# INNOVATIVE SOLUTIONS USING NITROGEN-CONTAINING STEELS

## ИННОВАЦИОННЫЕ РЕШЕНИЯ С ИСПОЛЬЗОВАНИЕМ АЗОТСОДЕРЖАЩИХ СТАЛЕЙ

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**Abstract:** *The report provides examples of two innovative solutions using nitrogen-containing steels. The use of nitrogen-containing steels allows to increase the durability and reliability of products; to reduce the thickness of work sections; to reduce the cost of maintenance and repair downtime. The proposed solutions: 1. Austenitic corrosion resistant cast steel with 0,5%N. After homogenizing heat treatment the steel surpasses traditional cast austenitic steels at yield strength at ~1.5-2 times, impact toughness ~ 4.5 times, hardness - by about 25%. It is recommended for the manufacture of cast valves. 2. The martensitic steel grade with 0,11-0,17% N. This steel is well proved as a material for the manufacture by cold heading of very high strength corrosion resistant fasteners.*

***KEYWORDS**: NITROGEN-CONTAINING STEELS, CAST STEEL, HIGH STRENGTH, CORROSION RESISTANCE, CORROSION RESISTANT FASTENERS, CAST VALVES*

### 1. *Introduction*

The report provides examples of two innovative solutions using nitrogen-containing steels. As an interstitital element, nitrogen ensures considerable solid solution strengthening. In nitrogen steel, dispersional hardening is also possible on account of nanoparticles of chromium nitride CrN. Alloying with nitrogen increases the resistance to local corrosion. Since nitrogen effectively stabilizes austenite, its introduction in steel reduces the consumption of expensive austenite stabilizers such as Ni, Co, and Cu. Nitrogen as an alloying element in the composition of corrosion resistant steels provides a simultaneous combination of their strength, ductility and toughness, corrosion and wear resisting. The use of nitrogen-containing steels allows to increase the durability and reliability of products; to reduce the thickness of work sections; to reduce the cost of maintenance and repair downtime.

#### *2.1. Austenitic corrosion resistant cast steel with 0,5%N.*

Many products of complex shape require manufacturing by casting. The problem of increasing the strength of cast corrosion-resistant products can be solved, including, through the use of nitrogenous steels. Our proposed solution: austenitic corrosion resistant high strength casting steel 05Kh22AG15N8MFL (0.05C21Cr0.5N15Mn8NiV) with nitrogen concentration 0,45–0,62% [1].

This steel has good fluidity in the process of mold casting. When crystallized, it is not prone to the formation of hot cracks. After the heat treatment, the cast steel has an austenitic structure, (% of δ-ferrite =5÷0, depending on nitrogen concentration), hardened with nano sized nitride particles of the MeN type, ~ 10 nm in size [2]. Its high yield strength in the absence of hardening deformation treatment (in the presence of coarse-grained structure) can be explained not only by solid solution strengthening of austenite by nitrogen, but also by the effect of dispersion hardening due to the presence of nano sized nitride particles. In cross-sections from 20 to 50 mm the mechanical properties of steel do not depend on the morphology of the cast structure.

**Mechanical properties (tensile testing, impact test).** After homogenizing heat treatment, this steel exceeds not only traditional Russian austenitic cast steels (without nitrogen in their chemical composition), but European and American nitrogen containing steels [2, 3]. Fig.1 illustrates a comparison of strength and ductility levels of proposed steel and the same mechanical properties levels of cast austenitic steel grades. New cast steel exceeds traditional cast austenitic steels by a factor of ~1.5 - 2 in terms of the yield strength, ~3 - 4.5 in terms of the impact, and 15-25% in terms of the hardness).

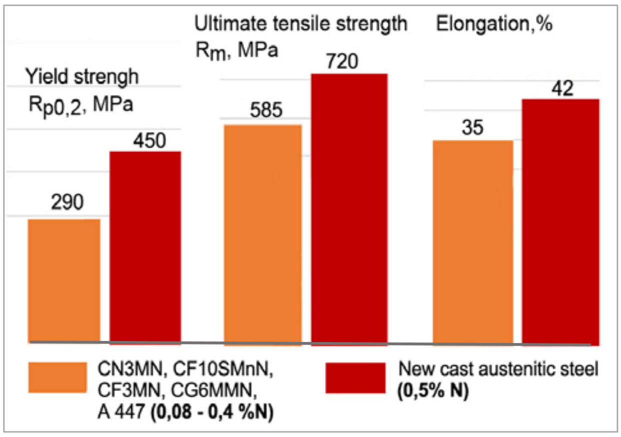


Fig.1. Characteristics of strength and plasticity in tensile testing of a new cast austenitic nitrogen containing steel and European and American cast steel grades (with a nitrogen content of up to 0.3%).

