Perspective high-strength pipe steel with increased corrosion cold resistance

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The scientists of Nosov Magnitogorsk State Technical University developed the new steel with 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti alloying system. Phase transformations of undercooled austenite were examined via dilatometric analysis using Gleeble 3500 complex. Metallographic analysis of the structure, which is forming during continuous cooling, is carried out. Thermokinetic and structural diagrams of steel were built. The conditions of controlled rolling and accelerated cooling of the developed steel are suggested; they provide increased strength ($\sigma_{\text{т}}$=520-560 N/mm^2, $\sigma_{\text{в}}$=600-673 N/mm^2; δ_5=26-23.5 %; HBW 207-229), cold resistance down to -70 °C (KCV^{-70}=252-245 J/cm^2; KCU^{-60}=330-295 J/cm^2), as well as increased corrosion resistance in carbon dioxide and hydrogen sulfide environments (HIC, SSC). Providing of such favourable combination of properties makes it possible to use the new steel for manufacture of pipes of different strength classes in oil and gas industry, for operation in the Far North regions.

Key words: high-strength pipe steels, C-Mn-Cr-Nb-Ti alloying system, continuous cooling, phase transformations, structure, thermokinetic diagram, controlled rolling and accelerated cooling, mechanical properties, cold resistance, corrosion resistance.
DOI: 10.17580/cisisr.2023.02.12

Introduction

Manufacture of new steels with simultaneous combination of high strength and ductility as well as cold resistance at the temperature -70 °C and increased corrosion resistance in H_2S- and CO_2-containing environments is required for operation of pipes and equipment at gas, gas-condensate and oil deposits in the Far North and Arctic regions [1-12].

It is known that the main concepts of development of high-strength low-alloy structural steels are formed in the following way [13]:

- lowering of carbon content in steel;
- lowering of content of harmful impurities and non-metallic inclusions;
- replacement of solid solution strengthening by dispersion one;
- grain refinement via thermomechanical treatment and microalloying;
- forming of optimal metal structure using accelerated cooling mechanisms.

The scientists of Nosov Magnitogorsk State Technical University developed the new high-strength steel with 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti alloying system. It should provide the following complex of mechanical properties: increased strength ($\sigma_{\text{т}} \geq$ 500 N/mm^2, $\sigma_{\text{в}}$=580-950 N/mm^2; $\delta_5 \geq 20$ %; HBW, KCV^{-70}=252-245 J/cm^2; KCU$^{-60} \geq$ 100 J/cm^2). Additionally, customers of pipe steels for oil and gas industrial complex are interested in increased resistance against hydrogen and hydrogen sulfide cracking.

The chemical compositions, which were molten according to the selected alloying system, were characterized by the following properties:

- restricted carbon content to provide optimal microstructure, which guarantees high cold resistance and resistance against corrosion cracking in hydrogen sulfide environments (HIC, SSC);
- increased manganese content to provide stable level of mechanical properties due to solid solution strengthening with lower carbon content, without worsening its resistance against hydrogen cracking;
- increased chromium content to provide resistance against carbon dioxide corrosion;
- microalloying by niobium and titanium to create the required conditions for controlled rolling, and to reach high cold resistance values;
- high steel cleanness for impurities (sulfur and phosphorus).

Microstructure is the most important factor having influence on resistance against hydrogen and hydrogen sulfide cracking. It is caused by steel chemical composition (from one side) and by thermal deformation treatment, that steel is subjected in the process of sheets manufacture (from other side). So, it was found out that the most homogenous and dispersive are microstructure components and the most close are they to the state of thermodynamic equilibrium, the most resistant are they to the effect of hydrogen sulfide containing environments [14-18]. Pearlite strips can be nodes of cracks formation and propagation in the structures of ferrite-pearlite type, which are forming in low-alloy steels during cooling with small speed. Analysis of cracked areas displays that cracks are forming either inside pearlite itself, or very close to a separation boundary between ferrite and pearlite [19, 20].

