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CORROSION RESISTANCE OF THE PRODUCED BY UKRAINIAN ENTERPRISES MAIN STRUCTURAL MATERIALS FOR THE PRIMARY CIRCUIT OF PRESSURIZED WATER REACTORS TO SUBSTANTIATE ITS APPLICATION AND FURTHER LICENSING

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INTRODUCTION

Ukraine and Eastern European countries that operate russian-designed VVER power units (VVER-1000, VVER-440) are intensively working to diversify suppliers of nuclear fuel, equipment and core components. The intensification of work is due to the fact that until recently, almost the entire infrastructure to support the operation of these power units, including the manufacturing of nuclear fuel, rod cluster control assemblies (RCCA) for VVER-1000 reactors and follower assemblies for VVER-440 reactors, remained in the RF.

A new nuclear fuel from an alternative supplier, Westinghouse company, was introduced due to the successful implementation of the Ukraine Nuclear Fuel Qualification Project (UNFQP)[1] [2] [3]. Westinghouse company has established the manufacturing of nuclear fuel for VVER-1000 reactors and plans to manufacture fuel for VVER-440 reactors, but is unable to provide both Ukrainian and EU NPPs operating VVER reactors with absorbing rods, which are an integral part of the nuclear fuel cycle. In the short term, the manufacturing of RCCAs and follower assemblies will be organized at the enterprises of the SE «NNEGC «Energoatom» using the structural materials produced at Ukrainian enterprises. Scientific support for this work is provided by the NFC STE NSC KIPT (Kharkiv city) and the E.O. Paton Electric Welding Institute (Kyiv city).

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[1] A.M. Abdullayev, V.Z. Baydulin, A.I Zhukov. «Design and Performance of South Ukraine Nuclear Power Plant Mixed Cores with Westinghouse Fuel", Proceedings of IAEA Technical Meeting on Fuel Design and Licensing of Mixed Cores for Water Cooled Reactors" (December 12–14, 2011, Vienna, Austria). P. 101–102.

[2] J. Hoglund, O. Riznychenko, R. Latorre, P. Lashevych. Performance of the Westinghouse WWER-1000 fuel design. International conference on WWER fuel performance, modelling and experimental support. Helena Resort (2011), 245–256.

[3] V. Skalozubov, S. Melnik, O. Pantak, V. Gryb, V. Spinov, Yu. Komarov. Analysis of experience, safety and prospects of diversification of nuclear fuel at nuclear power plants, Technology Audit and Production Reserves – № 4/1(48), 2019, DOI:10.15587/2312-8372.2019.180740

Moreover, SE «NNEGC «Energoatom» has signed a number of agreements on intentions for the construction of small modular reactors (SMRs) in Ukraine. Currently, several promising SMR designs from well-known companies are being considered: SMR-160 (Holtec), AP300™ (Westinghouse), IPWR (NuScale Power) and Rolls-Royce SMR. The construction of SMRs in Ukraine will necessarily involve localization of manufacturing of components and structural elements at Ukrainian enterprises, as this has become a common practice in recent years when signing contracts, for example, between SE «NNEGC «Energoatom» and Westinghouse company.

The above examples are SMRs with pressurized light water with coolant temperatures up to 350°C at power operation and possible transients. VVER reactors currently operated at Ukrainian NPPs are also pressurized water reactors with coolant parameters under normal operating conditions up to 350°C, 16.5 MPa for VVER-1000 and up to 316°C, 12.3 MPa for VVER-440.

In addition to zirconium alloy used to manufacture fuel rod claddings (E110, Zirlo®), guide thimbles and spacer grids (Zirlo®, Zr+1%Nb, Zr+2.5%Nb), the main structural material of the VVER core elements and reactor internals are nuclear grade chromium-nickel steels Cr18Ni10Ti (06Cr18Ni10Ti, 08Cr18Ni10Ti, 12Cr18Ni10Ti) and chromium-nickel alloy 42CrNiMo. Ukrainian enterprises have established the manufacturing of these chromium-nickel steels and alloy, as well as products made of them, including weldless tubes. However, these structural materials have not been comprehensively studied and operated under the conditions of the VVER primary water chemistry.

The objective of the study is to evaluate the main characteristics of corrosion resistance (general corrosion rate, degree of the oxide film dissolution) of austenitic chromium-nickel stainless steels of grades 06Cr18Ni10Ti, 08Cr18Ni10Ti and chromium-nickel alloy 42CrNiMo manufactured by Ukrainian enterprises to substantiate their application as the main structural material of primary circuits of the VVER and SMR pressurized water reactors and to obtain a set of scientific data necessary for further licensing of their application.

1. 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 manufacture of these tubes is currently mastered by some Ukrainian enterprises.