The new cast steel is not prone to cold brittleness: it is keeping the impact toughness at least 2.3 MJ/m$^2$ with cooling to -70 ° C [2, 3]. At elevated temperatures (in the 200-350 ° C range) steel has a yield strength of 200-230 MPa, high ductility (El = 47-55%), exceeding not only foundry steels, but also conventionall deformable stainless steels. These statements are illustrated in the table. 1 and by Fig.2.

Table 1. Cold and heat resistance of the new cast steel 05Kh22AG15N8MFL

| Steel grade | Mechanical properties | Testing temperature, $^oC$ | | | | |
|---|---|---|---|---|---|---|
| | | -70 | -40 | +200 | +300 | +350 |
| New austenitic cast steel | $Rp_{0,2,}$ MPa | 558 | 506 | 229 | 214 | 211 |
| | $R_m$, MPa | 841 | 851 | 575 | 547 | 542 |
| | El/ RA, % | 24/25 | 47/50 | 55/57 | 45/39 | 47/52 |
| | KCU, MJ/m$^2$ | 2,31 | 2,46 | - | - | - |
| AISI 316 | $Rp_{0,2,}$ MPa | | | 160 | 150 | 140 |
| | $R_m$, MPa | | | 400 | 360 | 340 |
| | El, % | | | 23 | 18 | 16 |

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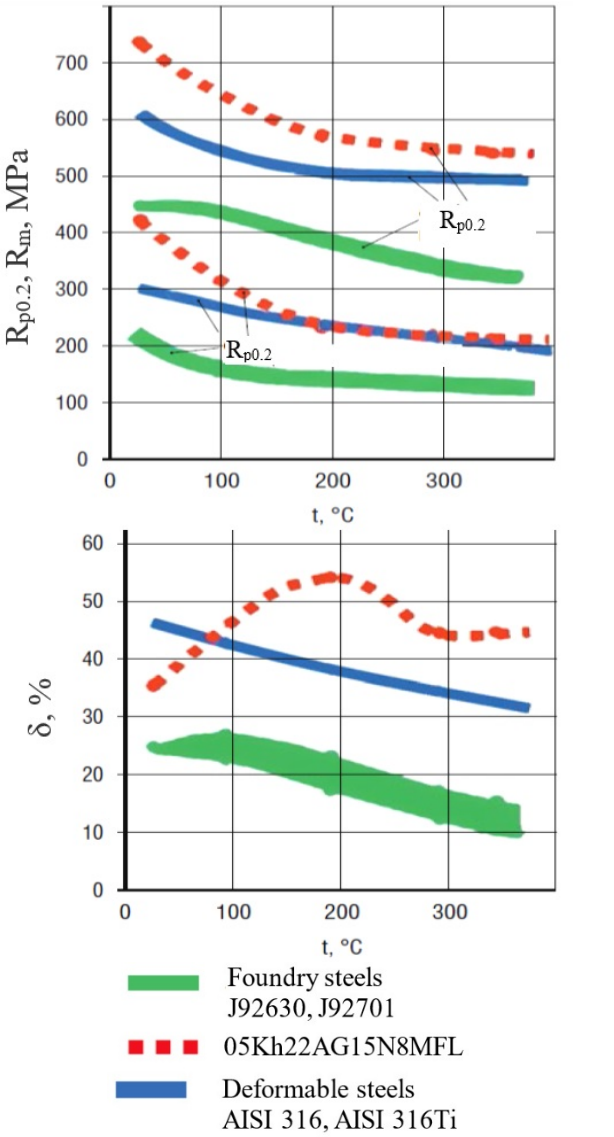


Fig.2. Characteristics of strength (a) and plasticity (b) in tensile testing of a new cast austenitic nitrogen containing steel and conventional foundry and deformable stainless steels steel grades at elevated temperatures

**The fatigue strength** of the annealed 05Kh22AG15N8MFL corrosion-resistant austenitic cast steel containing 0.47% N was investigated*. The fatigue curve of the 05Kh22AG15N8MFL steel (Fig. 4) was constructed on the basis of the experiments at maximum stresses ranging between 200 and 600 MPa. The curve allows us to assess the fatigue life in the fields of both low cycle fatigue (up to $10^5$ load cycles) and high-cycle fatigue. With decreasing the applied stress, the fatigue life increases.

