

# INFLUENCE OF NITROGEN ADDITION ON PHYSICAL-CHEMICAL PROPERTIES AND CORROSION RESISTANCE OF STAINLESS STEELS

## ВЛИЯНИЕ ДОБАВКИ АЗОТА НА ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА И СОПРОТИВЛЕНИЕ КОРРОЗИИ НЕРЖАВЕЮЩИХ СТАЛЕЙ

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**Abstract:** Researched were the physico-chemical properties, hardening and corrosion resistance of Cr18Ni10N type austenitic chromium-nickel stainless steels of different purity by the impurities and with different nitrogen content: from impurity level to 0.220%. It is demonstrated that nitrogen alloying is beneficial both for hardening and improvement of corrosion resistance of steel under conditions when nitrogen has the form of solid solution. Addition of 0.186-0.220% of nitrogen doesn't reduce intercrystalline corrosion in standard environment of 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.01M KSCN and improves resistance to general and pitting corrosion in chloride-containing environments. Pure nitric steel shows higher resistance to intercrystalline, general and pitting corrosion in chloride solutions than normal purity steel.  
**KEYWORDS:** AUSTENITIC STEEL, NITROGEN ALLOYING, CORROSION RESISTANCE

### 1. Introduction

Austenitic steels of type Cr18Ni10N have been widely used as corrosion resistant, heat resistant, cryogenic steels [1–6].

Due to complexity and multifactor impact of nitrogen there are no clear criteria for selection of proper nitrogen content and resulting structure for different purpose steels yet.

Similar to the carbon the nitrogen ensures solid solution steel hardening and dispersion strengthening due to generation of nitrides and carbonitrides. Within such process the nitrogen has higher impact on solid solution hardening and improves mechanical hardening due to smaller atom diameter compared to carbon.

Nitrides in Cr-Ni steels are more dispersed and evenly distributed compared to carbides allowing to get high values of resistance, ductility and toughness at the same time.

Grain-boundary strengthening of nitric steels is also effective due to release of dispersed nitrides and carbonitrides along the boundaries and subboundaries, and grain refining upon heat treatment.

Stable Cr-Ni and Cr-Mn austenitic steels alloyed with nitrogen are often reinforced with cold plastic yield and aging.

The increase of the concentration of N and N+C can result to increase of the effects of aging both during and after deformation due to a larger supersaturation of the solid solution. It can decrease the temperature of the austenite decomposition and thus can results to decrease of the solid solution doping as well as the stability of the austenite. Thus processes of the structure formation (including recrystallization) change and corrosion resistance and other special properties deteriorate. In particular, of long-term strength can decrease due to formation of such nitrides and carbonitrides as Cr<sub>23</sub>(CN)<sub>6</sub>, Cr<sub>2</sub>(CN). In this case, to save the properties is necessary to change the alloying of steel: to reduce the nitrogen content or to add other alloying elements.

Thermomechanical treatment is effective for nitrogen steels under proper treatment schedule. Under high-temperature thermomechanical treatment the heating temperatures can be higher than for nitrogen-free steels [7, 8].

Alloying with nitrogen improves resistance to local and intercrystalline corrosion [4–6]. However, since corrosion resistance

depends heavily on steel structure the specific temperatures of nitride discharge and solution should be taken into account.

The present work is devoted to experimental study of nitrogen alloying impact on hardening and corrosion resistance of austenitic Cr-Ni steel of different purity provided that nitrogen exists in solid solution form.

### 2. Material and Experiment

For this study the material was steel type Cr18Ni10N with nitrogen content of 0.186 % and 0.220 % and steel type Cr18Ni10Ti was used for comparison; chemical content of both steels see in Table 1.

The steels were produced and preliminary treated as follows. Hot-rolled industrially melted steel Cr18Ni10Ti.

Nitrogen-alloyed steels were melted in laboratory using burden material with different content of residual elements. Steel 2 (Cr18Ni10N, N=0.186 %) was produced in induction furnace by remelting nitrogen-free steel with similar chemical composition with addition of pure burden materials up to required composition.

Steel 3 (Cr18Ni10N, N=0.220 %) was melted in induction vacuum furnace, following pure materials were used as burden: ingot iron grade, electrolytic nickel, electrolytic manganese, pure chrome, nitrogenized ferrochrome, granulous aluminum.