Table 1

Materials composition

Material	Technical Specifications	Mass fraction of elements, %							
		C	Si	Mn	Mo	Cr	Ni	Fe	S
Cr18Ni10 Ti	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	<0.20	1.0-1.5	41.0-43.0	Base	<0.6	<0.01

The preparation of samples for corrosion tests was carried out in accordance with the requirements of GOST 9.908-85. 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, H_3BO_3 – 3 g/dm^3, NH_3 – 3 mg/dm^3, KOH – 12.3 mg/dm^3, $pH_{25} = 7.2$. The testing was divided into stages. The duration of the stages was 75; 150; 300; 500; 1000; 1,800; 2,500; 6,000; 6,500; 7000; 8,000; 9,000 and 10,000 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 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.

The high-temperature corrosion resistance of materials was evaluated basing on the results of high-temperature tests at temperature range 350 – 1200°C in a water steam environment in a tubular furnace at atmospheric pressure. The maximum isothermal exposure time was 1 hour. Distilled water heated to boiling temperature was used to obtain steam. Water steam was additionally heated to a temperature of 250-300°C before entering the tubular furnace. A certain section of the steam pipeline was equipped with additional heater for that. The length of the uniform temperature area in the furnace (main kiln area of the furnace) was 500 mm. The initial temperature of the sample was in the range 100 – 300°C. The heating rate of the sample from the initial temperature to 1000°C was more than 20°C per second (the temperature was reached in less than 35 seconds). The heating rate from 1000°C to 1225°C exceeded 2°C per second (heating in less than 100 seconds).

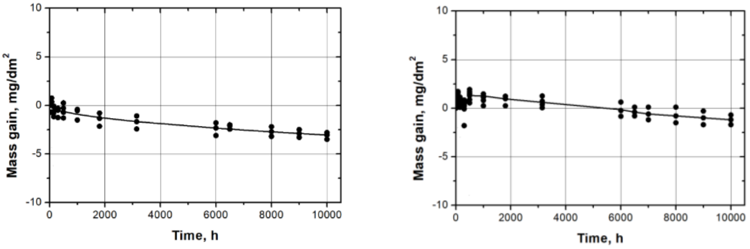
2. Results of testing of core materials under normal operating conditions

2.1. Autoclave testing

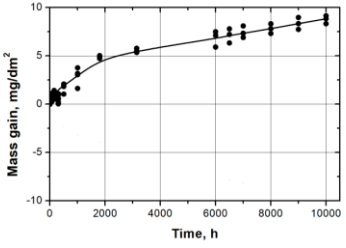
The generalized results of mass change of 42CrNiMo alloy and 06Cr18Ni10Ti and 08Cr18Ni10Ti steels samples after autoclave testing are given in Figure 1. The obtained results revealed that corrosion of 06Cr18Ni10Ti steel samples is accompanied by a mass loss (Figure 1.a).

Based on information in literature sources, the main mechanism of mass loss is the dissolution of the oxide film surface layers[4] [5]. The most intensive mass change was observed at the first stages of testing (up to ~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 exposure.

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



a (06Cr18Ni10Ti) *b* (08Cr18Ni10Ti)



c (42CrNiMo)

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

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[4] В.С. Красноруцький, І.А. Петельгузов, В.М. Грицина, М.В. Трет’яков, О.О. Слабоспицька, В.А. Зуйок, О.В. Архіпенко, В.І. Кузнєцов, Д.А. Соколов, В.М. Гладишев. Дослідження впливу ВХР на корозійні процеси матеріалів активної зони реакторів ВВЕР // Питання атомної науки і техніки. 2010. №5. Серія: Фізика радіаційних пошкоджень і радіаційне матеріалознавство (96), с. 58-66.

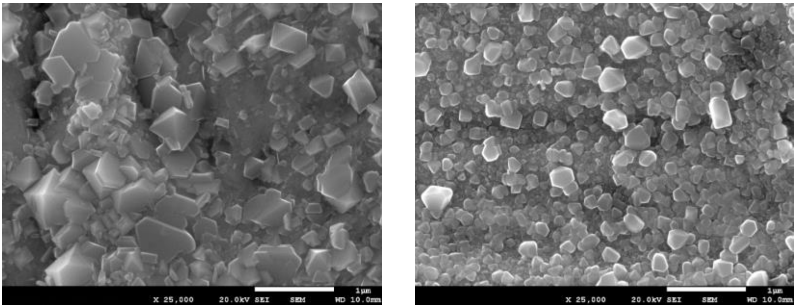
[5] Р.К. Мелехов, В.І. Похмурський. Конструкційні матеріали енергетичного обладнання. Властивості. Деградація. Київ: «Наукова думка», 2003, с. 384.

Corrosion of 42CrNiMo samples is characterized by a constant mass gain, in contrast to 06Cr18Ni10Ti and 08Cr18Ni10Ti samples. The rate of mass gain of 42CrNiMo samples at the initial stages of testing (up to 1,800...2,500 hours) 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 (Figure 1.c) is damping, which indicates the protective properties of the oxide films. The mass gain of 42CrNiMo samples was almost 9 mg/dm^2 after 10,000 hours of exposure.