After heat treatment, this steel contained up to 5% ferrite in the structure and exhibited a good combination of strength and ductility. Due to alloying with nitrogen, the steel at such type of loading does not undergo transformation of austenite to martensite, and its fatigue strength on the basis of $10^7$ cycles is 210 MPa, which is equal or close to the yield strength of traditional hot-worked and then solution-treated 18-10 type corrosion resistant steels. The smooth fatigue curve of the cast steel indicates that its structure is free from coarse defects and no formation of strain-induced martensite occurs under the action of applied stresses (Fig. 4). This test confirmed the beneficial effect of alloying with nitrogen not only on the static but on the cyclic strength.

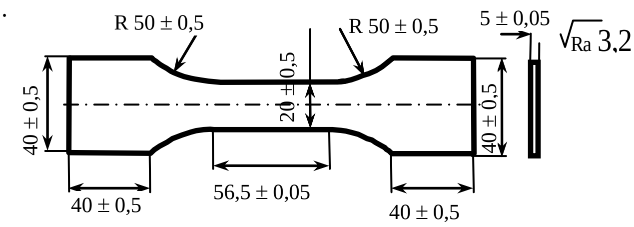


Fig.3. Sample for fatigue tests

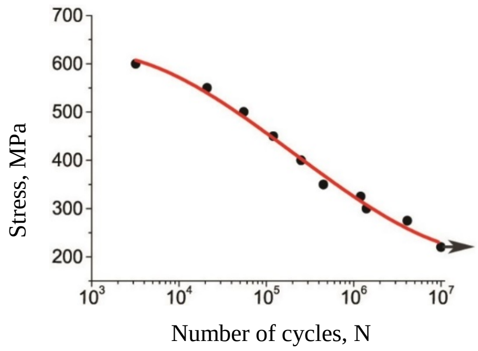


Fig. 4. Fatigue curve of the flat cast samples of the 05Kh22AG15N8MFL steel after heat treatment under conditions of repeated tension.

**Wear resistance.** The cast steel has a high wear resistance. The Hadfield steel (110G13L) was used as a standard of wear resistant material when the relative wear resistance $\boldsymbol{\varepsilon}$ in the dry friction on the abrasive was tested. ($\boldsymbol{\varepsilon} = \Delta M_s / \Delta M_t$ where $\Delta M_s$ is weight loss of standard, $\Delta M_t$ is weight loss of the tested samples). It was demonstrated that wear resistance of the cast steel 05Kh22AG15N8MFL (specimens with nitrogen concentration 0,47 and 0,62% N) is comparable to that of the Hadfield steel: ***ε= 0,94-1,08*** ***(***depending on nitrogen concentration in tested steel 05Kh22AG15N8MFL).

High wear resistance is an advantage of structure material, but especially for providing of normal technological process we developed, on the base of catting experiments using different catting parameters, the optimal catting technology (which is saving cutters, with a minimum time of cutting (turning)).

**Corrosion resistance** of cast steel was investigated. It was shown that steel 05Kh22AG15N8MFL is not prone to intergranular corrosion; steel has a high resistance to pitting corrosion. Their corrosion resistance parameters – calculated Pitting Resistance Equivalent (PREN), which depends on Cr, Mo and N concentrations in steels and the experimentally detected Critical Pitting Temperature (CPT) in comparison with the parameters of common stainless steels are shown in table 2.

