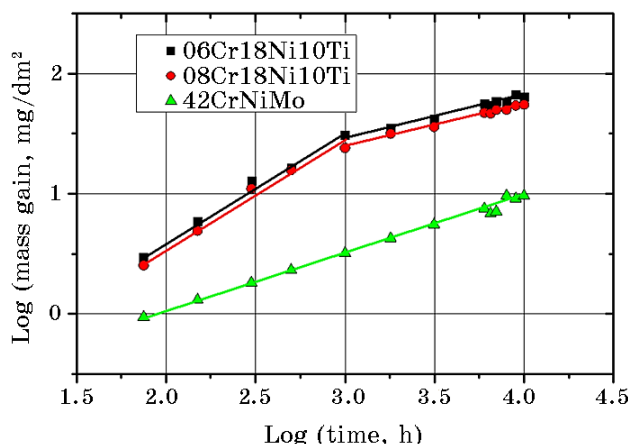


Fig. 7. Mass change of samples after autoclave testing at 350°C and 16.5 MPa and chemical removal of oxide films in logarithmic coordinates.

42CrNiMo samples in logarithmic coordinates are superimposed on one segment. The index n of formula 1 for the 42CrNiMo alloy is 0.510. If n is calculated for short-term (up to 1000 hours) and long-term (more than 1000 hours) test periods, it will be 0.509 and 0.546, respectively.

5. DISCUSSION OF RESEARCH RESULTS

The results of corrosion resistance tests of steels 06Cr18Ni10Ti, 08Cr18Ni10Ti and 42CrNiMo alloy in the model solution of the VVER-1000 primary coolant at a temperature of 350°C and a pressure of 16.5 MPa were obtained. At the first stage of the research, the corrosion resistance of the alloys was estimated basing on the mass change, the appearance of the samples, and the morphology of the oxide films.

The results of the autoclave tests revealed that the 42CrNiMo alloy samples oxidize with mass gain unlike the Cr18Ni10Ti steel samples. After 10000 hours of testing, the mass gain of the 42CrNiMo alloy samples was 9 mg/dm², and that of Cr18Ni10Ti steels was 2–3 mg/dm².

TABLE 3. Constants for calculating the amount of oxidized metal for steels 06Cr18Ni10Ti, 08Cr18Ni10Ti and 42CrNiMo alloy.

Material	0–1000 hours		1 000–10 000 hours	
	n	A	n	A
42CrNiMo	0.509 ± 0.04	0.0878 ± 0.03	0.546 ± 0.07	0.0630 ± 0.03
06Cr18Ni10Ti	0.817 ± 0.04	0.1084 ± 0.03	0.347 ± 0.02	2.6526 ± 0.66
08Cr18Ni10Ti	0.720 ± 0.05	0.1692 ± 0.06	0.352 ± 0.01	2.1686 ± 0.27

A greater mass gain of the 42CrNiMo samples does not mean that this alloy possesses lower corrosion resistance. During the corrosion process of stainless steels, two mutually competing processes occur: the formation of an oxide film, which results in a mass gain; and the dissolution/spalling of the surface layers of the oxide film—mass loss. The mass loss of Cr18Ni10Ti samples under the conditions of the primary coolant is caused by the formation of an oxide film with several layers of different composition. The outer layer of the oxide film partially dissolves in the corrosion environment under certain conditions, which results in a mass loss. In some cases (significant fluctuations in the pH of the corrosion environment, a high flow rate of the coolant), the mass loss can result in a negative value of the mass index of corrosion. It is possible to establish the valid corrosion rate only after establishing the actual amount of metal lost during corrosion, which is possible only after removing the remains of the oxide film from the surface.

The results of the removal of oxide films revealed that not all corrosion products are transferred to the aqueous environment during autoclave tests. The amount of metal that transforms into oxides increases with increasing exposure time of autoclave tests.

Figure 8 shows the mass change of stainless-steel samples after autoclave tests and chemical removal of oxide films in comparison with data from literature sources obtained during inspection of pipes at ZNPP-3, NVNPP-2, KolNPP-2, Paks NPP-3 [22, 27, 28]. The results obtained during the performance of this research are in the range of experimental results obtained at NPPs. This indicates that the test parameters and the composition of the corrosion environment were selected correctly, and the influence of irradiation on corrosion process-

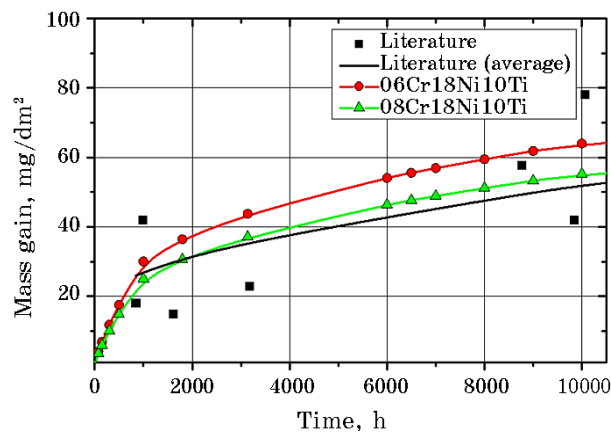


Fig. 8. Mass change of stainless steels according to the results obtained during the performance of this research and according to the results in literature sources [27].

es is not significant.

