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Local Corrosion of Austenitic Steels and Alloys

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Abstract

The principles of doping of austenitic unstabilized Cr-Ni and Cr-Mn-Ni steels resistant against pitting, slit, and intergranular corrosion (IGC) in weakly and strongly oxidative media are considered. The features of the effect of individual and joint doping with nitrogen, molybdenum, and silicon steels on their resistance to local corrosion have been studied. The ambiguous effect of joint doping with nitrogen and molybdenum of Cr-Mn-Ni steels on their resistance against pitting corrosion is revealed. It has been established that the presence of silicon, in addition to nitrogen and molybdenum, is a prerequisite for eliminating the propensity to the IGC after a long release of chromium-nickel steels. The introduction of silicon into Cr-Ni steel with 0.03% C, with a balanced content of Cr, N, Mo, and Si, equates it with a particularly low-carbon steel containing 0.003% C. Based on the above doping principles, a number of austenitic steels are designed for production equipment that is resistant to local corrosion in chloride-containing media and nitric acid.

Keywords: stainless steel, pitting corrosion, intergranular corrosion, crevice corrosion, weakly oxidative and strongly oxidative media environment, alloying, cold deformation, stable and unstable austenite, α'-phase, δ-ferrite

1. Introduction

The issues of reducing the metal capacity in industry, reducing the costs of repairing metal products, and increasing their service life and reliability are associated with the protection of the metal fund against corrosion. The use of stainless steels and alloys is an important direction in combating metal losses from corrosion in various industries and, above all, in those where metal products are used in corrosive aggressive environments. The greatest losses from corrosion are characteristic for the chemical industry and thermal and nuclear power.

In this case, the damage and failure of equipment in most cases are caused by the destruction of stainless steels as a result of their corrosion cracking, pitting, and intergranular corrosion.

In the chemical engineering industry, stainless chromium-nickel and chromium-nickel-molybdenum stabilized austenitic steels with a relatively high content of carbon 12Kh18N10T and 10Kh17N13M2T have been widely used as materials combining high strength with good processability in the metallurgical division. As a result of the development of industry and the increasing role of the economic factor, the shortcomings of these steels have also been revealed, in particular, low resistance against local corrosion in chloride-containing media. Therefore, low-carbon non-stabilized steels of 03Kh18N11, 03Kh17N14M3, and 03Kh19N10AГ3 types were developed and mastered by industry, which significantly increased the reliability of the welded equipment. At the same time, these steels are also prone to pitting corrosion with prolonged thermal exposures to the IGC, and their strength properties are even lower than those of 12Kh18N10T and 10Kh17N13M2T steels due to low-carbon content.

Increasing the resistance against local corrosion of austenitic steels is achieved as a result of reducing the content of carbon in them and doping with elements passivating the metal surface. It is known [1–3] that molybdenum inhibits active dissolution of steel, reduces the critical passivation current, and increases the critical temperature of pitting in chloride-containing media.

The use of nitrogen as an alloying element also makes it possible to obtain steels with high corrosion resistance. Like carbon, nitrogen forms a solid solution in the gland and promotes stabilization of the γ-phase. Like molybdenum, nitrogen reduces the propensity of steels to release intermetallic and carbide phases [3, 4].

The increased stability of the austenite of nitrogen-containing steels makes it possible to obtain from them highly corrosion-resistant low-magnetic products with a time resistance of the break of 2100–2150 N/mm^2 and a relative magnetic permeability of not more than 1.05 [5].

The introduction of nitrogen into the steel contributes to preventing or inhibiting the formation of border discharges in it and increasing its corrosion resistance [6]. However, the presence of only nitrogen or molybdenum in the metal is insufficient to completely eliminate the tendency to pitting corrosion [7, 8].

A high ability to self-passivate can have heat-treated steels alloyed together by nitrogen and molybdenum [2, 7–9]. Such steels in the cold-deformed state are also characterized by sufficient resistance to cracking during hydrogenation in chloride-containing media [10].

Increasing the resistance of austenitic steels against pitting corrosion is achieved by introducing silicon into them as an alloying element [11]. But silicon reduces the solubility of carbon, increases its thermodynamic activity, and accelerates the process of separating carbide phases, which can lead to a decrease in the resistance of the steel against intergranular corrosion [12].

In weakly oxidative environments, the influence of silicon on the propensity of austenitic steels to intergranular corrosion can be either positive or negative [13].

As follows from [14, 15], in steels Kh16N15M3 and Kh18N11 containing 0.03% C, an increase in the concentration of silicon leads to an increase in their propensity to the IGC in a weakly oxidative medium after tempering at temperatures above 650°C and to a decrease after heating below 650°C. Alloying with silicon in an amount of ≥3.29% of steel Kh20N20, containing not more than 0.032% C, suppresses its tendency to intergranular corrosion irrespective of the duration of tempering at 650°C within 1–100 h [16]. However, an increase in the silicon content to 5.40% in the same steel (with 0.015% C and 0.1% P) reduces its passivating ability [17].

The ambiguity of the influence of silicon on the corrosion resistance of tempered steels is caused by the formation of chromium-depleted border zones as a result of accelerating the release of excess phases, on the one hand, and facilitating the passivisability of these zones, thereby suppressing (complete or partially) their selective dissolution on the other. The resulting effect depends on which of these two factors is most prevalent [13].

