

CORROSION AND PROTECTION OF METALS

Effect of Interstitial Elements on Pitting and Intercrystalline Corrosion of Austenitic Chromium-Nickel Steel

A. S. Kudriavtsev^{a,*}, K. A. Okhapkin^a, and S. A. Suvorov^a

^aNational Research Center Kurchatov Institute—Central Research Institute of Structural Materials Prometey, St. Petersburg, 191015 Russia

*e-mail: mail@crism.ru

Received December 26, 2016

Abstract—The possibility of improving the resistance of austenitic chromium-nickel steel of 09Kh18N9 and 08Kh16N11M3 grades to pitting and intercrystalline corrosion under the conditions of standby mode of a fast neutron reactor facility has been investigated. Corrosion tests lasting up to 15000 h have demonstrated that the corrosion rate decreases significantly upon the decrease in the carbon content and the increase in the nitrogen content.

Keywords: chromium-nickel steel, reactor facility, pitting and intercrystalline corrosion, interstitial elements

DOI: 10.1134/S2075113318060138

INTRODUCTION

Austenitic corrosion-resistant steel of 09Kh18N9 (10Kh18N9) and 08Kh16N11M3 grades represents the most common construction material for equipment and piping of reactor facilities (RF) of liquid-sodium-cooled nuclear power plants [1]. Processability and high level of service properties provided production and safe operation of the reactor vessel and high-temperature equipment and sodium pipelines and steam superheater units during the operation of fast neutron reactor power units. However, during the prelaunch period, which, according to the experience gained in construction and start-up of nuclear power plant units, takes no less than 2–3 years, the conditions for formation and development of localized corrosion damage (including pitting corrosion) of equipment and piping could occur (Fig. 1).

For instance, equipment manufactured of Kh18N9 and Kh16N11M3 steel can be exposed to the atmosphere, including moist air containing chlorides, during storage, transportation, mounting, and operational start-up. Along with the temperature decrease (for example, at nighttime), condensation of moisture from the air containing chlorides can occur on the metal surface and, after subsequent temperature increase, the moisture evaporates, completely or partially, leaving an accumulation of concentrated chloride solutions. Deposition of dust and hygroscopic salts like CaCl₂ and MgCl₂ promotes long-time holding of these solutions on the steel surface.

It is rather complicated to completely avoid long-term contact of steel with atmospheric air containing

chlorides leading to pitting corrosion. In addition, steel of 09Kh18N9 and 08Kh16N11M3 grades is unstabilized; i.e., it does not contain strong carbide-forming elements like titanium and niobium, which bond excess carbon and, thus, prevent depletion of grain boundaries in chromium during operational heating, which could promote a tendency to crystalline corrosion.

The objective of the present study was to investigate the possibilities of improving the resistance of steel of 09Kh18N9 and 08Kh16N11M3 grades to pitting and intercrystalline corrosion by means of introduction of interstitial elements.

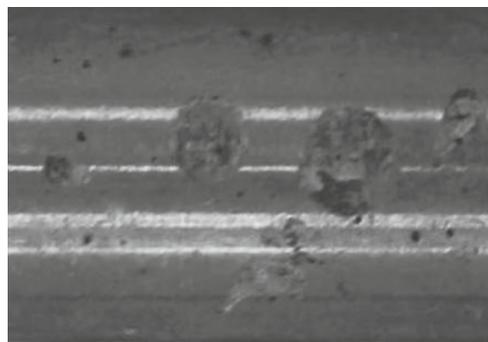
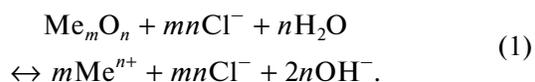


Fig. 1. Pittings on the piping of Kh18N10 steel formed in the standby mode on the sites where condensed moisture from marine atmosphere dried up.

MECHANISMS OF CORROSION DAMAGE AND WAYS TO IMPROVE THE RESISTANCE OF Kh18N9 AND Kh16N11M3 STEEL TO PITTING CORROSION

Pitting corrosion of equipment and piping made of construction steel of 09Kh18N9 and 08Kh16N11M3 grades under exposure to atmospheric air proceeds under conditions of the surface contact with moisture containing chlorides under deposits of external impurities (dust and hygroscopic salts). Upon reaching a critical concentration of chlorides and localized lack of oxygen on the surface active sites, a reversible breakdown of protective passive (oxide) film occurs as a result of substitution of chlorine ions for the surface oxygen ions [2, 3].