2.2. Appearance of samples

The surface of the 42CrNiMo samples became a solid dark yellow (straw) color without cracks and defects, with high reflectivity after autoclave tests. The surface of 06Cr18Ni10Ti and 08Cr18Ni10Ti samples had the same dark gray color. 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 and Cr18Ni10Ti samples, it is noticeable that, compact pyramidal-shaped microcrystalline precipitates formed during autoclaving (Figure 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 most of the pyramidal precipitates on the 42CrNiMo samples have a quadrangular base (Figure 2.a), and on the Cr18Ni10Ti samples they have a pentagonal base (Figure 2.b). The surface morphology of the samples was studied at all stages of testing and it almost does not differ from the micrographs given in Figure 2.



a *b*

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

2.3. Estimation of the amount of metal transformed into oxide under long-term autoclave tests by chemical removing of 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 exposure, and Cr18Ni10Ti samples – 2...3 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 due to 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, 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 estimate the mass of the material that transformed into oxide during testing. The removal of the oxide film is regulated by ISO 8407:1991. The methods specified in this standard are designed to remove corrosion products without significant dissolution of the base metal. This allows to accurately estimate 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, 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 90-160°C[6].The micrograph of the 08Cr18Ni10Ti sample surface after 3500 hours of autoclave exposure and after different stages of the oxide film removal process is given in Figure 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 as a result of

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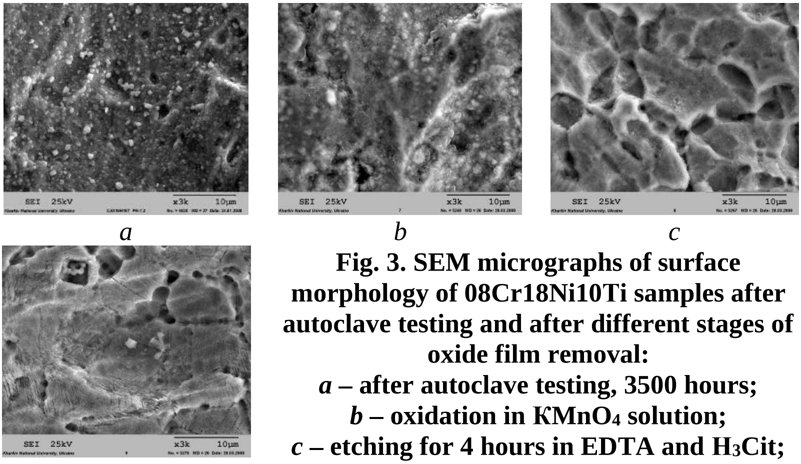
[6] Kinnunen, Petri. «ANTIOXI – Decontamination Techniques for Activity Removal in Nuclear Environments.» VTT Technical Research Centre of Finland: Espoo, Finland (2008)

sequential treatment of the samples with the 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 materials, 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. It makes this recipe acceptable for chemical removal of the oxide film without significant effect on the base metal.



a *b* *c*

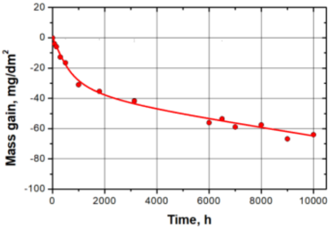
Fig. 3. SEM micrographs of surface morphology of 08Cr18Ni10Ti samples after autoclave testing and after different stages of oxide film removal:
***a* – after autoclave testing, 3500 hours;**
***b* – oxidation in $KMnO_4$ solution;**
***c* – etching for 4 hours in EDTA and H_3Cit;**
***d* – etching for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

d

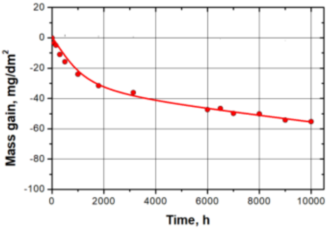
It should be noted that the specified recipe had a significant effect on the metallic base of the 42CrNiMo samples. The weight loss of the samples due to processing reached 3 mg/dm^2 in one cycle. To reduce the effect on the base metal it was decided to reduce the processing temperature from 160°C to 95°C. 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 luster. Since this method of removing oxide films formed under 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 Figure 4. According to the obtained results, not all of 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.

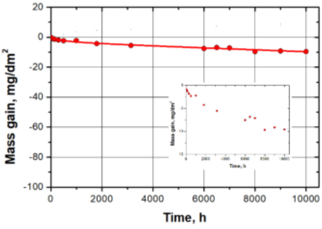
At the initial stages of testing (up to 1000...1,800 hours), all steel samples were characterized by a high rate of oxidation, that was evidenced by a more intense mass change after removing the remains of the oxide film. The rate of mass loss decreases with increasing autoclave exposure time. The first 1000 hours of testing resulted in a metal mass loss of ~30 mg/dm^2 for 06Cr18Ni10Ti samples (Figure 4.a) and ~25 mg/dm^2 for 08Cr18Ni10Ti (Figure 4.b), which corresponds to an average mass loss rate of 0.030 mg/(dm^2·h) and 0.025 mg/(dm^2·h), respectively. The average rate of mass loss over 10,000 hours was ~0.0064 mg/(dm^2·h) for the 06Cr18Ni10Ti samples and ~0.0055 mg/(dm^2·h) for the 08Cr18Ni10Ti. In accordance with the existing ideas about corrosion, such damping curve of the dependence of the mass change on the autoclave exposure time confirms the protective properties of the oxide films formed on the samples.