The ingots were hot-forged and hot-rolled. Final treatment of all steels – hardening (solution heat treatment) from austenite region from 1050 °C in water.

Mechanical properties of all steels were defined with pulling test on coupons according to GOST 1497-84.

Thermal conductivity is defined by a special apparatus in the temperature range of 20–100 °C using a differential non-contact thermocouple by constructing a temperature-time dependency as follows. One end of the coupon is dipped into boiling water with temperature T<sub>2</sub> (i.e. T<sub>2</sub>=const=100 °C), while the rod itself is inserted in plastic foam to prevent heat exchange between side surface and environment. On the other end the temperature is measured with thermocouple within equal time periods t until it becomes constant. At the initial time the rod has temperature T<sub>0</sub>, then the temperature grows and reaches T<sub>2</sub> asymptotically (under t=∞).

Table 1. Chemical composition of investigated steels

No.	Steel	Chemical composition, wt. %*								
		C	Cr	Ni	Mn	Mo	S	P	Al	N
1	Cr18Ni10Ti	0.10	17.7	9.5	1.19	0.10	0.007	0.027	0.11	<0.01
2	Cr18Ni10N (N=0.186 %)	0.05	18.1	9.6	0.82	<0.10	0.018	0.025	0.12	0.186
3	Cr18Ni10N (i.f., N=0.220 %)**	0.007	19.1	9.3	1.42	0.012	0.004	0.002	0.035	0.220

\* – base is Fe; \*\* – i.f. – impurity free

Temperature conductivity coefficient is defined by the following formula:

$$(1) \quad \alpha = \frac{2 \cdot L^2}{5 \cdot t_3} \ln \left( \frac{T_2 - T_0}{T_2 - T_3} \right),$$

where  $T_3$  – temperature measured on the other end of the rod at the time  $t_3$ ;

$L$  – length of the rod.

Thermal-expansion coefficients and crystalline transformation effects are defined with dilatometer DIL805 under following test schedule: heating from room temperature to the temperature of 1200 °C under 5 °C/sec, holding for 1 min. and further cooling under 50 °C/sec to 50 °C.

Resistance to general, intercrystalline and pitting corrosion in different environments is evaluated. Tests are done using electrochemical station Zive MP2.

Tendency to general corrosion is defined in sea water (3% NaCl) and in acid environment (0.5M H<sub>2</sub>SO<sub>4</sub>), including purging with H<sub>2</sub>S, by determination of potentials and critical current density of passivation. The test consisted of evaluation of open circuit potential ( $E_{ocp}$ ) during 3 hours; establishment of polarization curve from negative potential values (cathode region) to repassivation region (in acid environment) or to the potential of stable pitting formation (in sea water).

Potential equal to maximum current density in active dissolution region is taken as critical potential of passivation ( $E_{cp}$ ); potential of full passivity ( $E_{fp}$ ) – is the potential behind which development current density is reduced by no more than 1  $\mu$ A/cm<sup>2</sup> (for 0.5M H<sub>2</sub>SO<sub>4</sub>) or the potential upon which the current density is equal to 3 % from critical current density (for 0.5M H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>S); at that the critical current density of passivation ( $i_{cp}$ ) is determined as current density at critical potential of passivation, and current density in a passive state ( $i_p$ ) – as minimum density of current in passive region. The potential which didn't result in current density decrease under increase of potential is taken as the potential of repassivation; for tested steels the threshold value of current density is 5  $\mu$ A/cm<sup>2</sup> (for 5M H<sub>2</sub>SO<sub>4</sub>) or 1 mA/cm<sup>2</sup> (for 0.5M H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>S).

Resistance to intercrystalline corrosion is defined using method of potentiodynamic development in solution of 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.01M KSCN according to GOST 9.914-91. The tests were dedicated to plot the potentiodynamic curve of forward (from cathode region into anode region) and backward sweep of potential (from anode region to cathode region) for all coupons. Relation of calculated total charge of potentiodynamic curve of backward sweep of potential ( $Q_c$ ) to forward one ( $Q_a$ ) characterizes the resistance of the coupon to intercrystalline corrosion: if it is lower than 0.11, the coupon is recognized as resistant to intercrystalline corrosion.