Ferrite-bainite structure, which is obtained in the process of accelerated cooling during thermomechanical treatment (controlled rolling with consequent accelerated cooling), is characterized by essentially smaller banded orientation and size of the elements of ferrite matrix in comparison with ferrite-pearlite structure. It is acknowledged that such structure has smaller number of possible points of origination of hydrogen cracks. The authors of the work [21] examined influence of cooling rate on steel resistance against hydrogen cracking. Carbon diffusion in austenite during the process of transformation decreases as a result of cooling speed increase and homogenous ferrite and low carbon bainite microstructure is forming in the case if final cooling temperature will be higher that temperature of martensite transformation. It leads to higher steel resistance against hydrogen cracking.

However, not all types of ferrite-bainite structures are favourable from the point of view of resistance against hydrogen (HIC) and hydrogen sulfide (SSC) cracking. When forming high-strength components (such as lath bainite, martensite, M/A component) in the areas of primary or secondary segregation of alloying elements, cracks can originate and propagate along consistent components of such structure.

The main requirements to structural state of steel, providing increased resistance against hydrogen and hydrogen sulfide cracking, can be formulated in the following way:

- absence of pearlite banding;
- obtaining of ferrite-bainite structure without banding;
- absence of extended areas in solid structural components (martensite, high-carbon bainite);
- absence of extended non-metallic inclusions (MnS, oxides).

Study of structural and phase transformations of overcooled austenite, mechanical and corrosion resistance properties of the steel with 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti alloying system is the aim of this work.

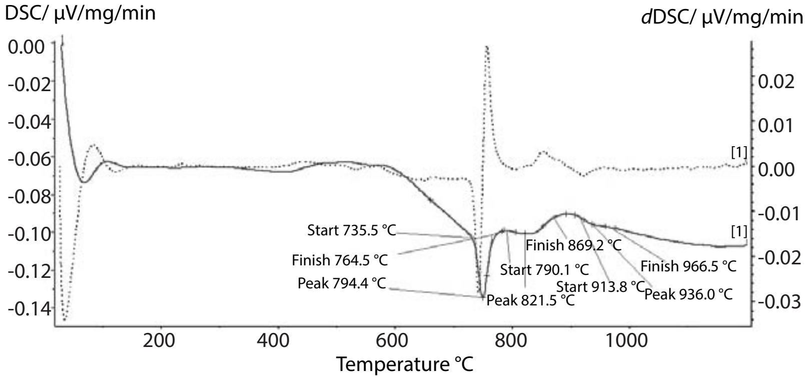


Fig. 1. Experimental curve of differential scanning calorimetry of steel during heating with rate 10 °C/min

Material and testing technique

Melting and rolling of the experimental samples of hot-rolled coiled sheets of the steel with 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti alloying system were conducted on the base of the scientific and production complex "Engineering center Termodeform MGTU". Hot rolling was carried out using hydraulic press P6334 (roughing stage) and laboratorial reversing tot rolling mill 500 duo (finishing stage), which ic combined with the unit for accelerated cooling.

Critical points were determined via the method of differential scanning calorimetry (DSC), using the sensor of synchronous thermal analysis STA Jupiter 449 F3 (NETSCH), doen to the temperature 1000 °C with speed 10 °C/min in the argon environment (argon purity 99,998 %), as well as via dilatometric analysis using the research complex Gleeble 3500.

Mechanical tests were carried out according to the standard techniques:

- stretching testing according to the GOST 1497;
- impact bending testing at lowered temperatures according to the GOST 9454;
- hardness measuring via Brinnell according to the GOST 9012.