Table 2. Comparison of corrosion resistance parameters of conventional stainless steels and 05Kh22AG15N8MFL cast steel

| Steel grade | %Cr | % Mo | % N | PREN[1] | CPT ,°C[2] |
|---|---|---|---|---|---|
| AISI 316 | 16.5 | 2.1 | 0.05 | 24.2 | 15 |
| Type 317 | 18.5 | 3.1 | 0.06 | 29.7 | 18,9 |
| AISI 904L | 20.5 | 4.5 | 0.05 | 36.2 | 40 |
| 05Kh22AG15N8MFL | 20-22 | 0,8-1,5 | 0,5 | 30-33 | 40-43 [3] |

* The fatigue tests were performed according to GOST 25.502-79 "Fatigue testing methods" with an Instron 8801 setup at 30 Hz under conditions of repeated tension at cycle asymmetry R = 0.1 at room temperature. The test base was $10^7$ cycles. The flat samples (type IV according to GOST 25.502-79) 3 mm thick and 100 mm long (Fig. 3) were ground and polished on cloth

[1] *Pitting Resistance Equivalent N = %Cr + 3.3 %Mo + 16 %N*
[2] *Critical Pitting Temperature (CPT), ASTM G-48A (72 h in 6% solution $FeCl_3$);*
[3] *RU-standard (5 h in 10% solution $FeCl_3$)*

**Weldability**. As well as the deformable steel prototype, the cast steel can be welded, in common ways for stainless steels. The strength of weld is 85-95% of the strength of the base metal.

On the finishing stage of tests 05Kh22AG15N8MFL stainless steel they were experimental (pilot) castings produced from it (fig. 5). Samples of castings metal showed a high level of mechanical properties.

Fig.5 Cast blanks for a high-strength corrosion-resistant 05Kh22AG15N8MFL (0.05C21CrN15Mn8NiV) steel regulator: $Rp0_{.2}$ = 400 MPa; $R_m$ = 680 MPa; *A*5 = 37%; *RA* =50%; *KCV*–70 = 1.8MJ/m$^2$;

*2.2. Conclusions on the steel 05Kh22AG15N8MFL*

The studies revealed the following advantages of the new cast stainless steel 05Kh22AG15N8MFL:

- ✓ Austenitic structure with 0-5% of δ-ferrite. (Steels CF10SMnN, CF3MN, A 447, CG6MMN, CN3MN can contain up to 20% ferrite).
- ✓ Significantly higher level of mechanical properties caused by solid solution strengthening of austenite by nitrogen and by the effect of dispersion hardening due to the presence of nano sized nitride particles in solid solution.
- ✓ A markedly higher level of corrosion resistance than that of conventional stainless steels without nitrogen.
- ✓ Wear resistance is at the level of Hadfield steel.
- ✓ Fatigue strength (based on $10^7$ cycles) of 225 MPa is close to the yield strength of traditional stainless steels: 18-10 (hot-rolled, followed by solution treatment).
- ✓ Weldable steel.

The use of steel 05Kh22AG15N8MFL will:

- save Ni (due to stabilization of austenite steel with nitrogen);
- save material in the product (due to the higher level of mechanical properties);
- ensure high reliability of products and steel constructions;
- reduce operating costs (due to reduction of repair costs).

*3.1. Martensitic steel grade with 0,11-0,17% N.*

Martensitic steel 05Kh16N5AB (0.05C16CrNNb) with 4–5% Ni and ~0.11–0.17% N is a high strength, weldable, corrosion- and wear resistant steel, having good manufacturability [4–6]. Applications under consideration include the following branches. (1) The manufacture of bolts and screws, which are capable to replace bolts and screws made of 614V, VT16, and VT35 expensive titanium alloys and martensitic stainless steels like 07Kh16N6 (0.07C16Cr6Ni), which are prone to intergranular corrosion, austenitic steels 12Kh18N9T (0.12C18Cr10NiTi), which are having low strength level, and other stainless steels, with improvements in strength and cost [4–6]. (2) The manufacture of flat springs and shafts for submersible electric oil pumps, in place of 12Kh18N9T steel, with increase in the working life by a factor of 2–3 for springs and 2.8 for shafts [6]. (3) The manufacture of sealing surfaces in cryogenic valves in place of 03Kh9K14N6M3D (ЭП921, 0.03C9Cr14Co6Ni3MoCu) steel, with no loss of working life or reliability [6]. The composition of 05Kh16N5AB (0.05C16CrNNb) steel and recommendations for its use were incorporated in Russian State Standard GOST 5632–2014 "Alloyed stainless steels and alloys, corrosion-resistant and heat-resistant. Grades» (October 24, 2014).