The resistance to pitting corrosion is evaluated according to GOST 9.912-89 by the average conditional speed of pitting corrosion. The tests included 24-hours holding of pre-weighted coupons in solution of ferric chloride (III) and following weighting. The speed of pitting corrosion  $V_m$  is determined by the weight loss using a formula:

$$(2) \quad V_m = \frac{\Delta m}{S \cdot t},$$

where  $\Delta m$  – total weight loss for parallel (tested at the same time) coupons, grams,

$S$  – total area of parallel coupons, m<sup>2</sup>,

$t$  – duration of the test, hours.

### 3. Results and Discussion

Steel hardness index grows with increase of nitrogen content in steels 2 – 3 Cr18Ni10N (Table 2). During the elongation all steels show high ductility (see Table 2) while pure steel 3 has the highest ductility index: El = 63% and RA = 84%.

Thermal conductivity of steel Cr18Ni10N within 25–100 °C is appropriate for austenitic high-resistance steels: for steel 3 temperature conductivity coefficient  $\alpha = 3.8$  mm<sup>2</sup>/sec.

Table 2. Mechanical properties of the investigated steels

No.	Steel	UTS, MPa	YS, MPa	El, %	RA, %
1	Cr18Ni10Ti	515	230	47	51
2	Cr18Ni10N (N=0.186 %)	715	355	25	67
3	Cr18Ni10N (i.f., N=0.220 %)	750	400	63	84

Analyzed dilatograms of nitric steel heating showed that under the heating at ~5 °/sec within 50–1200 °C excessive nitrides may be discharged and dissolved. The discharge can happen under 400–700 °C, dissolution – above 1000 °C. This process should be controlled as together with improvement of hardness it can reduce the toughness and corrosion resistance.

Coefficient of thermal expansion for different temperature ranges corresponds to regular values by the order and, for example, for steel Cr18Ni10N within 50–300 °C (without excessive phase discharge) equals to 20.46·10<sup>-6</sup> K<sup>-1</sup>. Average linear coefficients for ranges of 50–800 °C and 50–1200 °C equal to 25.28·10<sup>-6</sup> K<sup>-1</sup> and 31.72·10<sup>-6</sup> K<sup>-1</sup> respectively. This difference results from phase content change and can be used for express-control of transformation processes. Also this difference should be considered during the size change evaluation. The products made from nitric steel should not be heated above 300 °C after the hardening to preserve the nitrogen in solid solution, as mentioned before [9].

Polarization curves of tested steels in acid environment are characterized with soft transition from cathode region into anode region, peak of active dissolution is clear and located in the range of -150–113 mV for steel 2 (see polarization curve of steel 2 Cr18Ni10N in the Fig.1) and in the range of -147–271 mV for steel 3. The width of passive region is 1145 mV for steel 2, and 996 mV for steel 3. It is estimated that repassivation starts immediately from or soon after the initiation of oxygen discharge. After the test the surface of coupons is highly etched and rough, borders of working area are clear (see Fig. 2).

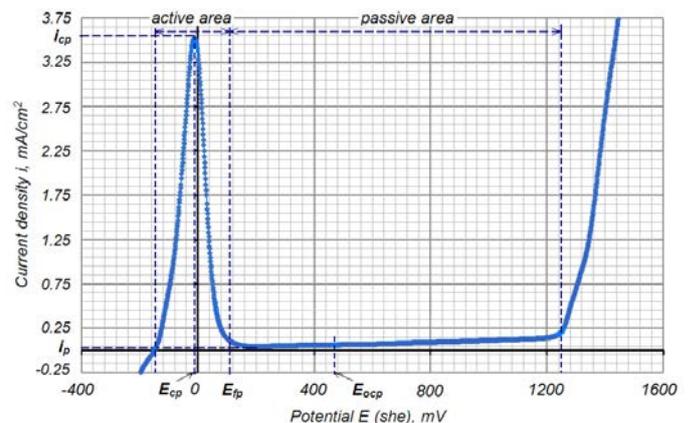


Fig. 1. Polarization curve for steel 2 Cr18Ni10N (N=0.186 %), environment 0.5M H<sub>2</sub>SO<sub>4</sub>, development speed – 1 mV/sec:

$E_{cp}$  – critical potential of passivation;  $E_{fp}$  – potential of full passivity;  $E_{ocp}$  – open circuit potential;  $i_p$  – current density in a passive state;  $i_{cp}$  – critical current density of passivation; she – standard hydrogen electrode

During the test in 0.5M H<sub>2</sub>SO<sub>4</sub> and purging with H<sub>2</sub>S polarization curves of tested steels also have smooth transition from cathode to anode region; the peak of active dissolution is located in the range of -147–510 mV for steel 2 and -182–623 mV for steel 3. The passivation is sharp and abrupt, the width of passive region is 701 mV and 688 mV for steels 2 and 3 respectively. Probably the repassivation starts immediately or soon after the oxygen discharge.

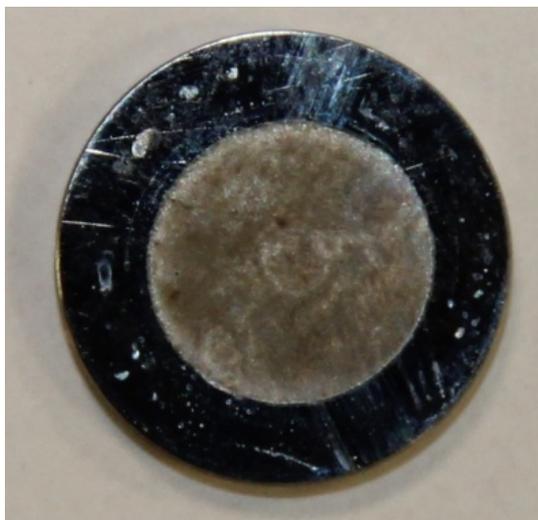


Fig. 2. Appearance of coupon made from steel 2 Cr18Ni10N (N=0.186 %) after testing in environment 0.5M H<sub>2</sub>SO<sub>4</sub> (coupon outer diameter is 19 mm, working area diameter is 11 mm, coupon thickness is 2.4 mm)

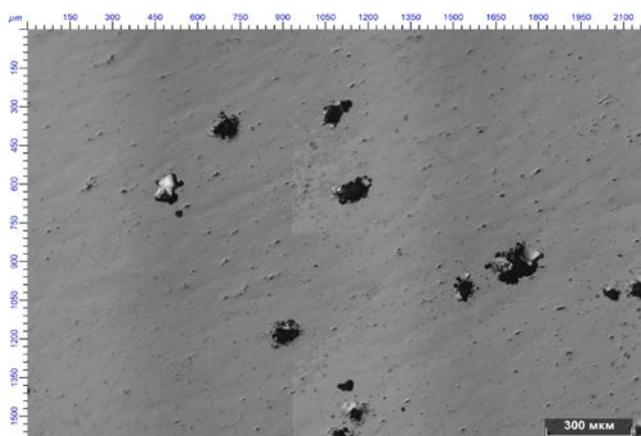


Fig. 3. Appearance of pittings formed on the coupon surface under testing in 3% NaCl



Fig. 4. Appearance of coupon made from steel 2 Cr18Ni10N (N=0.186 %) after testing in environment 3% NaCl

Within the active dissolution region black film appears on all surfaces (probably due to the porosity). This film has no protecting properties and peels after critical potential of passivation  $E_{cp}$  is reached. Based on the work [9] it is estimated the approximate composition of such film is nickel sulphide Ni<sub>2</sub>S. The surface is evenly etched, the depth of etching is small but the surface is evenly rough: there are clear black points on the surface of coupons made from steel 2. It is presumed that such points are resulted from selective dissolution of alloy components.

Appropriate electrochemical data on testing steel resistance to general corrosion in acid environment (including purging with hydrogen sulfide) see in Table 3.