A reversible reaction proceeds at a breakdown potential with a formation of soluble metal (Me) chlorides, particularly, iron chlorides (FeCl_2 , FeCl_3) as well as those of chromium, nickel, and molybdenum [2]:



An active-passive element is realized on the metal surface as a result of localized crippling of a passive film, where the cathode reaction of oxidant reduction proceeds on a passive site of surface:



and the reaction of the metal active dissolution proceeds on the anode site, where the oxidizer (oxygen) concentration is not sufficient to provide reduction of a passive film:



Simultaneously, under effect of the emerging difference of potentials, negative ions (OH^- , Cl^-) are transferred inside the pitting. Solutions of salts of the FeCl_2 and FeCl_3 type that are formed inside the pitting are subject to hydrolysis with release of free hydrogen ions. Here, chlorides, which are not consumed during corrosion, are accumulated inside the pitting. According to [4, 5], the pH value inside the pitting can decrease to values lower than 1, while the concentration of chlorides can exceed 100 g/kg.

To lower the probability of the pitting corrosion formation during storage, transport, mounting, and operational start-up, as well as during standby modes of nuclear power plant units, steel with increased resistance to pitting corrosion should be used as construction materials for equipment and piping.

Improving the resistance of the passive film to the impact of chlorides can be achieved by increasing the concentration of elements exhibiting high affinity for oxygen, including chromium and molybdenum.

PREN (pitting resistance equivalent number [6]) serves as a commonly accepted qualitative measure of resistance of steel to pitting corrosion, which is described by the following formula for austenitic steel:

$$\text{PREN} = \% \text{Cr} + 3.3\% \text{Mo} + 30\% \text{N} \quad (4)$$

(the contents of elements are shown in the weight percent, wt %).

As seen from formula (4), a substantial improvement of the resistance to corrosion of 09Kh18N9 and 08Kh16N11M3 steel with retention of their grade composition can be expected only under the condition of an elevated nitrogen content. Moreover, its equilibrium value should not be surpassed in order to maintain high-temperature structural stability of the steel.

INTERCRYSTALLINE CORROSION OF AUSTENITIC CHROMIUM-NICKEL STEEL

Owing to susceptibility of unstabilized steel to intercrystalline corrosion (ICC), it is not advisable to apply it in contact with steam-water media except for dry steam. However, under real operating conditions of the reactor equipment, circumstances for emergence of intercrystalline corrosion can be realized only upon short-term acidic deactivation or upon water leakage on the surface of heated equipment because of an accident.

Austenitic steel of Kh18N9 and Kh16N11M3 types, after sensitization heating following the welding thermal cycle or after long-term service of the equipment at temperatures exceeding 500°C, can exhibit a tendency toward intercrystalline corrosion related to formation of chromium carbides along the grain boundaries and to depletion of the localized sites adjacent to the boundaries in chromium content upon heating within the critical temperature range. At a reduced content of chromium, passivation becomes difficult, while at the chromium content below 12% the corrosion resistance of the boundaries decreases drastically, which leads to acceleration of intercrystalline corrosion in aggressive media [7]. The tendency toward ICC at temperatures exceeding 500°C occurs the faster, the higher the concentration of carbon in steel.

The resistance of steel to ICC can be improved by means of the decrease in carbon concentration. Here, the effect of nitrogen on the tendency of steel to ICC is ambiguous. At low concentrations, nitrogen can decrease the resistance of steel to ICC significantly, while at contents of 0.1% and higher its effect is not substantial [7]. Therefore, the maximum decrease in the carbon content within the grade composition of steel of Kh18N9 and Kh16N11M3 types along with the increasing nitrogen content is supposed to improve the resistance to ICC.

Table 1. Plan of experimental melts

Melt no.	Content of chemical elements, wt %		
	C	N	C + N
1	0.08	0.02	0.1
2	0.05	0.05	0.1
3	0.02	0.08	0.1

MATERIALS AND METHODS

In the framework of the study, it was planned to melt three industrial casts of steel of 09Kh18N9 and 08Kh16N11M3 grades with varied contents of carbon and nitrogen with their constant total content (Table 1). The maximum content of carbon was accepted as proximate to maximum values of the grade composition (0.09%).

The metal melting was performed at the Chelyabinsk Metallurgical Plant in vacuum-induction furnaces with casting into forms, bar weight of ~500 kg. The actual contents of carbon and nitrogen in the steel slightly varied from the preset values (Tables 2, 3); however, they remained within the accepted limits necessary to perform the experiment.