Based on the results of measuring the mass change of the samples, it can be concluded that the corrosion rates of 06Cr18Ni10Ti and 08Cr18Ni10Ti steels are almost the same. The rate of transformation of metal to oxide for the 42CrNiMo alloy is much lower and is 0.0022 g/(dm²·h) in the first 1000 hours, in contrast to the average rate for Cr18Ni10Ti steels, which is about 0.0550 mg/(dm²·h) during the same time interval. In longer tests (more than 1 000 hours), the corrosion rate decreases by almost 2 times and for the 42CrNiMo alloy is 0.0010 mg/(dm²·h), while for Cr18Ni10Ti steels the corrosion rate decreases by almost 4–5 times.

To estimate the mass loss, it is necessary to use formula 1 with the coefficients given for each studied material (Table 3). Calculations revealed that during one reactor cycle (7500 hours) of Cr18Ni10Ti steels operation in the core, a mass loss of metal is almost 54 mg/dm² (average value for 06Cr18Ni10Ti and 08Cr18Ni10Ti), that is equal to 0.68 μm. The next reactor cycle will result in the loss of only 0.19 μm of metal. For the 42CrNiMo alloy, losses for the first and second reactor cycles will be 0.1 μm and 0.04 μm, respectively. Calculations revealed that the 42CrNiMo alloy is more resistant to corrosion damage under the conditions of the primary coolant.

An equally important parameter that characterizes the corrosion resistance of the 42CrNiMo alloy is the dissolution index of the oxide film, which has a low value. While for Cr18Ni10Ti steels, it is ≈ 30%. The surface area of Cr18Ni10Ti stainless steel components in the primary circuit of VVER-1000 is 12.500 m², and in the first reactor cycle, the transfer of corrosion products in the reactor core will amount to 20.25 kg. While the transfer of corrosion products into the circuit will be minimal or absent for 42CrNiMo alloy components.

CONCLUSIONS

1. The paper presents the results of corrosion tests of 06Cr18Ni10Ti, 08Cr18Ni10Ti steels and 42CrNiMo alloy tubular samples in a model environment of the primary coolant of a light water reactor at a temperature of 350°C and a pressure of 16.5 MPa for 10 000 hours. The corrosion resistance of the samples was estimated by the mass change of the samples after testing, the appearance of the samples, the microstructure of the oxide films and the amount of oxidized metal.
2. The results of autoclave tests in an aqueous environment at a temperature of 350°C and a pressure of 16.5 MPa revealed that, unlike the Cr18Ni10Ti steel samples, the 42CrNiMo samples oxidized with mass gain. After 10 000 hours of testing, the mass gain for the chrome-nickel alloy was only ≈ 9 mg/dm², and for steels—0--2 mg/dm².
3. After autoclave tests, the surface of 42CrNiMo alloy samples and

06Cr18Ni10Ti and 08Cr18Ni10Ti steel samples had different colours but high reflectivity. Based on the general idea of corrosion, the high reflectivity of the surface and the absence of loose deposits on the surface indicate the high corrosion resistance of the studied materials. The study of the morphology of the oxide films surface revealed that during autoclaving, compact pyramidal-shaped microcrystalline precipitates form on their surface.

4. The kinetics of mass change in of 06Cr18Ni10Ti and 08Cr18Ni10Ti steel samples after testing and after chemical removal of oxide films had a similar character. The mass of the samples during the entire time of the autoclave tests did not change significantly (0–2 mg/dm²). Chemical removal of the oxide film from the surface revealed that for 10 000 hours of testing, corrosion losses were up to 55 mg/dm².

5. It was established that the dissolution coefficient of oxide films, which is the ratio of the mass of the oxide film components that has transferred into the corrosion environment, to the total mass of oxide that was formed during oxidation, is equal to zero for the 42CrNiMo alloy. Moreover, this coefficient was 30% on average for steels 06Cr18Ni10Ti and 08Cr18Ni10Ti. This indicates that the transfer of corrosion products into the coolant will actually be absent for the 42CrNiMo alloy.