a (06Cr18Ni10Ti)



b (08Cr18Ni10Ti)



c (42CrNiMo)

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

Based on the results of measuring the mass change of the 42CrNiMo samples after removing the oxide films (Figure 4.c), the rate of transformation of the metal into the oxide for this alloy is much lower and is 0.0022 mg/(dm^2·h) in the first 1000 hours, in contrast to the average rate for Cr18Ni10Ti steels, which is about 0.0255 mg/(dm^2·h) for the same period of time. Longer tests (more than 1000 hours) resulted in the decrease of the mass loss rate of 42CrNiMo samples by almost 2 times and it was 0.0010 mg/($dm^2 \cdot h$), while for Cr18Ni10Ti steels, a decrease by 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 Figure 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 measurement the mass change during autoclave testing and after removing the oxide films. The results of estimation the mass of lost metal due to 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 to estimate the following:

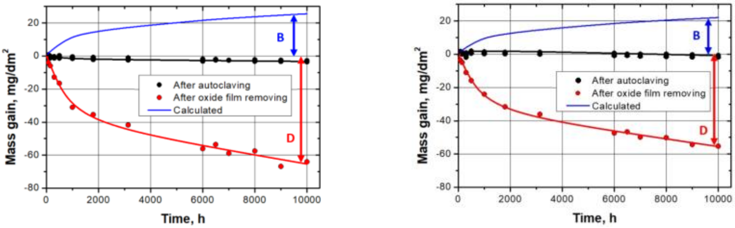
- dissolution coefficient of outer surface layers of oxide films due to corrosion of 06Cr18Ni10Ti, 08Cr18Ni10Ti steels and 42CrNiMo alloy;
- the kinetics of the corrosion products transfer to the corrosion environment at the initial stage (up to 1000 hours) and during long-term (more than 2000 hours)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

2.4. Dissolution coefficient of outer surface layers of oxide film

On the basis of gravimetric data of the mass change (Figure 1), one can draw a false conclusion that the 42CrNiMo alloy 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 (Figure 4), which, in turn, allows to calculate 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 as a result of sequential treatment of samples with the proposed solutions, only the oxide layer is removed, without significant dissolution of the base metal.

Figure 5 shows the summarized results of measurement the mass change of 06Cr18Ni10Ti (Figure 5.a) and 08Cr18Ni10Ti (Figure 5.b) 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 10,000 hours of testing in the aqueous environment of the VVER-1000 primary coolant composition at a temperature of 350°C and a pressure of 16.5 MPa, the mass gain of the samples would be almost the same: ~25.6 mg/dm^2 and 22.0 mg/dm^2 for 06Cr18Ni10Ti and 08Cr18Ni10Ti samples, respectively (Table 2).



a *b*

Fig. 5. Mass change of 06Cr18Ni10Ti (a) and 08Cr18Ni10Ti (b) samples at different stages of testing:

— – calculated mass change of the sample taking into account absorbed oxygen;

● – mass change of studied sample;

● – mass change of sample without taking into account the oxide film (after oxide removal)

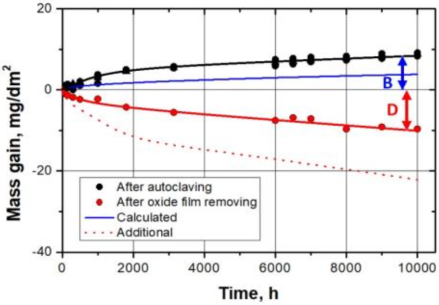


Fig. 6. Mass change of 42CrNiMo samples at different stages of testing

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/dm^2) almost coincides with the mass gain of the samples during the test (9.15 mg/dm^2). But this is not valid, because the amount of lost metal should be ~22 mg/dm^2 (additional curve in Figure 6). Therefore, it can be assumed that the recipes developed and tested for austenitic stainless steels do not allow to completely remove the oxide film from the surface of the 42CrNiMo sample. Therefore, it is likely that the recipes need to be adapted for processing the 42CrNiMo alloy. But the obtained results allowed to confidently conclude that the dissolution coefficient of oxide films on 42CrNiMo samples is insignificant or even equal to zero.

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

2.5. Corrosion kinetics 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 thermomechanical 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.

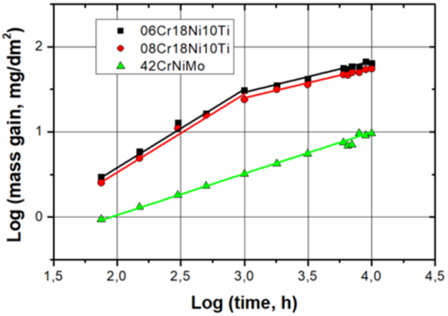


Fig. 7. Mass change of samples after autoclave testing at 350°C and 16,5 MPa and chemical removal of oxide films in logarithmic coordinates

The corrosion kinetics of metals and alloys can be approximated by several laws: linear, parabolic, cubic, and logarithmic. 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:

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

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 1.0 to 3.0. 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 Figure 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 results of autoclave exposure 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 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.