Niobium and titanium made it possible to bond certain amounts of carbon and nitrogen; however, the concentrations of these elements was not sufficient to bond all the carbon, so that both of these types of steel cannot be considered as stabilized.

After the facing, the bars were forged by hammers into bar strips with a size of 50 × 190 × 1010 mm. Thermal treatment consisted of austenitization at 1050°C, holding for 1 h, and cooling in air. Workpieces to produce samples were cut of the bar strips crosswise.

Accelerated tests for pitting corrosion were performed to compare the tendency of metal with varied chemical composition toward formation of pittings. The tests were performed using flat samples with a size

of 15 × 60 × 2 mm according to GOST 9.912-89 via a chemical method in 10% solution of iron trichloride (FeCl₃ · 6H₂O). The test duration was 5 h.

The testing cell scheme is shown in Fig. 2. The prepared and weighed samples 1 were fixed on a wire in polyvinyl chloride insulation 2, the wire was fixed on a glass rod 5, and the samples were hung in chemical glasses 3 with a volume of 1 L and covered with 10% solution of iron trichloride in water 4 (FeCl₃ · 6H₂O).

Long-term tests of the samples simulating the conditions of standby corrosion during storage, mounting, or operational startup of RF equipment are the most representative in terms of estimating the damageability of construction steel under operational conditions.

The following conditions were accepted for the long-term corrosion tests of steel of 09Kh18N9 and 08Kh16N11M3 grades in terms of standby corrosion:

- corrosive media—3% solution of NaCl in distilled water;
- baseline duration of the tests—15000 h;
- temperature of the tests—23 ± 2°C;
- intermediate examinations of the samples and their weight loss—after 1000, 3000, and 15000 h.

The samples and the cell used to perform long-term corrosion tests were the same as for the accelerated tests. The weight loss was determined by means of analytical scales (VLR-200) with an accuracy of 0.00005 g (second class).

Intercrystalline corrosion (ICC) tests of the samples were performed in order to compare and select the optimal composition of steel of 09Kh18N9 and 08Kh16N11M3 grades from various melts of basic and upgraded compositions according to the resistance index to intercrystalline corrosion with consideration of the welding thermal cycle in the heat-affected zone (HAZ). For this purpose, the material was subject to sensitization heating. These testing conditions were considered more aggressive, since for the unstabilized

Table 2. Chemical composition of the investigated melts of steel of 09Kh18N9 grade

Melt	Weight content of chemical elements, %						
	C	Mn	Si	Cr	Ni	Cu	Mo
Grade composition	0.07–0.10	1.20–2.00	≤0.80	17.00–19.00	8.00–10.00	≤0.25	—
N1	0.09	1.47	0.43	18.00	9.01	0.03	0.01
N2	0.06	1.42	0.45	17.74	9.35	0.01	0.01
N3	0.02	1.47	0.44	17.68	9.20	0.01	0.01
Melt	Ti	S	P	N	Al	Nb	PREN
Grade composition	≤0.10	≤0.020	≤0.020	—	—	—	—
N1	0.01	0.006	0.011	0.02	0.07	0.01	18.60
N2	0.05	0.002	0.012	0.05	0.08	0.10	19.24
N3	0.02	0.003	0.012	0.09	0.06	0.10	20.38

Table 3. Chemical composition of the investigated melts of steel of the 08Kh16N11M3 grade

Melt	Weight content of chemical elements, %						
	C	Mn	Si	Cr	Ni	Cu	Mo
Grade composition	≤0.08	1.0–1.70	0.40–0.80	15.00–17.00	10.00–12.00	≤0.20	2.00–2.50
NM1	0.08	1.32	0.70	16.15	10.98	0.03	2.26
NM2	0.06	1.45	0.57	15.72	11.10	0.03	2.30
NM3	0.02	1.26	0.61	15.62	11.11	0.02	2.38
Melt	Ti	S	P	N	Al	Nb	PREN
Grade composition	≤0.10	0.020	0.020	–	–	–	–
NM1	0.01	0.003	0.011	0.01	0.06	0.01	23.91
NM2	0.05	0.002	0.011	0.06	0.06	0.11	25.11
NM3	0.05	0.002	0.01	0.06	0.07	0.10	25.27

steel the resistance to ICC was required, while sensitization heating was not mandatory.