**Mechanical properties (tensile testing, impact test).** Steel 05Kh16N5AB can be used for the manufacture of critical parts of machines, including fasteners, operating at temperatures from -70° C to + 300° C. After hardening heat treatment steel has the following tensile test characteristics:

- $R_m \geq$ 1400 MPa,
- $Rp_{0,2} \geq$ 1100 MPa,
- El ≥ 20%,
- RA ≥ 60 MPa.

Static tensile testing of M8 ready-made bolts has shown that the rupture of bolts occurs with the breaking force of P = 3,600 kg. Bolts are not sensitive to distortions under the head and under the nut during tensile testing.

Impact tests on specimens with a sharpy notch (according to Charpy) showed that 05Kh16N5AB steel is cold resistant, steel retains its plasticity at lower climatic temperatures (fig. 6)..:

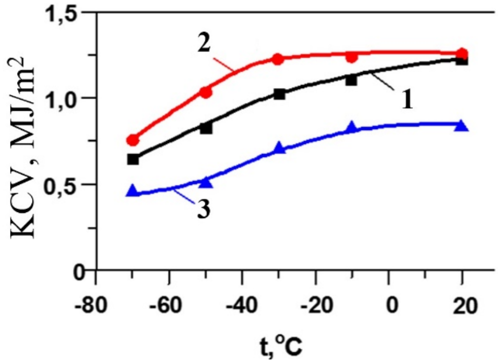


Fig.6 Temperature dependence of fracture toughness for 05Kh16N5AB steel Sharpi-specimens after different treatments: 1 – water quenching; 2, 3 – heat treatment at different temperatures after water quenching.

**The fatigue strength.** Testing of smooth samples by the method of cantilever bending after hardening heat treatment demonstrated fatigue strength on the basis of $10^7$ cycles 770 MPa. After tests on high-cycle fatigue alternating load (Pmax = 1400 kg and Pmin = 140 kg) bench tests of the bolts were carried out. After the operating time 500 000 cycles the bolts were removed from the stand without damage.

**Corrosion resistanc**e. Comparative corrosion tests of steels 07Kh16N6B (without nitrogen) and 05Kh16N5AB were carried out. Below are the results of these studies.

Tendency to pitting and crevice corrosion in 6% $FeCl_3$ for 5 hours at 20° and 50° C was studied. Steel 05Kh16N5AB has corrosion rate ($v_{cor}$) at 20 and 50$^o$C 4,5-5 and 2-2,5 times lower than steel 07Kh16N6B corrosion rate (fig.7).

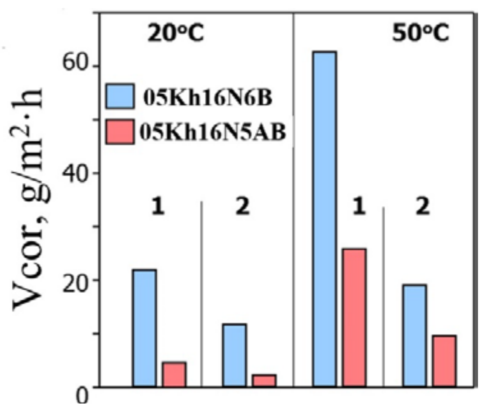


Fig. 7. The rate of pitting (1) and crevice (2) corrosion when testing samples by chemical method

Pitting corrosion tests using anodic polarization showed that nitrogen positively affects the resistance characteristics of pitting - $E_{PO}$ and $E_{PR}$ potentials (fig. 8).

Stress-corrosion cracking tests under tension in air and in 3.5% of NaCl solution with deformation rate $\varepsilon \cdot = 2 \cdot 10^{-7}$ $s^{-1}$ demonstrated that the strength of 05Kh16N5AB steel is much higher than 07Kh16N6B at the same level of plasticity.

The tendency to intergranular corrosion (boiling 24 h in a solution of $CuSO_4$ + $H_2SO_4$) was investigated. These experiments showed that steel 05Kh16N5AB is not prone to intergranular corrosion.

Test on resistance to atmospheric corrosion demonstrated that steel 05H16N5AB is not prone to corrosion in the industrial atmosphere.