Table 3

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

Material	0 – 1000 hours		1000 – 10,000 hours	
	n	*A*	*n*	*A*
42CrNiMo	1.96	0.0084	1.83	0.0063
06Cr18Ni10Ti	1.22	0.0659	2.88	16.6324
08Cr18Ni10Ti	1.39	0.0848	2.84	9.0169

2.6. Discussion of research results

The results of corrosion resistance tests of 06Cr18Ni10Ti, 08Cr18Ni10Ti steels 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 10,000 hours of testing, the mass gain of the 42CrNiMo samples was 9 mg/dm^2, and that of Cr18Ni10Ti steels was 2...3 mg/dm^2. A greater mass gain of the 42CrNiMo samples does not mean that this alloy possess 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 operating conditions of the VVER 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 due to corrosion process, which is possible only after removing the remains of the oxide film from the surface.

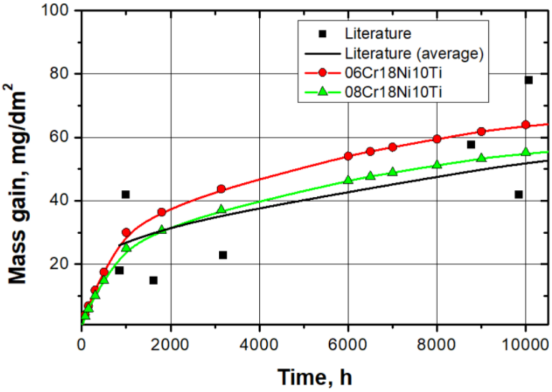


Fig. 8. Mass change of stainless steels according to the results obtained during the performance of this research and according to the results in literature sources[7]

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 autoclave exposure.

Figure 8 shows the mass change of stainless steel samples under autoclave tests and chemical removal of oxide films in comparison with data from literature sources obtained during inspection of pipes at Paks NPP. 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 processes 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 into oxide for the 42CrNiMo alloy is much lower and is 0.0022 g/(dm^2·h) in the first 1000 hours, in contrast to the average rate for Cr18Ni10Ti steels, which is about 0.0550 mg/(dm^2·h) during the same time interval. In longer tests (more than 1000 hours), the corrosion rate decreases by almost 2 times and for the 42CrNiMo alloy is 0.0010 mg/(dm^2·h), while for Cr18Ni10Ti steels the corrosion rate decreases by almost 4-5 times.

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[7] G. Nagy, P. Tilky, Á. Horváth, T. Pintér & R. Schiller (2001) Kinetic and Statistical Analysis of Primary Circuit Water Chemistry Data in a VVER Power Plant, Nuclear Technology, 136:3, 331-341, DOI: 10.13182/NT01-A3249

To estimate the mass loss, it is necessary to apply 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/dm^2 (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 m^2, 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.

3. Results of testing the construction materials of the reactor core under conditions of overheating

3.1. High-temperature corrosion kinetics of the 08Cr18Ni10Ti steel

Corrosion tests of 08Cr18Ni10Ti samples in a water steam environment for 1 hour in the temperature range from 350°C to 1225°C were carried out within this research. Increasing the time of isothermal exposure results in a mass gain of samples at all temperatures. The corrosion kinetics of 08Cr18Ni10Ti samples at 1 hour testing in a water steam environment in the temperature range from 350°C to 1225°C is decaying (Figure 9), i.e. the curve can be characterized as a power-law dependence.

The dependence of the average corrosion rate for 1 hour on the test temperature of 08Cr18Ni10Ti steel samples in water steam (Figure 10) reveals a low rate of mass gain for the samples up to a temperature of 800°C. At the same time, the mass gain does not exceed 100 mg/dm^2. A sharp mass gain is observed at a temperature above 800°C. Mass gain for samples that were exposed for 1 hour at a temperature of 1200°C was almost 4080 mg/dm^2.

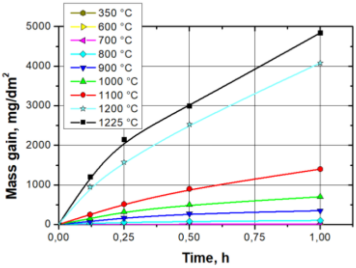


Figure 9. Corrosion kinetics of 08Cr18Ni10Ti samples in a water steam environment

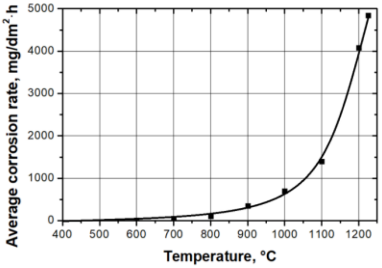


Figure 10. Dependence of the average corrosion rate of 08Cr18Ni10Ti samples on the test temperature in a water steam environment

The appearance of the samples surface changed during the testing from dark gray color over gray and brown to gray color with a metallic luster after testing at a temperature of 1225°C (Figure 11).