Despite numerous studies, the effect of doping on the resistance to local corrosion of cold-deformed austenitic stainless steels with a stable and unstable austenite remains unclear.

2. Methodology of research

The investigated steels 22Kh18N5AM3D2S2 (EP 995) [18], 22Kh18N5AM3S2 (EP 996) [19], and 15Kh21G9N9AM2-Sh [20] were produced under industrial conditions. The first two were melted in 1-t induction furnace and the third in a 5-t electric arc furnace with a subsequent ESR. Forged bars with a cross section of 83 × 83 mm were rolled onto a wire rod with a diameter of 8 mm and then stretched onto billets with diameters of 3.0 and 1.5 mm. The workpiece with a diameter of 3.0 mm was quenched with heating from 1120 to 1150°C and cooling in water to study the microstructure and the resistance against IGC. Hardened billets with a diameter of 1.5 mm were pulled onto a wire 0.8 mm in diameter (deformation rate of 72%), from which samples were prepared for corrosion and mechanical and electrochemical tests.

The remaining meltings were produced in an induction furnace with a capacity of 40 kg. Forged blanks of 35 × 35 mm were rolled onto a wire rod with a diameter of 8 mm and stretched onto billets with diameters of 3.0 and 1.5 mm. After quenching from 1070 to 1150°C (depending on the content of carbon and nitrogen), 1.5-mm-diameter billets were drawn to a wire 0.8 mm in diameter, from which samples were prepared for the research.

Tests of steels for resistance against pitting and crevice corrosion were carried out under conditions of uniaxial tension equal to $0.8\sigma_b$. For this purpose cold-worked specimens were wound with wire of the same steel, passed into glass cylinders, filled with $10\%FeCl_3 \cdot 6H_2O$ solution (GOST 9.912-89, ASTM G48A), and loaded into adapted creep machines.

The anodic potentiodynamic polarization curves were taken at room temperature in a chloride solution of 1.0-n H_2SO_4 + 1.0-n NaCl by means of a potentiostat P-5848 in automatic mode at a polarization rate of 3.6 V/h using a standard silver chloride electrode, a computer IMM-IM3. Samples with a surface area of 5 cm² were mechanically polished, degreased, and activated with a current of 2×10^{-3} A/cm² for 5 min.

Resistance against IGC was tested on samples with a diameter of 3.0 mm after their tempering at 550–750°C for 1, 10, 100, and 500 h according to the standard method of AMU GOST 6032. Mechanical tests of cold-deformed wire samples were carried out in accordance with GOST 10446.

The microstructure was studied with a Neofot-2 light microscope. The composition of the phases was determined by the X-ray diffraction method; δ-ferrite and α'-phase (martensite of deformation) were detected from the value of the magnetic permeability of the samples, which was determined on a ballistic installation in a magnetic force field equal to 39.8 × 10^4 A/m (500 Oe).

3. Corrosion behavior of cold-deformed austenitic steels

Testing of samples under conditions of uniaxial tension in a 10% solution of $FeCl_3 \cdot 6H_2O$ made it possible to reveal the effect of the separate and combined alloying with nitrogen and molybdenum for unstabilized Cr-Ni and Cr-Mn-Ni cold-worked steels on pitting and crevice corrosion resistance. The results of the tests are shown in **Table 1**.

From the data obtained, it follows that steel without nitrogen and molybdenum, as well as separately doped with molybdenum or nitrogen, with both stable and unstable austenite, tends for pitting and crevice corrosion. These steels are destroyed after 7–30 h in contact with the wound wire because of the formation of deep pitting. The low resistance of samples against local corrosion is confirmed by the nature of the anodic potentiodynamic curves (**Figure 1**). The critical passivation current and the total passivation current, indicating the ability to pass into the passive state of 17Kh18N9 and 17Kh18AN10 steels, are maximum and are, respectively, $(2–5) × 10^{-3}$ and $(1–5) × 10^{-5}$ A/cm^2 (**Figure 1**, curves 1 and 2). On the polarization curves in the region of complete passivation, secondary activation maximum and unstable current jumps are seen associated with the formation of self-passivating pits.

Elimination of the tendency to pitting corrosion of cold-deformed Cr-Ni and Cr-Mn-Ni steels with a stable austenite structure (magnetic permittivity 1.05 Gs/Oe) is achieved, as can be seen from **Table 1**, when they are jointly doped with nitrogen and molybdenum. All nitrogen-doped chromium-nickel steels containing molybdenum do not collapse under prolonged stress tests. They are characterized by high resistance against pitting and crevice corrosion, which confirms the previously obtained data [8, 21, 22]. Areas of secondary activation absent on a polarization curve 3 steel 12Khl8N13AM3 (see **Figure 1**) are alloyed with nitrogen and molybdenum. The critical passivation current is minimal, and the region of potentials of total passivation is much wider than on curves 1 and 2 of steels 17Kh18N9 and 17Kh18AN10 (**Figure 1**). The surface of the 12X18H13AM3 steel samples remained light after the tests, without any trace of corrosion. The appearance of δ-ferrite and the formation of an α'-phase in the structure of nitrogen-containing Cr-Ni-Mo steels (1–3, see **Table 1**) do not reduce their resistance to local corrosion.