The tests were carried out according to the method AMU GOST 6032-2003 [8] in the boiling solution of cupric sulfate (50 g/L CuSO_4) and sulfuric acid (250 cm³/L H_2SO_4 , $d = 1.83 \text{ g/cm}^3$) in distilled water in contact with copper turnings. The samples of each melt were placed into a glass flask over the copper chips and then filled with the solution and boiled for 8 h with a back-flow condenser.

The samples, whose compositions are shown in Tables 2 and 3, were used to perform ICC corrosion tests. Three samples from each melt were tested; one served as a reference sample. Prior to the test, the sam-

ples of each melt were subjected to sensitization thermal treatment at 650°C for 1 h.

After the test, the samples (including the reference ones) were bent in a special former with bending radius of 2 mm and examined by means of 10-power magnifier for the presence of corrosion cracks that signified a tendency to ICC.

RESULTS AND DISCUSSION

Estimation of the Resistance of the Experimental Compositions to Pitting Corrosion

Results of the accelerated tests in 10% solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ demonstrated an improved resistance to pitting corrosion with the increase in the nitrogen content, which was reflected in the decrease in the average relative weight loss values and the number of pittings (Table 4). Note the close weight loss values of the NM1 and NM2 samples, while a significantly larger amount of pittings was observed in the NM2 melt sample. This phenomenon was presumably related to the fact that corrosive processes in the NM1 samples proceeded in the formed pittings, so that they were substantially deeper.

The results demonstrated the following:

—Upon an increase in the molybdenum content in chromium-nickel steel to 2.0–2.5%, the corrosion loss decreased sharply and the number of pittings per unit area decreased.

—Upon an increase of the nitrogen content to 0.06–0.09% with an appropriate limitation of the carbon content in steel of Kh18N9 and Kh16N11M3 types, the corrosion loss and the number of pittings per unit area decreased (except for the NM1 melt samples, where the formed pittings were developing rapidly broad and deep).

—Even a slight increase in the PREN value (by 1.5–2 units) by doping of austenitic steel of Kh18N9 and Kh16N11M3 types with nitrogen led to improvement of the resistance to pitting corrosion.

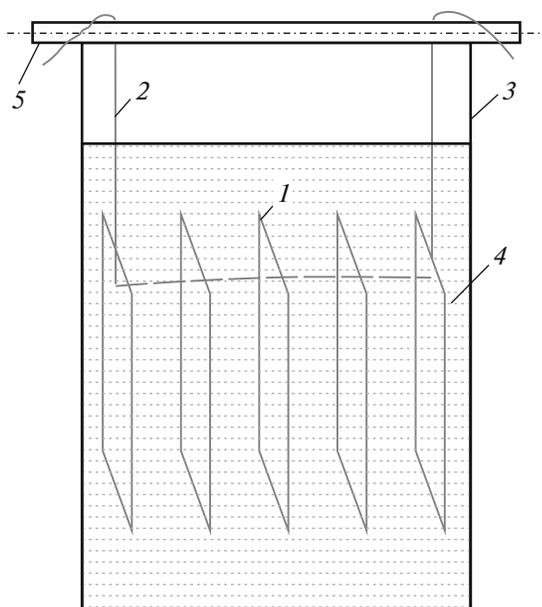


Fig. 2. The cell for testing of the samples for pitting corrosion.

Table 4. Results of tests for pitting corrosion of samples of steel of Kh18N9 and Kh16N11M3 grades in 10% FeCl₃ · 6H₂O solution

Steel grade	Melt	C, wt %	N, wt %	Average relative weight loss, g/cm ²	Number of pittings per 100 cm ²
Kh18N9	N1	0.09	0.02	0.00322	90
	N2	0.06	0.05	0.00268	85
	N3	0.02	0.09	0.00246	77
Kh16N11M3	NM1	0.08	0.01	0.00026	6
	NM2	0.06	0.06	0.00026	26
	NM3	0.02	0.06	0.00018	5

Table 5. Results of tests for pitting corrosion of samples of basic metal of steel of Kh18N9 and Kh16N11M3 grades in 3% NaCl solution

Steel grade	Melt no.	Average corrosion rate × 10 ⁴ , g/(cm ² h), within given period of tests		
		1013 h	3029 h	15130 h
Kh18N9	N1	0.00063	0.00030	0.00004
	N2	0.00050	0.00025	0.00003
	N3	0.00037	0.00019	0.000028
Kh16N11M3	NM1	0.00052	0.00018	0.00004
	NM2	0.00043	0.00015	0.00002
	NM3	0.00024	0.00012	0.00001

Long-Term Corrosion Tests

The results of the long-term tests of the steel samples of Kh18N9 and Kh16N11M3 grades are shown in Table 5.