700 °C 900 °C 1000 °C 1100 °C 1225 °C

Fig. 11. Appearance of 08Cr18Ni10Ti samples after testing in a water steam environment

3.2. High-temperature corrosion kinetics of the 42CrNiMo alloy

The results of corrosion testing of 42CrNiMo samples in a water steam environment for 1 hour in the temperature range from 350 °C to 1225 °C revealed that the corrosion kinetics of this alloy is decaying (Figure 12). This indicates to the protective properties of the oxide film, formed during corrosion testing in a water steam environment.

The rate of mass gain increased with increasing the test temperature, as evidenced by the dependence of the average corrosion rate during 1 hour on the test temperature (Figure 13). A characteristic feature of the corrosion resistance of the 42CrNiMo samples in the water steam environment is that the corrosion rate is much lower compared to the 08Cr18Ni10Ti steel. The dependence curve of the average corrosion rate of the 42CrNiMo samples is similar to the curves for the 08Cr18Ni10Ti steel. A sharp mass gain of the samples was observed at a temperature above 800°C, and at a temperature of 1200°C in 1 hour of testing it was 105 mg/dm^2.

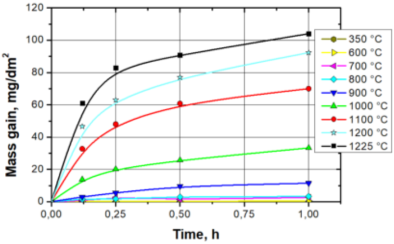


Fig. 12. Corrosion kinetics of the 42CrNiMo samples in a water steam environment

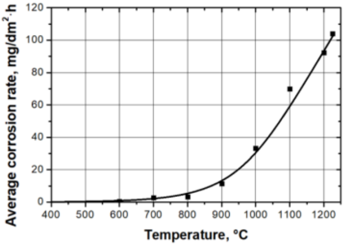


Fig. 13. Dependence of the average corrosion rate of 42CrNiMo samples in 1 hour on the test temperature in a water steam environment

The appearance of the surface changed from brown over black and dark green to gray color at the end of the test at a temperature of 1225°C (Figure 14).


700 °C 900 °C 1000 °C 1100 °C 1225 °C

Fig. 14. Appearance of *42*CrNiMo samples after testing in a water steam environment

3.3. High-temperature corrosion kinetics and the formation of hydrogen gas during the oxidation of materials

In the case of a severe accident with deteriorated heat removal, nuclear fuel can be heated to high temperatures due to the residual heat generated by the shutdown reactor. This generates steam in the reactor core, which reacts with the core structural materials. During oxidation, the material takes up oxygen and the residual hydrogen is released into the core according to the reaction:

$$Me + H_2O \rightarrow MeO_2 + 2H_2, \tag{2}$$

A large amount of hydrogen can be produced, amounting to thousands of cubic meters as a result of the reaction of a large amount of metal (Me). This is extremely dangerous, both in terms of explosion and fire hazard and in terms of the formation of gas bubbles in the reactor core that impede coolant circulation, which can aggravate the accident by stopping the removal of heat from the fuel.

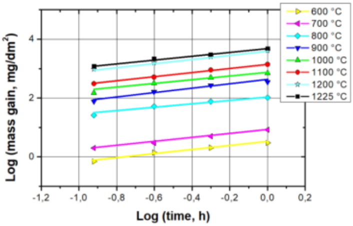
Based on the above reaction (2), the amount of hydrogen released directly depends on the amount of metal oxidized, i.e., to determine the amount of hydrogen formed during the oxidation of 08Cr18Ni10Ti steel and 42CrNiMo alloy, it is necessary to evaluate the high-temperature oxidation kinetics of these materials.

The oxidation rate depends significantly on temperature, surface area, and reaction time, and for most metals is described by the following formula:

$$\left(\frac{\Delta m}{S}\right)^n = K_0 \cdot exp^{\left(\frac{-Q}{RT}\right)} \cdot t\ , \tag{3}$$

where: Δm – mass change of sample, mg; S – surface area of sample, dm^2; t – exposure time, hours; K_0 – proportionality factor; n – the degree of reaction; T – temperature, K; Q – activation energy of the process, cal/mol; R – the universal gas constant, (1.987 cal/(mol·K).

The average value of the degree of reaction n was determined to be 1.45 (from 1.40 to 1.54) based on the experimental data of the mass change of 08Cr18Ni10Ti samples after high-temperature testing with respect to the exposure time in logarithmic coordinates (Figure 15). The activation energy of the process was determined to be 45 kcal/mol based on the dependence of the corrosion index (K) on 1/T (Figure 16).