Austenitic steels with a super-equilibrium content of nitrogen after cold plastic deformation make it possible to obtain articles with yield strength of up to 3600 N/mm^2 or higher [23]. At

| Steel (nominal melt number)	$\sigma_{\text{в}}$ (N/mm²)	Time to failure (h)	Phase composition	μ (Gs/Oe)	PRE
Cr-Ni steels					
22Kh18N5AM3D2S2 (1) (EP995)	2300	6500*	$\gamma + \alpha'$	7.5	30.3
22Kh18N5AM3S2 (2)	2670	6500*	$\gamma + \alpha'$	8.7	29.5
05Kh20N5AM2D2 (3)	1760	3000*	$\gamma + \delta + \alpha'$	15	29.2
03Kh18N9S2AM2 (4) 1920 3000* γ 1,05 28,0	1920 3000* γ 1,05 28,0	3000*	γ	1.05	28.0
03Kh17N13S2AM2 (5)	1915	1000*	γ	1.05	28.3
I2Khl8N13AM2 (6)	1815	1000*	γ	1.05	32.1
20Kh20N13 (7)	1610	20–30	γ	1.05	20.0
17Kh18AN10 (8)	1825	10–20	γ	1.05	21.8
07Khl8N10M3 (9)	1770	15–20	$\gamma + \alpha'$	10.1	27.4
17Khl8N9 (10)	1895	7–10	$\gamma + \alpha'$	7.5	17.8
Cr-Mn-Ni steels					
25Kh18G9N13M2 (11)	1820	10–15	γ	1.05	24.6
10Kh18G13AN4 (12)	1880	5–10	γ	1.05	22.1
25Kh18G9AN5M2 (13)	2240	1500*	γ	1.05	31.0
25Kh18G9AN5M2S2 (14)	2410	1500*	γ	1.05	31.2
15Kh21G9N9AM2-Sh (15)	2215	1500*	γ	1.05	35.8
10Kh18G9AN5M2S2 (16)	2000	5–10	$\gamma + \alpha'$	4.1	28.7
05Kh18G9AN5M2S2 (17)	1690	5–10	$\gamma + \delta + \alpha'$	7.3	29.1
05Kh18G9AN5M2S2 (18)	1650	1500*	γ	1.05	33.2

*Specimens taken from testing without failure.

Table 1. Properties, phase composition, and time to failure of cold-deformed wire specimens 0.8 mm in diameter of Cr-Ni and Cr-Mn-Ni steels in 10% $FeCl_3 \cdot 6H_2O$ solution with tensile stress of $0.8\sigma_{\text{в}}$ under conditions, simulating pitting, and crevice corrosion.

the same time, it is known [24] that when they crystallize a large part of the nitrogen passes into nitrides of relatively large sizes. During subsequent heating, coarse particles of excess phases are retained within the structure, ineffective for steel strengthening and reducing its resistance to local corrosion.

In this regard, for the production of high-strength cold-deformed semifinished products, along with low-carbon steels with super-equilibrium nitrogen content, the use of nitrogen-containing steels with an increased carbon concentration, obtained by standard methods using nitrided ferroalloys, is effective. Studies are under way to test the compositions of corrosion-resistant Cr-Mn-Ni steels alloyed together by nitrogen and carbon [25], which significantly expands the γ-region on the equilibrium-phase diagram and improves the properties of steels [26].
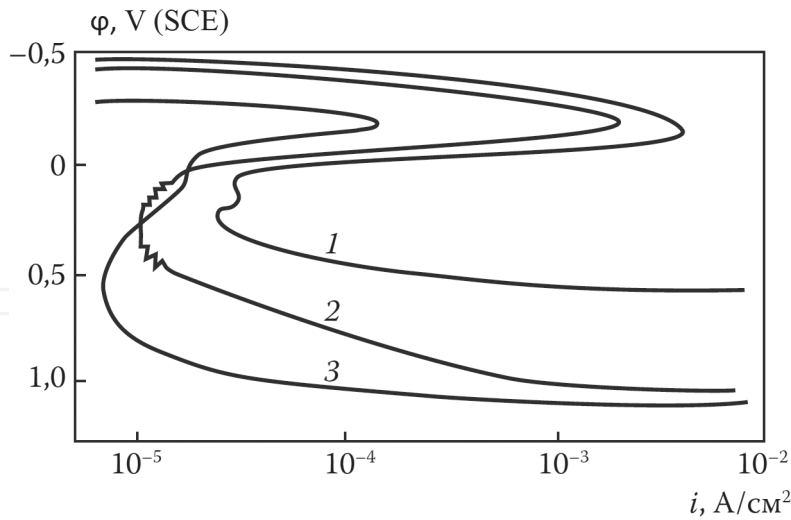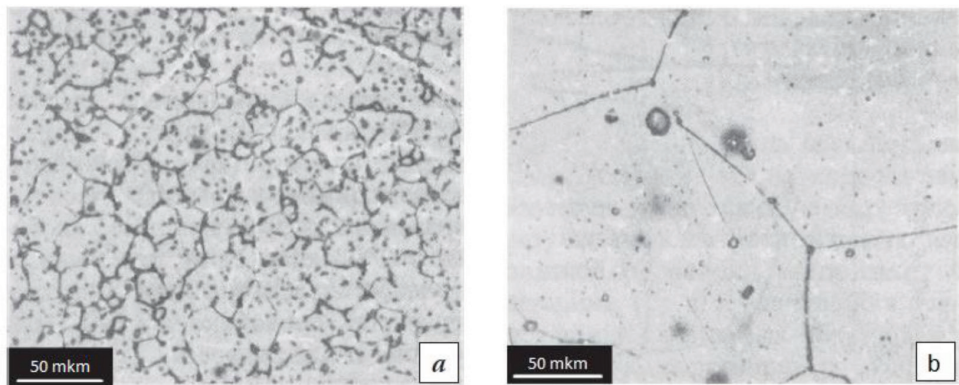
Figure 1. Anodic potentiodynamic polarization curves for cold-deformed steels 17Khl8N9 (1), 17Kh18AN10 (2), and 12Kh18N13AM3 (3) in 1.0-n H_2SO_4 + 1.0-n NaCl solution.