Dynamics of the corrosion rate reduction over time is demonstrated on the histogram (Fig. 3). As seen from the figure, the corrosion rate for Kh18N9 and Kh16N11M3 steel under conditions simulating standby corrosion decreased significantly upon increase in the holding time from 1013 h to 15130 h.

During the first examination of the samples after 1013 h of the tests, neither tracks of corrosion nor pittings of visible size (upon 4- and 10-power magnification) were observed. The dependence was established as a result of weighing, where the weight loss decreased upon increase in nitrogen content and decrease in carbon content in the investigated melts. Deviation of the weight loss data for certain samples from the average values did not exceed ±37%. The calculated corrosion rate under these conditions can be estimated as less than 0.0005 mm/year for all the melts, except for basic N1 and NM1 (0.0007 and 0.00058 mm/year, respectively) ones, as well as the N2 melt (0.00056 mm/year).

Upon the second examination carried out after 3029 h of the tests, individual pittings with a diameter

of up to 0.1 mm were observed (at 10-power magnification) on the surface of samples of N1, N2, N3, and NM1 melts. The calculated corrosion rate decreased for all the melt samples. The samples of the Kh16N11M3 steel with the minimal concentration of carbon and the maximal concentration of nitrogen demonstrated the highest resistance to pitting corrosion, which confirmed the conclusions of the accelerated tests performed for these melt samples in 10% solution of iron trichloride (FeCl₃ · 6H₂O).

The third examination performed after 15130 h of tests did not demonstrate any significant development of pittings in any of the investigated samples. The corrosion rate decreased 5- to 10-fold for all the melt samples. The samples with the minimal content of carbon and the maximal content of nitrogen demonstrated the highest resistance to pitting corrosion, which confirmed the conclusions of the accelerated tests performed for samples of these melts in 10% solution of iron trichloride (FeCl₃ · 6H₂O).

The tendency to reduction of the corrosion rate of the investigated samples can be explained by the known mechanism of slowing down of the growth of formed pittings with the increase of their depth [9]. Here, for the melts with the maximal content of nitro-

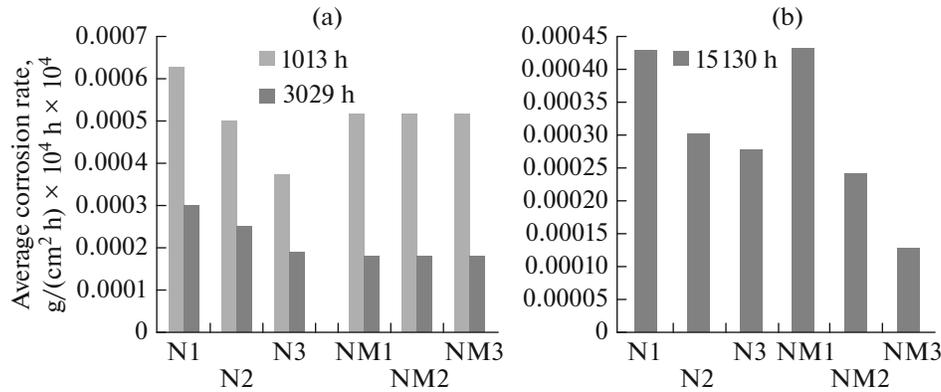


Fig. 3. Dynamics of changes in the corrosion rate over time of Kh18N9 and Kh16N11M3 steel of different melts under conditions of standby corrosion in 3% NaCl solution.

gen and the minimal content of carbon, this tendency persisted.

Note that the duration of the corrosion tests in 3% NaCl solution (15000 h) exceeded the maximum possible time of exposure to the most aggressive corrosive media during storage, transport, mounting, and operational startup of equipment for nuclear power plants.

Estimation of Resistance of the Experimental Compositions to Intercrystalline Corrosion

The results of ICC tests of steel of 09Kh18N9 and 08Kh16N11M3 grades with basic and upgraded compositions subjected to sensitization thermal treatment are provided in Table 6.

As seen from Table 6, the samples of all the melts of Kh18N9 and Kh16N11M3 steel with basic and upgraded compositions exhibited a tendency toward intergranular corrosion to a greater or lesser extent. Substitution of nitrogen for carbon did not completely exclude the possibility of the tendency toward ICC, although it reduced it substantially. Here, the melt samples N3 and NM3 with the minimal content of carbon (0.02%) demonstrated the highest level of properties preventing the development of ICC.