Table 3. Electrochemical data gathered upon corrosion resistance testing of steel in the acid environment

No.	Steel	$E_{ocp}$ , mV	$E_{cp}$ , mV	$E_{fp}$ , mV	$i_{cp}$ , mA/cm <sup>2</sup>	$i_p$ , μA/cm <sup>2</sup>
acid environment (0,5M H <sub>2</sub> SO <sub>4</sub> )						
2	Cr18Ni10N (N=0.186 %)	473	-11	113	3,55	52,4
3	Cr18Ni10N (i.f., N=0.220 %)	-135	0	271	11,0	8,35
acidic (0,5M H <sub>2</sub> SO <sub>4</sub> ) compressed hydrogen sulphide H <sub>2</sub> S						
2	Cr18Ni10N (N=0.186 %)	-132	463	510	135	871
3	Cr18Ni10N (i.f., N=0.220 %)	-189	607	623	176	81,9

Purging of solution with hydrogen sulfide equally activates both steels: current density grows in regions of active dissolution and passivation, potential of passivation shifts to positive end and passivation region is narrowed. Probably, all steels show some change of passive state due to generation of sulfide components together with their oxides: during the testing the black film was formed in the active region. Such film had no protective properties and disappeared before the passivation begins. This behavior is typical for nickel in sulfuric environments.

According to the results, if external potential is absent steel 2 Cr18Ni10N stays passive in acid environment; steel 2 has higher corrosion resistance parameters in acid environment. During test in 0.5M H<sub>2</sub>SO<sub>4</sub> and purging with H<sub>2</sub>S both steels remain in active state, i.e. they have low corrosion resistance in this environment.

During the general corrosion resistance test in 3% NaCl (sea water) the polarization curves of all coupons do not have the regions of active dissolution, i.e. they remain passive during the whole test period. At that the open circuit potential has higher negative value than potential of pitting formation. Due to this, open circuit potential and potential of pitting formation ( $E_{pf}$ ) (the potential corresponding to current density of 1 mA/cm<sup>2</sup> is taken as the potential of pitting formation) are calculated. In this environment all coupons demonstrated formation of clear pitting and insignificant general corrosion: the work area of all coupons remains glassy and pittings are equal by kind on all coupons, see Fig. 3. Pittings on tested coupons are clear and evenly distributed on the coupon surface, however steel 2 demonstrates larger pittings (see Fig. 4). All steels are exposed to gap corrosion in sea water: there are tracks of gap corrosion (appeared as big etches in the form of circles or circular sectors) along the boundaries of working area (at points of contact between waterproof gasket and metal surface).

The electrochemical data collected during testing in 3% NaCl see in Table 4.

Table 4. Electrochemical data gathered upon corrosion resistance testing of steel in the sea water

No.	Steel	$E_{ocp}$ , mV	$E_{pf}$ , mV
2	Cr18Ni10N (N=0.186 %)	-9	664
3	Cr18Ni10N (i.f., N=0.220 %)	32	785

According to the results, steel 3 Cr18Ni10N is more resistant to corrosion in chlorine-containing environments – potential of pitting formation for this steel is 120 mV upward than for steel 2 in average.

Results of intercrystalline resistance evaluation (see Table 5) demonstrated that tested steels are resistant to corrosion of this type as the ratio between backward sweep curve charge and forward sweep curve charge  $Q_c/Q_a$  for all steel is less than 0.11. During the test the coupons showed minimal etching and retained glassy surface.

Table 5. Results of intercrystalline corrosion resistance test

No.	Steel	$Q_c/Q_a$	Resistance to intercrystalline
2	Cr18Ni10N (N=0.186 %)	0,0002	resistant
3	Cr18Ni10N (i.f., N=0.220 %)	$6 \cdot 10^{-7}$	resistant

The tested steels showed similar resistance to pitting corrosion evaluated by the average conditional speed of pitting corrosion (see Table 6).

Table 6. Results of pitting corrosion resistance test

No.	Steel	$S, 10^{-4} \text{ m}^2$	$\Delta m, \text{ grams}$	$V_m, \text{ grams} \cdot \text{m}^{-2} \cdot \text{hours}^{-1}$
1	Cr18Ni10Ti	2,99	0,1586	11,06
2	Cr18Ni10N (N=0.186 %)	4,27	0,1661	16,22
3	Cr18Ni10N (i.f., N=0.220 %)	3,14	0,0997	6,61

At that, resistance of pure steel 3 Cr18Ni10N to intercrystalline and pitting corrosion is higher than of commercial steel 2. Nitrogen steel (2 Cr18Ni10N) and nitrogen-free steel (1 Cr18Ni10Ti) of regular commercial melting had similar pitting corrosion resistance value, but lower than pure steel (3).