It was shown [27] that doping with copper facilitates the passivation of steel and increases its technological plasticity, ensuring the achievement of high strength due to large degrees of deformation [19, 28, 29].

The possibility of cold working of metals with high degrees of deformation is also ensured by sufficient solubility of excess phases in the structure of the steel during its high-temperature hardening (**Figure 2**), which simultaneously increases the corrosion resistance of the metal. On the polarization curve of 22Kh18N5AM3D2C2 steel (**Figure 3**, curve 1), there are no secondary activation regions; the current in the total passivation region does not exceed 10^{-5} A/cm^2, which characterizes a stable passive-state steel in a wide range of potentials. With a time resistance of 2300 N/mm^2, the steel 22X18H5AM3Д2C2 (EP 995) in a cold-deformed state is not prone to pitting and crevice corrosion and can withstand 6500 h without breaking in a chloride-containing medium at a stress of 0.8 σ_B (**Table 1**).

In accordance with technical conditions developed, industrial batches of steel 22Khl8N5AM 3D2S2 (EP 995) have been prepared for corrosion-resistant marine cable structures 3 ×19(1 +9+9) and 3 ×7(1 +6) with an improved aggregate strength (16,200 and 13,100 N).

Figure 2. Microstructure of steel 22Kh18N5AM3D2S2 (EP 995) after water quenching from 1120°C (a) and 1150°C (b).
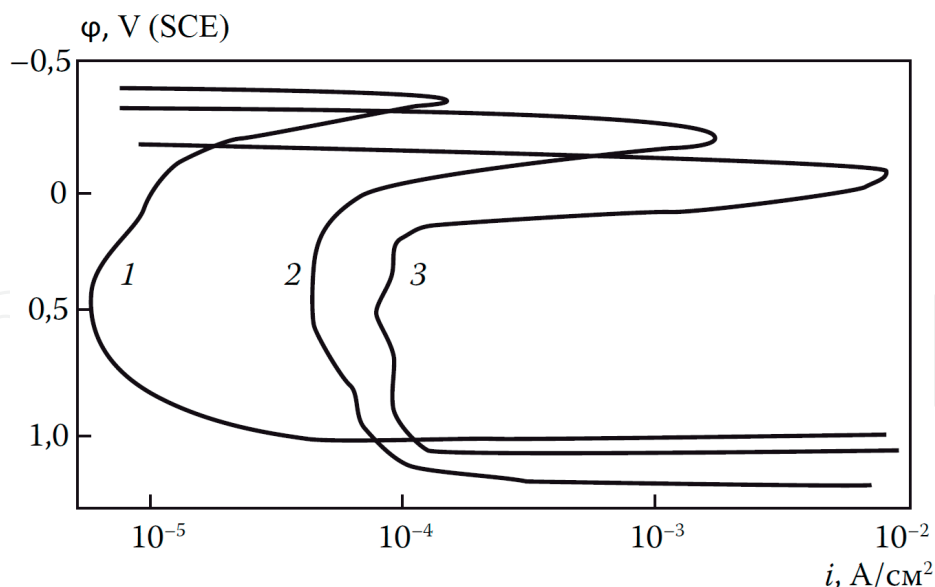
Figure 3. Anodic potentiodynamic polarization curves for cold-deformed steels 22Khl8N5AM3D2S2 (1) and15Kh21G9 N9AM2-Sh (2) in 1.0-n H_2SO_4 + 1.0-n NaCl solution and especially low-carbon alloy 02KhN40MB in chloride electrolyte after 100 h aging at 375°C (3).

As can be seen from **Table 1**, with separate doping with nitrogen and molybdenum, there is no significant increase in resistance to pitting corrosion of cold-deformed Cr-Mn-Ni steels. Samples of steels 25X18G9N13M2 and 10X18G13AN4 (melts 11 and 12) are destroyed after 5–15 h. Elimination of the propensity to local corrosion of Cr-Mn-Ni-like Cr-Ni steels is achieved by their joint doping with nitrogen and molybdenum. As a result, the samples survive the tests without failure for 1500 h (melting 13–15, 18). However, the high corrosion resistance of manganese steels, unlike chromium-nickel steels, is realized only if the former have a stable austenite structure, without the inclusion of δ-ferrite and α-phase, which increase the tendency to pitting corrosion and reduce the time to fracture of the samples to 5–10 h (melting 16 and 17).