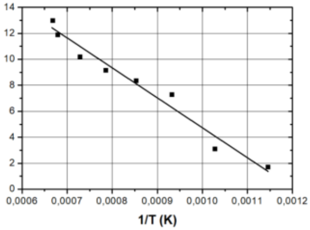
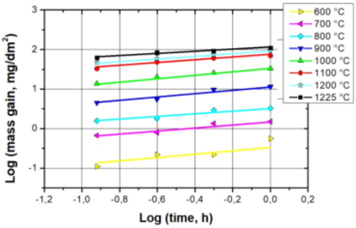


Fig. 15. Mass change of 08Cr18Ni10Ti samples at high-temperature testing in logarithmic coordinates

Fig. 16. Temperature dependence of the corrosion index of steel 08Cr18Ni10Ti

The experimental data on the mass change of 42CrNiMo samples with time (Figure 12) are approximated by a power law expression with a power factor in the range from 2.6 (for 800°C) to 3.6 (for 1225°C). An average value of the degree of reaction *n* was 3.1 and was determined for each of the test temperatures (600...1225°C) based on the data of the mass change of 42CrNiMo samples with time during high-temperature testing in logarithmic coordinates (Figure 17).

The the dependence of the corrosion index K on 1/T is quite accurately approximated by two segments, each characterized by its own activation energy (Figure 18). The decrease in the oxidation rate at high temperature may be due to a slight spalling of the surface layers of the oxide film. To confirm the fact that the activation energy changes with increasing test temperature, it is necessary to carry out additional clarifying tests. However, all experimental data can be approximated by a single dependence with a slope of 37095, which corresponds to an activation energy of 73.5 kcal/mol, with a reliability of $R^2 = 0.923$.



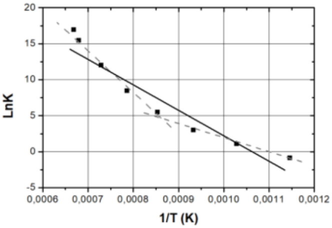


Fig. 17. Mass change of *42*CrNiMo samples at high-temperature testing in logarithmic coordinates

Fig. 18. Temperature dependence of the corrosion index of *42*CrNiMo

Generalized data on the constants for calculating the amount of oxidized metal for 08Cr18Ni10Ti steel and 42CrNiMo alloy are shown in Table 4.

Table 4

Constants for calculating the amount of oxidized metal for 08Cr18Ni10Ti steel and 42CrNiMo alloy

Material	n	Q, kcal/mol	K_o
08Cr18Ni10Ti	1.45	45.0±3.2	$8.43 \cdot 10^{11}$
42CrNiMo	3.10	73.5±8.7	$1.24 \cdot 10^{17}$

The corrosion kinetics (mass change) of austenitic steels Cr18Ni10Ti and 42CrNiMo alloy in a water steam environment at temperatures of probable accidents associated with core overheating (from 350°C to 1200°C) were estimated when performing this work. The constants of the formula that describes with sufficient accuracy the experimental results of the mass change of samples versus exposure time and test temperature were determined. This formula can be applied to calculate both the corrosion kinetics and the release of hydrogen gas during the oxidation of the studied materials.

4. Verification of models for calculations

4.1. Corrosion kinetics at normal operating temperatures of core materials

To evaluate the applicability of the proposed formula for calculating the amount of dissolved material of austenitic steels 06Cr18Ni10Ti, 08Cr18Ni10Ti and 42CrNiMo alloy under conditions simulating the parameters of the primary coolant, there was built a dependence on the mass change of samples under autoclave testing at 350°C and 16.5 MPa and chemical removal of oxide films obtained experimentally and calculated by Formula 1 according to the data given in Table 3 (Figure 19).

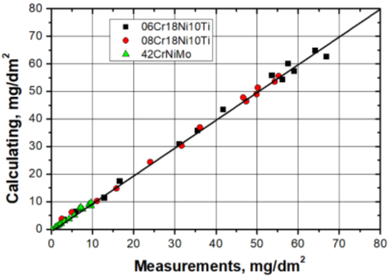
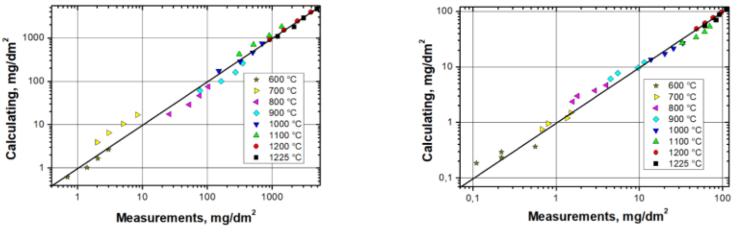


Fig. 19. Dependence of the experimental data on the amount of dissolved material due to corrosion at a temperature of 350°C and a pressure of 16.5 MPa on the calculation data

Based on the comparative values shown in Figure 19, the obtained formulas allow calculating with high comparability the amount of metal dissolved under corrosion process in the environment and under parameters that simulate the primary coolant. Namely: for 06Cr18Ni10Ti $R^2 = 0.994$; 08Cr18Ni10Ti $R^2 = 0.992$, and for 42CrNiMo $R^2 = 0.980$.