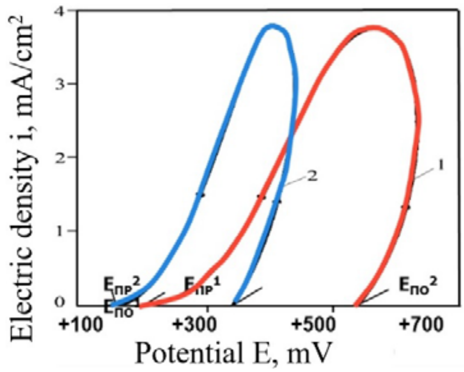


Fig. 8. Polarization curves for anodic polarization in a 3.5% solution of NaCl steels 05Kh16N5AB (1) and 07Kh16N6B (without nitrogen) (2)

**Wear resistance.** Nitrogen alloyed steel 05Kh16N5AB has a higher wear resistance by 25% than its prototype without nitrogen (07Kh16N6B).

**The weldability.** The steel is weldable. When welding wire ("noodles") from the same steel (instead of a filler rod) microhardness of different zones of welded steel specimens 05Х16Н5АБ has almost the same level HV ~450. Its weld doesn't need in additional heat treatment.

**Manufacturability.** Steel 05Kh16N5AB needs simple (and economical) heat treatment: hardening is possible in water, or in air. No quenching in oil is required. (Removing process of oily scale increases the cost of fasteners). This steel has: good ability to cold plastic deformation, to cold planting; high plasticity (El ≥ 20%, deformation up to failure of 75%). Its good plasticity allows to produce fasteners with any form of heads; allows to produce them with the absence of rejects caused by the formation of cracks during cold upsetting.

Fig. 9. Bolts produced from high-strength and corrosion-resistant nitrogen containing steel 05Kh16N5AB by cold upsetting technology

### *3.2. Conclusions on the steel* 05Kh16N5AB

The studies revealed the following advantages of the martensitic stainless steel 05Kh16N5AB:

- ✓ Efficiency. The steel does not contain expensive alloying elements (Mo, Co, etc.); it contains <18% Cr, ~ 5% Ni.
- ✓ Good manufacturability.
- ✓ High strength, weldable, corrosion- and wear resistant steel.

The use of steel 05Kh16N5AB L will:

- Economy of alloying elements (steel does not contain expensive Mo, Co, Cu); Contains <18% Cr, ~ 5% Ni.;
- save material in the product (due to the higher level of mechanical properties);
- allow to produce fasteners with any form of heads; allows to produce them with the absence of rejects caused by the formation of cracks
- ensure high reliability and durability of products and steel constructions and parts;
- reduce operating costs (due to reduction of repair costs).

REFERENCES

1. High-strength cast non-magnetic corrosion-resistant steel and a product made of it. Patent RU №2445397, priority of 23.06.2010.

2. Kostina M.V., Muradyan S.O., Khadyev M.S., Korneev A.A.. Phase transformations in a corrosion-resistant high-chromium nitrogen-bearing steel // Russian metallurgy (Metally). 2011. Т. 2011. № 9. С. 813-825.

3. Kostina, M.V., Muradyan, S.O., Terent'ev, V.F., Blinov, E.V., and Prosvirin, D.V., Static and cyclic strength of austenitic corrosion_resistant cast Cr–Ni–Mn–Mo–N steel, Russ. Metall. (Engl. Transl.), 2015, vol. 2015, no. 5, pp. 367–375.

3. Bannykh, O.A., Blinov, V.M., Kostina, M.V., et al., On possibility of the use of nitrogen steel in the Russian valve industry, Armaturostroenie, 2014, no. 2 (89), pp. 63–71.

4. Kostina M.V., Bannykh O.A., Blinov V.M. Effect of plastic deformation and heat treatment on the structure and hardening of nitrogen-bearing steel 0KH16AN4B // Metal Science and Heat Treatment. 2001. Т. 43. № 7-8. С. 259-262.

5. Blinov, V.M., Kalinin, G.Yu., Kostina, M.V., Mushnikova, S.Yu., Popov, V.I., and Khar'kov, A.A., Effect of nitrogen on the corrosion and corrosion-mechanical properties of steels with a nitrogen martensite structure, Russian metallurgy (Metally). 2003. №4. С. 360-366.

6. Bannykh O.A., Blinov V.M., Kostina M.V., Lukin E.I., Blinov E.V., Rigina L.G. Effect of heat treatment on the structure and the mechanical and technological properties of corrosion resistant nitrogen-bearing 0KH16N4AFD steel for high- strength welding constructions of railway engineering // Russian metallurgy (Metally). 2015. Т. 2015. № 7. С. 571-575.