As a whole, local corrosion resistance for cold-deformed manganese steels depends on the quantitative ratio within them of (δ+ α′)-phase manganese on the one hand and molybdenum, nitrogen, and chromium on the other. Therefore, due to the balanced content of the alloying elements, the steel 15X21Г9H9AM2-Ш [20] of industrial melting with the structure of stable austenite with the total content of nitrogen and carbon of 0.53% has a sufficiently high corrosion resistance. On a polarization curve (see **Figure 3**, curve 2), areas of secondary activation are absent. In the potential range from 0 to 900–1000 mV, the steel is in a stable passive condition, which points to the absence of a tendency toward pitting corrosion.

4. Potential resistance of austenitic steels to pitting corrosion

The potential resistance of steels to pitting corrosion can be estimated using the so-called PREN (pitting resistance equivalent number), calculated by the formula PRE = % Cr + 3.3 (%Mo) + 16 (%N) [30, 31]. It is believed that the higher the PRE, the more resistant the steel against pitting corrosion.

Table 1 shows the PRE values of the investigated steels, which, as a rule, correspond to their level of corrosion resistance. Elevated PRE values are characteristic for samples that do not break down during testing. Reduced values indicate the propensity of steels to pitting and crevice corrosion. At the same time, as can be seen from **Table 1**, melts 3 and 17, having the same structure and practically equal values of PRE, are different in resistance to local corrosion. One survives 3000 h of testing, and the other quickly collapses. In the corrosion-resistant Cr-Ni alloy 4, the PRE (28.0) is less than the Cr-Mn-Ni melting 17 (29.1), prone to pitting corrosion, which contradicts the meaning of the equivalent.

The obtained data indicate that the PRE formula does not take into account the different influence of the stability of austenite and inclusions of the second phases on the resistance to pitting corrosion of Cr-Mn-Ni and Cr-Ni steels doped with nitrogen and molybdenum, as well as their tendency to pitting corrosion in the case absence of one of these elements in the chemical composition of steel.

## 5. Pitting corrosion of nickel alloys

An analysis of the published data shows that nickel alloys not doped with N and Mo are prone to pitting corrosion (**Table 2**).

The Inconel 600 alloy containing a low percentage of chromium and high nickel has the lowest resistance to pitting corrosion and is prone, according to [32], to intergranular corrosion cracking.

Inconel 625 and Inconel 718 alloys, despite the high molybdenum content (up to 10 and 3.3%, respectively), under certain conditions, also have low resistance against pitting corrosion. Appearance of such corrosion of these alloys after aging in supercritical pressure (SCP) water at 500°C for 500 h is shown in **Figure 4** [33]. In this case, the PRE values reach the maximum values.

Alloy	C, ≤	Cr	Ni	Mo	N	PRE	Propensity to PC
Inconel 600	0.15	14–17	≤72	–	–	14–17	There is
Inconel 690	0.05	27–31	≤58	–	–	27–31	There is
Inconel 625	0.10	20–23	≤58	8–10	–	46–56	There is [33]
Inconel 718	0.08	17–21	50–55	2.8–3.3	–	26–31	There is [33]
02KhN40MB	0.02	18–20	30–40	4–5	–	31–36	There is [1]
KhN30MDB	0.03	29	31	3.5	0.05	41	There is [4]
					0.12	42	No [4]

Table 2. The content of basic alloying elements and nitrogen (wt.%) in nickel alloys and their propensity for pitting corrosion (PC).
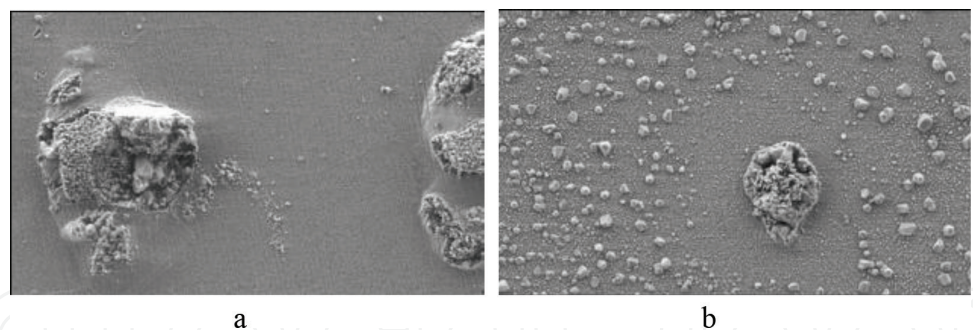
Figure 4. Pittings on the surface of nickel alloys Inconel 625 (a) and Inconel 718 (b) after their soak in water SCD at 500°C for 500 h.

The alloy ХН30МДБ (ЭК 77) [34], if its composition includes up to 0.05% N, also does not have sufficient resistance against pitting corrosion. However, an increase in the nitrogen content to 0.12% is sufficient to eliminate the propensity of the nickel alloy to pitting corrosion (**Table 2**) [4].