6. The dependences that approximate the corrosion kinetics of Cr18Ni10Ti steels and 42CrNiMo alloy were obtained. At the initial stages of corrosion (up to 1000 hours), the mass loss was described by a power law with indices of power of 0.817 and 0.720 for 06Cr18Ni10Ti and 08Cr18Ni10Ti steels, respectively. In longer tests, the power indices were 0.347 and 0.352, respectively. The results of measuring the mass change for the 42CrNiMo alloy samples, obtained over the entire period of the research, were described by one law with an index of power of 0.510.

7. Basing on the research results, it was concluded that the 42CrNiMo alloy possess higher corrosion resistance, and the oxide films that grow on its surface do not dissolve significantly in the corrosion environment, in contrast to the Cr18Ni10Ti steels with the dissolution coefficient of oxide films of 30%.

REFERENCES

1. V. G. Krickij, Yu. A. Rodionov, I. G. Berezina, E. V. Zelenina, A. V. Gavrilov, A. P. Shukin, A. I. Fedorov, M. G. Shedrin, and A. V. Galanin, *Formirovanie i Udalenie Otlozheniy v 1-om Konture AES s VVER* [Formation and Removal of Deposits in the 1st Circuit of the VVER Nuclear Power Plant] (Sankt-Peterburg: Beresta: 2011) (in Russian).
2. P. Cohen, *Water Coolant Technology of Power Reactors* (Am. Nucl. Soc.: 1980).
3. Y. Solomon, *An Overview of Water Chemistry for Pressurized Water Reactors*,

- Proceedings of Water Chemistry of Nuclear Reactor Systems* (Br. Nucl. Energy Soc.: 1978) p. 101.
4. B. A. Kalin, *Atomnyy Ehkspert*, Nos. 2–3 (2019) (in Russian).
 5. K. Fukuya, K. Fujii, H. Nishioka, and Y. Kitsunai, *J. Nucl. Sci. Technol.*, **43**, No. 2: 159 (2006).
 6. F. L. LaQue and M.A. Cordovi, *The Corrosion of Pressure Circuit Materials in Boiling and Pressurized-Water Reactors* (Special Report 69) (London: Iron Steel Inst.: 1961), p. 157.
 7. M. I. Solonin, V. P. Kondratev, S. N. Votinov, V. N. Rechytssky, Yu. Y. Kazennov, A. B. Alekseev, and V. P. Kolotushkyn, *Voprosy Atomnoi Nauki i Tekhniki*, **1**(52): 13 (1995) (in Russian).
 8. M. I. Solonin, A. B. Alekseev, Y. I. Kazennov, V. F. Khramtsov, V. P. Kondrat'ev, T. A. Krasina, V. N. Rechitsky, V. N. Stepankov, and S. N. Votinov, *Nucl. Mater.*, **233–237**: 586 (1996).
 9. M. I. Solonin, A. B. Alekseev, S. A. Averin, Yu. A. Burenkov, V. M. Chernov, B. K. Kardashev, V. P. Kondrat'ev, A. V. Kozlov, V. N. Rechitsky, and S. N. Votinov, *J. Nucl. Mater.*, **258–263**, Part 2: 1762 (1998).
 10. A. V. Vatulin, V. P. Kondratev, V. N. Rechickiy, and M. I. Solonin, *Metallovedenie i Termicheskaya Obrabotka Metallov*, **11** (593): 19 (2004) (in Russian).
 11. B. A. Gurovich, A. S. Frolov, D. A. Maltsev, E. A. Kuleshova, S. V. Fedotova, and I. V. Fedotov, *Materialy XI Konferencii po Reaktornomu Materialovedeniyu (NIIAR, Dimitrovgrad, May 27–31, 2019)* (in Russian).
 12. S. A. Kushmanov, I. N. Vasilchenko, V. V. Vyalitsyn, K. V. Zinin, I. I. Ionova, K. Yu. Kurakin, V. M. Makhin, A. N. Churkin, Yu. I. Mironov, S. E. Sirotkin, and V. D. Risovanyy, *Vopr. At. Nauki Tekh., Ser.: Obespechenie Bezop. AES*, **30**: 15 (2011) (in Russian).
 13. V. I. Prokhorov, V. D. Risovanyy, and S. A. Kushmanov, *Vopr. At. Nauki Tekh., Ser.: Obespechenie Bezop. AES*, **30**: 5 (2011) (in Russian).
 14. G. V. Kulakov, S. A. Ershov, Yu. V. Konovalov, M. V. Leonteva-Smirnova, V. N. Rechickiy, M. V. Skupov, and V. V. Fedotov, *Yadernoe Topливо Novogo Pokoleniya dlya AES: Tezisy Nauchno-Tekhnicheskoy Konferentsii AO 'TVEL' (Oct., 2018, Sochi)*, p. 37 (in Russian).
 15. G. V. Kulakov, S. A. Ershov, Yu. V. Konovalov, M. V. Leonteva-Smirnova, V. N. Rechickiy, M. V. Skupov, V. V. Fedotov, V. Yu. Shishin, and A. A. Sheldyakov, *Tezisy Dokladov na XI Konferentsii po Reaktornomu Materialovedeniyu (May 27–31, 2019, Dimitrovgrad)*, p. 37 (in Russian).
 16. G. V. Kulakov, Yu. V. Konovalov, A. V. Vatulin, A. A. Kosurov, V. Yu. Shishin, A. A. Sheldyakov, A. I. Romanov, O. A. Morozov, and O. B. Samoylov, *At. Energ.*, **130**, No. 4: 208 (2021) (in Russian).
 17. V. Zuyok, R. Rud, M. Tretyakov, N. Rud, Ya. Kushtym, I. Dykyy, I. Shevchenko, H. Rostova, and V. Shtefan, *Probl. At. Sci. Technol.*, No. 4 (140): 89 (2022).
 18. B. A. Gurovich, A. S. Frolov, D. A. Maltsev, E. A. Kuleshova, and S. V. Fedotova, *Sb. Tezisev Dokladov 15-y Mezhdunarodnoy Nauchno-Prakticheskoy Konferentsii po Atomnoy Ehnergetike, 2019*, p. 10 (in Russian).
 19. A. A. Slobodov, V. I. Zarembo, V. G. Krickij, L. V. Puchkov, and V. M. Sedov, *Zh. Prikl. Khim.*, **59**, No. 5: 1030 (1986) (in Russian).
 20. I. Yu. Dobrovolskaya, *Nauchno-Tekhnicheskoye Soveshchanie 'Vodno-*