4.2. Corrosion kinetics at accidental operating temperatures of core materials

To evaluate the applicability of the proposed formula for calculating the mass change under high-temperature oxidation (in proportion to the amount of water steam generated) of austenitic steels 06Cr18Ni10Ti, 08Cr18Ni10Ti, and alloy 42CrNiMo under accident conditions associated with overheating of the reactor core (temperature up to 1225°C, water steam), there was built a dependence of the mass change of samples at high-temperature oxidation obtained experimentally and calculated by formula 3 according to the data given in Table 4 (Figure 20).



a b

Fig. 20. Dependence of the experimental data on the mass change of samples under high-temperature oxidation on the calculated data for Cr18Ni10Ti steels (a) and 42CrNiMo alloy (b)

Based on the comparative values shown in Figure 20, the obtained formulas allow calculating the kinetics of high-temperature oxidation of the studied materials with high comparability. For steels Cr18Ni10Ti grade $R^2 = 0.991$ (Figure 20. a) and for 42CrNiMo $R^2 = 0.980$ (Figure 20.b).

CONCLUSIONS

1. The article 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/dm^2, and for steels – 0...-2 mg/dm^2.

3. After autoclave tests, the surface of 42CrNiMo alloy samples and 06Cr18Ni10Ti and 08Cr18Ni10Ti steel samples had different colors 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 of 06Cr18Ni10Ti and 08Cr18Ni10Ti 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/dm^2). Chemical removal of the oxide film from the surface revealed that for 10,000 hours of testing, corrosion losses were up to 55 mg/dm^2.

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. And 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 dependencies 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 1.22 and 1.39 for 06Cr18Ni10Ti and 08Cr18Ni10Ti steels, respectively. In longer tests, the power indices were 2.88 and 2.84, respectively. The results of measuring the mass change for the 42CrNiMo alloy samples, obtained over the entire period of testing, were described by one law with an index of power of 1.96.

7. The corrosion kinetics (mass change) of austenitic steels Cr18Ni10Ti and 42CrNiMo alloy in water steam environment at temperatures of probable accidents associated with core overheating (from 350 °C to 1200 °C) were established. Among the materials considered in this study, samples of

42CrNiMo alloy demonstrated the highest corrosion resistance at high temperatures in a water steam environment.

8. Under conditions of maximum design accidents associated with core overheating, the amount of hydrogen released during oxidation of the cladding made of chromium-nickel alloy 42CrNiMo will be almost forty times less than that of austenitic stainless steels Cr18Ni10Ti.
9. The constants of the formula that describes the experimental results of the mass change of samples over time and test temperature with sufficient accuracy were established. These formulas can be used both to calculate corrosion kinetics and hydrogen gas emission under oxidation of the studied materials.
10. The corrosion kinetics of Cr18Ni10Ti steels produced at Ukrainian enterprises is comparable to the corrosion kinetics of materials applied at operating NPPs with VVER reactors. The 42CrNiMo alloy possess higher corrosion resistance under normal operating conditions of a nuclear reactor and an almost 40 times lower rate of high-temperature (1200°C) oxidation compared to austenitic stainless steels Cr18Ni10Ti. The dissolution coefficient of the oxide film on Cr18Ni10Ti austenitic stainless steels is about 30%, while for the chromium-nickel alloy 42CrNiMo, no significant dissolution of corrosion products in the corrosion environment is observed.
11. Based on the research results, it can be concluded that Ukrainian enterprises have mastered the manufacturing of main structural materials of the pressurized water reactors primary circuit with high corrosion resistance in the primary coolant under power operation (350°C, 16.5 MPa) and in accidents associated with core overheating up to 1200°C.

SUMMARY

Ukrainian enterprises have established the manufacturing of austenitic chromium-nickel austenitic stainless steels of the Cr18Ni10Ti grade and chromium-nickel alloy 42CrNiMo, as well as components made of them, that will be applied to diversify nuclear fuel supplies and manufacture equipment and components of VVER reactor cores. In addition to the reactor pressure vessel internals, the main elements of the reactor core are nuclear fuel, rod cluster control assemblies for VVER-1000 and the follower assemblies for VVER-440. There is also a high probability that SMR components will be manufactured at Ukrainian enterprises using Ukrainian materials.

The substantiation of the application of new or developed materials, but manufactured using other technological processes, requires a comprehensive study. These materials and components manufactured at Ukrainian enterprises have not been thoroughly studied and operated under the conditions of the VVER primary water chemistry.

This article presents the results of studying the main characteristics of corrosion resistance of chromium-nickel austenitic stainless steels 06Cr18Ni10Ti, 08Cr18Ni10Ti and chromium-nickel alloy 42CrNiMo, produced at Ukrainian enterprises. According to the research results, it can be concluded that the structural materials exhibit high corrosion resistance in the conditions of the primary coolant at power operation (350°C, 16.5 MPa) and in accidents associated with core overheating up to 1200°C. The chromium-nickel alloy 42CrNiMo exhibits higher corrosion resistance; oxide films formed on its surface do not dissolve significantly in the VVER primary coolant, unlike austenitic steels Cr18Ni10Ti, having an oxide film dissolution factor of 30%. The rate of high-temperature oxidation (1200°C) of the chromium-nickel alloy 42CrNiMo is almost 40 times lower than that of austenitic steels Cr18Ni10Ti.

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