6. Intergranular corrosion of austenitic Cr-Ni steels

6.1. Increasing the resistance of steels against IGC in a weakly oxidative environment

The results of tests of samples in a solution of sulfuric acid and copper sulfate in the presence of copper chips according to the AMU GOST 6032 method after tempering at 650°C are given in **Table 3**. It shows that steel without Mo, doped with Si (1) or Si and N (2), is prone to IGC after tempering for 1–500 h [27]. The steels X16H15M3 [14] (3) and 03X20H19AM2 (4) alloyed together with nitrogen and molybdenum are corrosion-resistant after tempering only for 1 h. Alloying of these steels with silicon (see grade 03X17H13C2AM2 (5)) makes it corrosion-resistant after 100 H of heating.

Steel (nominal melt number)	C	Si	N	IGC resistance of steel tempered at 650°C (h)				
	Content (wt.%)			1	5	10	100	500
03Khl6NI4S2 [27] (1)	0.031	2.07	–	●	●	●	●	●
03Kh18N12AS2 (2)	0.029	1.53	0.16	●	●	●	●	●
Khl6N15M3 [14] (3)	0.032	≤0,4	0.12	○	●	●	●	●
03Kh20N19AM2 (4)	0.030	0.18	0.23	○	●	●	●	●
03Kh17N13S2AM2 (5)	0.034	1.71	0.20	○	○	○	○	●
03Kh17N13S2AM2 (6)	0.029	1.90	0.14	○	○	○	○	○
Khl6N15M3 [14] (7)	0.003	≤0.4	0.13	○	○	○	○	○

Light symbols, there is no IGC; dark symbols, there is IGC.

Table 3. Results of testing for IGC (AMU GOST 6032 procedure) resistance after tempering at 650°C steels with separate and combined alloying with N, Mo, and Si, containing ~0.03% C and steel Khl6N15M3 with 0.003% C.

Reducing the nitrogen content from 0.20 to 0.14% in this steel (6) eliminates its propensity to the IGC after a 500-h tempering. Similar corrosion resistance is possessed only by extremely low-carbon steel X16H15M3 (7), containing 0,003% of carbon [14].

Steel 03X17N13S2AM2 does not show a tendency to intergranular corrosion after tempering and other temperature and time parameters in the range 550–750°C (**Figure 5a**). This steel is much more resistant to IGC steel than the steel X16N15M3 with the same content of carbon and nitrogen (**Figure 5b**) [14], practically not inferior to especially low-carbon steel with 0.003% C (**Figure 5c**) and is not inclined to pitting and crevice corrosion (see **Table 1**, melting 5).

Thus, the introduction of silicon into the nitrogen-containing chromium-nickel austenitic steel with 0.03% C doped with molybdenum significantly improves its resistance against IGC and at a balanced content of Cr, N, Mo, and Si equates to a particularly low-carbon stainless steel containing 0.003% C.

The results of the investigations show that improvement of passivability and elimination of the propensity to pitting corrosion of cold-deformed austenitic chromium-nickel and stably austenitic chromium-manganese nickel steels with high- and low-carbon content are achieved by their joint doping with nitrogen and molybdenum.

However, to prevent a tendency for the IGC to leave after tempering in the investigated temperature-time range of stainless steels, their passivation with doping with nitrogen and molybdenum is insufficient. Apparently, this is due to the fact that when heated in the region of dangerous temperatures along the grain boundaries, chromium-depleted zones are formed as a result of the precipitation of excess phases. Therefore, the necessary condition for stability against IGC in the weakly oxidative environment of austenitic Cr-Ni steels after their long tempering at 550–750°C is the simultaneous presence in them of not only nitrogen and molybdenum but also a sufficient amount of silicon that improves, according to [13, 16, 17], the passivation of chromium-depleted boundary zones and reduction in tens or even hundreds of times the dissolution rate of tempered steels containing ≤ 0.032% C.
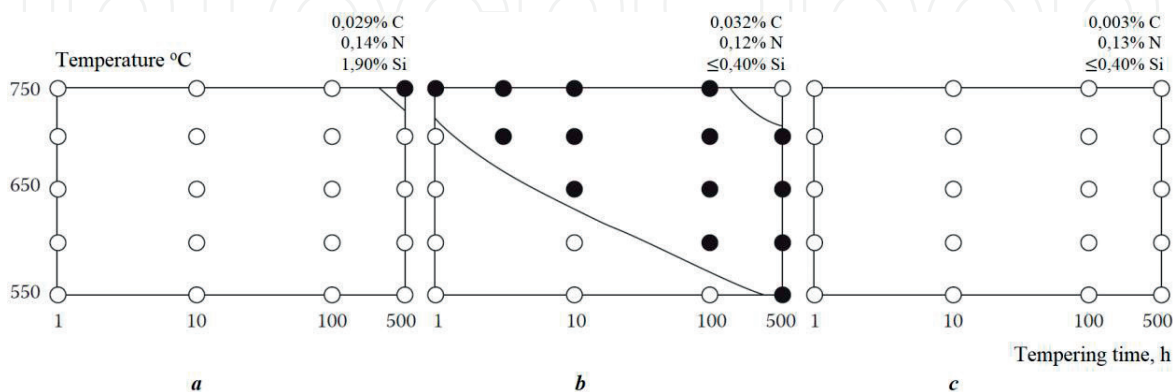
Figure 5. Resistance against IGC of nitrogen-containing steels 03Khl7N13S2AM2 (a) and Kh16N15M3 (b, c) with different contents of C and Si. Light symbols, there is no IGC; dark symbols, there is IGC.