On the basis of the investigation performed, it was concluded that the metal melts with the carbon content reduced to 0.02% applied for production of equipment and piping for nuclear power plants could substantially decrease the possibility of formation and development of intercrystalline corrosion during operation under conditions of acidic deactivation or water leakage on the surface of hot equipment from an accident.

Therefore, the performed comparative tests of various melts of Kh18N9 and Kh16N11M3 steel allowed establishing a clear positive effect of decreasing carbon content and additional doping with nitrogen reflected in the improved resistance to pitting and intercrystalline corrosion.

This conclusion along with the one made in [10] about the improvement of heat resistance of 08Kh16N11M3 grade steel through substitution of nitrogen for carbon made steel of 09Kh18N9 and 08Kh16N11M3 grades with a reduced content of carbon and an elevated content of nitrogen a prospective material for producing equipment and piping for nuclear power plants with a long-term cycle of mounting and operation.

Table 6. Results of tests for intergranular corrosion of samples of steel of 09Kh18N9 and 08Kh16N11M3 grades according to the method of AMU GOST 6032-2003

Sample	Presence of ICC cracks on the samples following bending					
	N1	N2	N3	NM1	NM2	NM3
Melt no. 1	Deep cracks	Deep cracks	No	No	No	No
Melt no. 2	Deep cracks	Deep cracks	Fine cracks	No	No	Fine cracks
Melt no. 3	No	Yes	No	Fine cracks	No	No
Melt no. 4	Deep cracks	Yes	No	Deep cracks	Fine cracks	No
Blank sample	No	No	No	No	No	No

CONCLUSIONS

(1) As a result of comparative corrosion tests of the samples of 09Kh18N9 and 08Kh16N11M3 steel of melts with varied chemical compositions applied under conditions of the standby mode of fast neutron nuclear reactors within time period up to 15000 h, it has been established that the corrosion rate decreases substantially with a reduction of carbon content and rise of nitrogen content.

(2) The melt samples with the minimal carbon content (0.02%) have demonstrated the highest resistance to the development of ICC.

(3) The advantages of applying semifinished products made of steel of 09Kh18N9 and 08Kh16N11M3 grades with reduced content of carbon and doped with nitrogen for equipment and piping for nuclear power plants with a long-term cycle of mounting and operation have been established.

REFERENCES

1. Karzov, G.P., Kudriavtsev, A.S., Markov, V.G., Grishmanovskaya, R.N., Trapeznikov, Yu.M., and Anan'eva, M.A., Development of constructional materials for nuclear power plants on fast neutrons with sodium coolant, *Vopr. Materialoved.*, 2015, no. 2 (82), pp. 23–33.
2. Rozenfel'd, I.L., *Korroziya i zashchita materialov* (Corrosion and Protection of Materials), Moscow: Metallurgiya, 1970.
3. Gerasimov, V.V. and Monakhov, A.S., *Korroziya reaktornykh materialov* (Corrosion of Materials for Nuclear Reactors), Moscow: Tsentr. Nauchno-Issled. Inst. Uprav., Ekon. Inf., 1994.
4. *Struktura i korroziya metallov i splavov: Spravochnik* (Structure and Corrosion of Metals and Alloys: Handbook), Ul'yanin, E.A., Ed., Moscow: Metallurgiya, 1989.
5. Bardal, E., *Corrosion and Protection*, London: Springer-Verlag, 2004.
6. *Encyclopedia of Corrosion Technology*, Schweitzer, Ph.A., Ed., New York: Marcel Dekker, 2004.
7. Číhal, V., *Mezikrystalová Koroze Ocelí a Slitin*, Prague: Stát. Naklad. Tech. Lit., 1978.
8. *GOST (State Standard) 6032-2003: Corrosion-Resistant Steels and Alloys. Test Methods of Intercrystalline Corrosion Resistance*, Moscow, 2005.
9. Landolt, D., *Corrosion and Surface Chemistry of Metals*, Boca Raton: CRC Press, 2007.
10. Kudriavtsev, A.S., Okhapkin, K.A., Trapeznikov, Yu.M., Artem'eva, D.A., and Kovalev, P.V., Optimization of service characteristics of the 08Kh16N11M3 steel by improving alloying system, *Vopr. Materialoved.*, 2015, no. 3 (83), pp. 38–46.

Translated by D. Marinin