- Khimicheskiy Rezhim Deystvuyushchikh AS (Sep. 19–21, 2000, Moskva)* (in Russian).
21. V. G. Kritskiy, 3rd Res. Coord. Meet. 'Modelling of Transport of Radioactive Substances in Primary Circuit of Water Cooled Reactors (Nov. 6–10, 2000, Buenos Aires, Argentina).
 22. N. Gabor, P. Tilky, T. Pintér, A. Horvath, and R. Schiller, *Nucl. Technology*, **136**: 331 (2001).
 23. State Standard 1987-01-01. Edinaya Sistema Zashity ot Korrozii i Stareniya. Metally i Splavy. Metody Opredeleniya Pokazateley Korrozii i Korroziionnoy Stoykosti. GOST 9.908-85. [Unified System of Corrosion and Ageing Protection. Metals and Alloys. Methods for Determination of Corrosion and Corrosion Resistance Indices. GOST 9.908-85] (Moskva: Izdatelstvo Standartov: 1990), p. 17 (in Russian).
 24. V. Krasnorutskyy, I. Petelguzov, V. Grytsyna, V. Zuyok, M. Tretyakov, R. Rud, O. Slabospyska, N. Ishchenko, and N. Svichkar, *Journal of Materials Sciences and Applications*, **2**, No. 2: 10 (2016).
 25. *ISO 8407:2021. Corrosion of Metals and Alloys – Removal of Corrosion Products from Corrosion Test Specimens.*
 26. V. A. Zuyok, R. A. Rud, I. A. Petelguzov, and M. V. Tretyakov, *Vopr. At. Nauki Tekh., Ser.: Fiz. Radiats. Povrezhdenii Radiats. Materialoved.*, No. 1 (65): 141 (2010) (in Russian).
 27. V. G. Kritskiy, Yu. A. Rodionov, P. S. Styazhkin, and E. V. Zelenina, *Meropriyatiya po Snizheniyu Moshnosti Dozy v Pomescheniyakh 1-go Kontura AES* [Measures to Reduce the Dose Rate in the Premises of the 1st Circuit of the NPP] (Sankt-Peterburg: 2010) (Prepr./VNIPIET.2010) (in Russian).
 28. V. G. Kritskiy, Yu. A. Rodionov, P. S. Styazhkin, and I. G. Beresina, *Masopereenos i Formirovanie Otlozheniy v 1 Konture AS s Reaktorami VVER i RBMK* [Mass Transfer and Deposit Formation in the 1st Circuit of NPP with VVER and RBMK Reactors] (Sankt-Peterburg: 2003) (Prepr./VNIPIET. No. 002-003, 2003) (in Russian).