6.2. New steels resistant to IGC in a strongly oxidizing environment

The main structural material for the manufacture of equipment producing nitric acid is steel 03Kh18N11 and its analog AISI 304L. Nitric acid is a strong oxidant, and the equipment used in its production has an inadequate service life due to corrosion damage.

In TsNIIchermet developed austenitic steels of the new system of doping Cr-Ni-N-Si (≤0.03% C, 14–17% Cr, 9–11% Ni, 2–4.5% Si) are intended for work in contact with highly oxidizing media [35–37]. The development is based on the nitrogen-containing steel 03Kh17AN9, which was doped with silicon in an amount that provides the formation of an austenite structure, and also the content of chromium and nickel was changed. The concentration of nitrogen and silicon in the steels was in the range of 0.08–0.145 and 2.0–4.5%, respectively.

The most positive results were obtained on the basis of two doping systems, (14–16)% Cr–11% Ni and (14–17)% Cr–9% Ni, with additions of nitrogen and silicon.

The metal for investigation was melted in a vacuum induction furnace and poured into 10 kg ingots that were forged on bobbins and rolled onto a 10-mm-thick sheet. The samples were quenched in water after heating to 1050°C. Resistance of steels against IGC was determined on polished cylindrical specimens with a diameter of 5 mm, a length of 60 mm according to a method simulating the method of DU GOST 6032. An analogue express method was used in which by using a more oxidizing medium, 27% HNO_3 + 40 g/l Cr^{6+} reduces the test time to 10 h.

The results of tests of steels for resistance against IGC are presented in **Table 4**. It can be seen that in comparison with steel 03Kh18N11, a decrease in chromium content from 16 to 14% at a nickel concentration of 11% and joint doping with nitrogen and silicon contributes to a 5–10-fold decrease in the mass loss of samples, and a decrease in chromium content from 17 to 14% and nickel to 9% is 5–28 times.

Steel	Test time (h)			$\Delta m_{st}/\Delta m$
	1	6	10	
	Mass loss Δm (g)			
03Kh18N11	0.014	0.327	1.046	–
03Kh16N11AS2	0.014	0.095	0.212	4.93
03Kh15N11AS2	0.015	0.078	0.127	8.24
03Kh14N11AS2	0.015	0.062	0.102	10.25
03Kh17N9AS2	0.012	0.091	0.194	5.39
03Kh15N9AS2	0.016	0.099	0.196	5.34
03Kh14N9AS4	0.002	0.021	0.037	28.27

Note: Δm_{st} и Δm, mass loss of standard steel 03Kh18N11 and new steels for 10 h.

Table 4. The change in the mass of the samples as a function of the time of testing for IGC in a strongly oxidizing medium.

The increase in resistance against intergranular corrosion in a highly oxidative environment of nitrogen-containing silicon-doped Cr-Ni steels should be attributed to its ability to enrich the surface layers, thereby increasing the protective properties of the passivating films.

In accordance with the new system of doping of Cr-Ni-N-Si, new austenitic steels 03Kh17N9AS2 and 03Kh14N9AS4 are developed that are not inclined to IGC in a strongly oxidative environment and are much more corrosion-resistant than standard steel 03Kh18N11.

It is generally accepted that the main cause of the destruction of steels under conditions of contact with an aggressive medium is local corrosion of the metal, which leads to a decrease in its working section. However, there are reasons to believe that another reason for the cracking of the metal can be its hydrogen saturation due to the development of delayed fracture phenomenon [38–41]. The results of the study showed that the new steels 03Kh17N9AS2 and 03Kh14N9AS4, designed for operation in highly oxidative media, also have an increased resistance to delayed fracture and hydrogen embrittlement [42, 43].

7. Local corrosion and choice of candidate steel for heat-exchange tubes of NPP with WWER

Historically, the steel 08X18H10T was chosen for heat-exchange pipes of the first domestic steam generators of NPPs with WWER. Despite all subsequent upgrades, this steel remained unchanged for steam generators [44]. While during this time at foreign nuclear power plants

Steel/alloy	NPP with	$\sigma_{0.2}$ $\sigma_{в}$ N/mm^2 Not less than	δ (%)	PRE	Resistance against the PC (○); inclination to PC (●)	Resistance against the IGC (○); inclination to IGC (●)
Applied steels and alloys						
AISI 304*	PWR	205 515	40	19	●	●
AISI 316*		205 515	40	25	●	●
Inconel 600*		205 550	35	15.5	●	●
Inconel 690		240 550	45	29	●	○ ●
08Kh18N10T	WWER	196 490	40	18	●	○ ●
Candidate steels						
03Kh17N13S2AM2	WWER	340 650	40	30	○	○
AISI 316LN		280 600	40	28	○	○ ●
AISI 316L [30]		170 485	40	26	●	○
AISI 316 Ti [30]		220 520	40	24	●	○

*Currently not applicable.

Table 5. Mechanical properties and resistance to pitting (PC) and intergranular (IGC) corrosion of steels and alloys used previously and currently for the production of heat-exchange tubes of nuclear power plants (NPP) with PWR and WWER.

with PWR, not a single generation of pipe system materials has been replaced [30]. The AISI 304 and 316 steels were replaced with nickel alloys—first, it was Inconel 600 and then the more corrosion-resistant Inconel 690 (see **Table 5**). However, recently this alloy also becomes a problem for NPPs with PWR. The instability of its corrosive behavior is close to the characteristics of the Inconel 600 alloy [45].