So, the tested nitric steels showed rather close values of resistance to different types of corrosion, however by the value of critical current and passivation potential, ratio between back curve charge and forward curve charge during evaluation of resistance to intercrystalline corrosion and by the average conditional speed of pitting corrosion they can be categorized as follows (see Table 7). Pure nitric steel showed high resistance to intercrystalline, general and pitting corrosion in chloride solutions than normal purity steel.

Table 7. Resistance of tested steels to different types of corrosion

No.	Steel	General corrosion			Intercrystalline corrosion	Pitting corrosion
		acid environment (0,5M H <sub>2</sub> SO <sub>4</sub> )	acidic (0,5M H <sub>2</sub> SO <sub>4</sub> ) compressed hydrogen sulphide H <sub>2</sub> S	sea water (3% NaCl)	0,5M H <sub>2</sub> SO <sub>4</sub> + 0,01M KSCN	100 g/l FeCl <sub>3</sub> ·6H <sub>2</sub> O
		categorizing by				
		combination of parameters	combination of parameters	$E_{pt}-E_{ocp}$	$Q_c/Q_a$	$V_m$
2	Cr18Ni10N (N=0.186 %)	1	nonresistant	2	2	2
3	Cr18Ni10N (i.f., N=0.220 %)	2	nonresistant	1	1	1

## 4. Conclusion

Alloying of austenitic Cr-Ni steel type Cr18Ni10N with nitrogen up to 0.220% is prospecting for improvement of hardness and corrosion resistance in mildly aggressive chloride environments (like sea water) provided that there is no additional discharge of nitrides. Corrosion resistance can be additionally improved by improving the purity of steels.

## 5. References

- Bannykh, O., Progress in the Research and Application of Nitrogen-Alloyed Steels. – In: Proceed. 10th Int. Conf. on High Nitrogen Steels, Moscow, MISiS, 2009, pp. 24–27.
- Berns, H., S. Riedner, V. Gavriljuk, High Interstitial Stainless Austenitic Steels, Part I: Constitution, Heat Treatment, Properties, Applications. – In: Proceed. 10th Int. Conf. on High Nitrogen Steels, Moscow, MISiS, 2009, pp. 129–139.
- Svyazhin, A.G., J. Siwka, L.M. Kaputkina, High-nitrogen steels – The current state and development trends. – In: Proceed. Int. Conf. Advanced Steels, China, Beijing, Metallurgical Industry Press, 2010, pp. 352–356.
- Mushnikova, S.Yu., Yu.L. Legostaev, A.A. Harkov, and other. An investigation on the influence of nitrogen on austenitic steel pitting resistance. – Issues of material science, 2 (38), 2004, pp. 126–135. (in Russian)
- Baba, H., T. Kodama, Y. Katada. Role of nitrogen the corrosion behavior of austenitic stainless steels. – Corrosion Science, 44, 2002, pp. 2393–2407.
- Mudali, UK, S. Ningshen, B. Raj. Passive Films and Localised Corrosion – Role of Nitrogen. – In: Proceed. 10th Int. Conf. on High Nitrogen Steels, Moscow, MISiS, 2009, pp. 271–280.
- Rakhshadt, A.G., L.M. Kaputkina, S.D. Prokoshkin, and other (Edtrs). Metal science and heat treatment of steel and cast iron, v. 3. Moscow, Intermet Engineering, 2007, 920 p. (in Russian)
- Schastlivtsev, V.M., V.I. Zeldovich, D.A. Mirzayev, and other. Development ideas of academician V.D. Sadovsky. Ekaterinburg, Inst. Metal Physics Ural Division RAS, 2008, 409 p. (in Russian)
- Andreev, Y.Y., T.V. Bobkov, A.V. Dub, and other. Thermodynamics of chemisorption of sulfur from thiocyanate on nickel during electrochemical passivation. – Protection of Metals and Physical Chemistry of Surfaces, 4 (49), 2013, pp. 444–450.

The results were obtained within the execution of state task of the Ministry of Education and Science of the Russian Federation.