There is every reason to believe that the problems of damage to heat-exchange pipes made of AISI 304 and 316 steels and Inconel 600 and 690 alloys have led to ignoring their propensity to local corrosion (**Table 5**). In this respect, steel 08Kh18N10T is also rather mediocre. It is prone to pitting corrosion [30] and, in certain cases, to the IGC.

Steel X16N15M3 [14] (see **Table 2**, steel 3) is an analog of AISI 316LN and is not prone to pitting corrosion (**Table 5**), but is resistant to MCC after tempering at 650°C for only 1 h.

Thus, among the candidate materials for heat-exchange pipes, the most promising, as can be seen from **Table 5**, is steel 03Kh17N13S2AM2, the chemical composition of which is developed on the basis of grade 03Kh18N9S2AM2 [46]. Steel has the highest mechanical properties and no tendency to local corrosion.

8. Corrosion resistance of steel for heat-exchange tubes of reactor with lead coolant

The new steel 03Kh18N13S2AM2VFBR-Sh (EP 302M-Sh) [47], designed on the basis of grades 03Kh18N9S2AM2 [46] and 10Kh15N9S3B-Ш, was proposed for manufacturing heat-exchange tubes of the steam generator of the said reactor. Pipes, made of steel 03Kh18N13S2AM2VFBR-Sh, will be operated simultaneously in liquid lead and chloride-containing steam-water medium.

The results of her tests, presented in **Table 6**, indicate that the rate of crevice and pitting corrosion of this steel is 2 orders of magnitude lower than the standard grades 08Kh18N10T, stainless in an aqueous medium, and 10Kh15N9S3B-Sh (EP 302-Sh) designed for operation in liquid lead. In tests for stress-corrosion cracking, samples from a new steel—Odinga rings—do not collapse, in contrast to standard steels, for 1000 h (**Table 7**).

Steel	SC rate	PC rate
	g/m²h	
03Kh18N13S2AM2VFBR-Sh	0.10	≤0.01
10Kh15N9S3B	25	9.6
08Kh18N10T	16	7.8

*On contact with a sealing sulfur-containing material.

Table 6. The slit (SC)* and pitting (PC) corrosion rate in 10% $FeCl_3 \cdot 6H_2O$ solution of the new 03Kh18N13S2AM2VFBR-Sh and standard steels.

03Kh18N13S2AM2VFBR-Sh	10Kh15N9S3B	08Kh18N10T
Tensile stress (N/mm²)		
523	552	295
Time to failure (h)		
1000*	43	10
*Samples are not destroyed.		

Table 7. Time before the destruction of the Odinga rings in 10% $FeCl_3 \cdot 6H_2O$ solution with tensile stress of $1.2\sigma_{0.2}$ of the new 03Kh18N13S2AM2VFBR-Sh and standard steels.

Corrosion indicators	03Kh18N13S2AM2VFBR-Sh	12Kh18N10T	AISI 316L
Weight gain (g/m²)	0.33	0.54	–
Corrosion rate (mg/m²h)	0.88	1.5	5.6

Table 8. Corrosion parameters of polished samples of steel 03Kh18N13S2AM2VFBR-Sh, 12Kh18N10T in an aqueous medium at 505°C, pressure 17 MPa for 1000 h [39], and AISI 316L steel at 480°C, 25 MPa pressure for 500 h [49].

Table 8 shows the results of gravimetric measurements of polished samples of steel 03Kh18N13S2 AM2VFBR-Sh after 1000 h of testing in an aqueous medium of an autoclave complex at 505°C, a pressure of 17 MPa, and a dissolved oxygen concentration of 30 ppb [48]. From the data obtained, it follows that the corrosion rate of the new steel in the water-coolant environment is almost 1.5 times lower than that of the grade 12Kh18N10T and several times smaller than that of the AISI 316L steel. The new steel after the tests remained without trace of corrosion, unlike the Inconel 625 and 718 alloys with pitting on the surface of the samples after they had been held in supercritical pressure (SCP) water with an oxygen concentration of 25 ppb at 500°C for 500 h (see **Figure 4**).

9. Conclusion

Results of investigation of the effect of joint and separate doping with nitrogen and molybdenum, cold deformation, inclusions of the α'-phase, δ-ferrite on the tendency to pitting corrosion of Cr-Ni and Cr-Mn-Ni steels with stable and unstable austenite, studying the influence of silicon, and nitrogen resistance to intergranular corrosion of Cr-Ni steels are essentially the principles of alloying unstabilized austenitic steels that are resistant to local corrosion in weakly and strongly oxidizing environments. On their basis, a number of austenitic steels of the following types have been developed: 22Kh18N5AM3D2S2 (EP 995), 22Kh18N5AM3S2 (EP996), 15Kh21G9N9AM2-Sh, 03Kh18N9S2AM2, 03Kh17N13S2AM2, 03Kh18N13S2AM2VFBR-Sh, 03Kh17N9AS2, 03Kh14N9AS4, 03Kh20N19AM2 (EC 176), 12Kh18N13AM3 (EP 878), etc. These steels are designed to produce equipment that is resistant to local corrosion in chloride-containing media and nitric acid.

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