Corrosion resistance of rolled products was determined via the following parameters:

- resistance against hydrogen cracking (HC) according to the technique of NACE TM-0284 standard, using the testing solution A with determination of cracking sensibility coefficient (CSR), crack length coefficient (CLR) and crack thickness coefficient (CTR);
- resistance against sulfide corrosion cracking under stress (SCCS) according to the technique of NACE TM-0177 standard, using the testing solution A via the method A and according to the standard ASTM G39 for 4-point bending in the A medium;
- speed of general corrosion of rolled products in CO_2-containing environment via the technique noted in the supplement 4 TTT-01.02.04-01 (version 3.0);
- speed of general corrosion of rolled products in H_2S-containing environment via the technique of NIPTs NefteGazServis No. 966814-006-593377520-2014.

To provide microanalysis according to the standard technique, polished micro-samples were prepared via pressing of samples in «Transoptic» resin at automatic press Simplimet 1000, in the Buechler samples preparation line. To reveal microstructure, the surface of polished samples was subjected to pickling in 4 % solution of nitric acid in ethyl alcohol via dipping of polished surface in a bath with reactant. Qualitative and quantitative analysis were carried out via a light microscope Axio Observer (Zeiss) with magnification 50-100 folds, using the software Thixomet PRO for processing

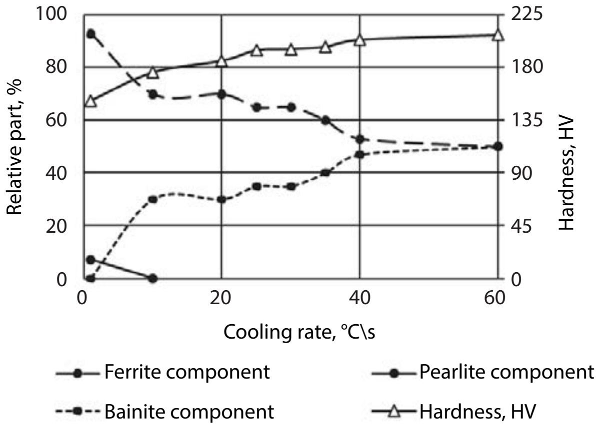


Fig. 2. Structural diagram of the steel 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti

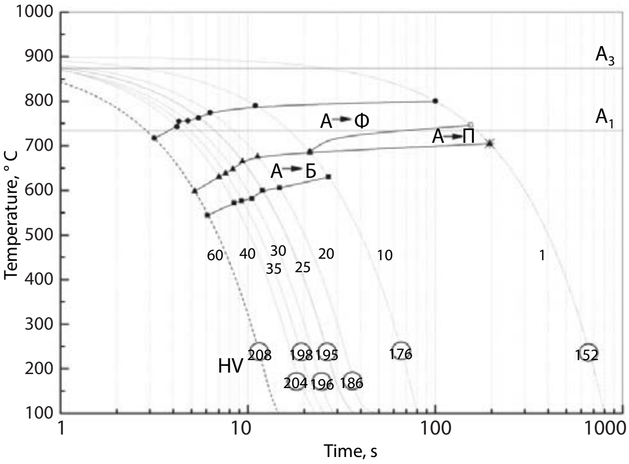


Fig. 3. Thermokinetic diagram of transformation of overcooled austenite in the steel 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti (А – austenite, Ф – ferrite, П – pearlite, Б –bainite)

of metallographic images, as well as via scanning electronic microscope (SEM) JSM 6490 LV.

Results and discussion

Critical points during heating, which were determined via the method of differential scanning calorimetry (DSC), were found for the examined chemical compositions, they made A_{c1} – 735 °C and A_{c3} – 869 °C (**Fig. 1**).

Based on analysis of the results of complex dilatometric, metallographic analyses and hardness measurement, regularities of structural and phase transformations, occurring in the steel 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti during continuous cooling were established, and the structural diagram (**Fig. 2**) and thermokinetic diagram (CCT) of undercooled austenite (**Fig. 3**) were built.

According to the obtained data, the following conditions should be implemented to provide the aimed microstructure and specified complex of properties:

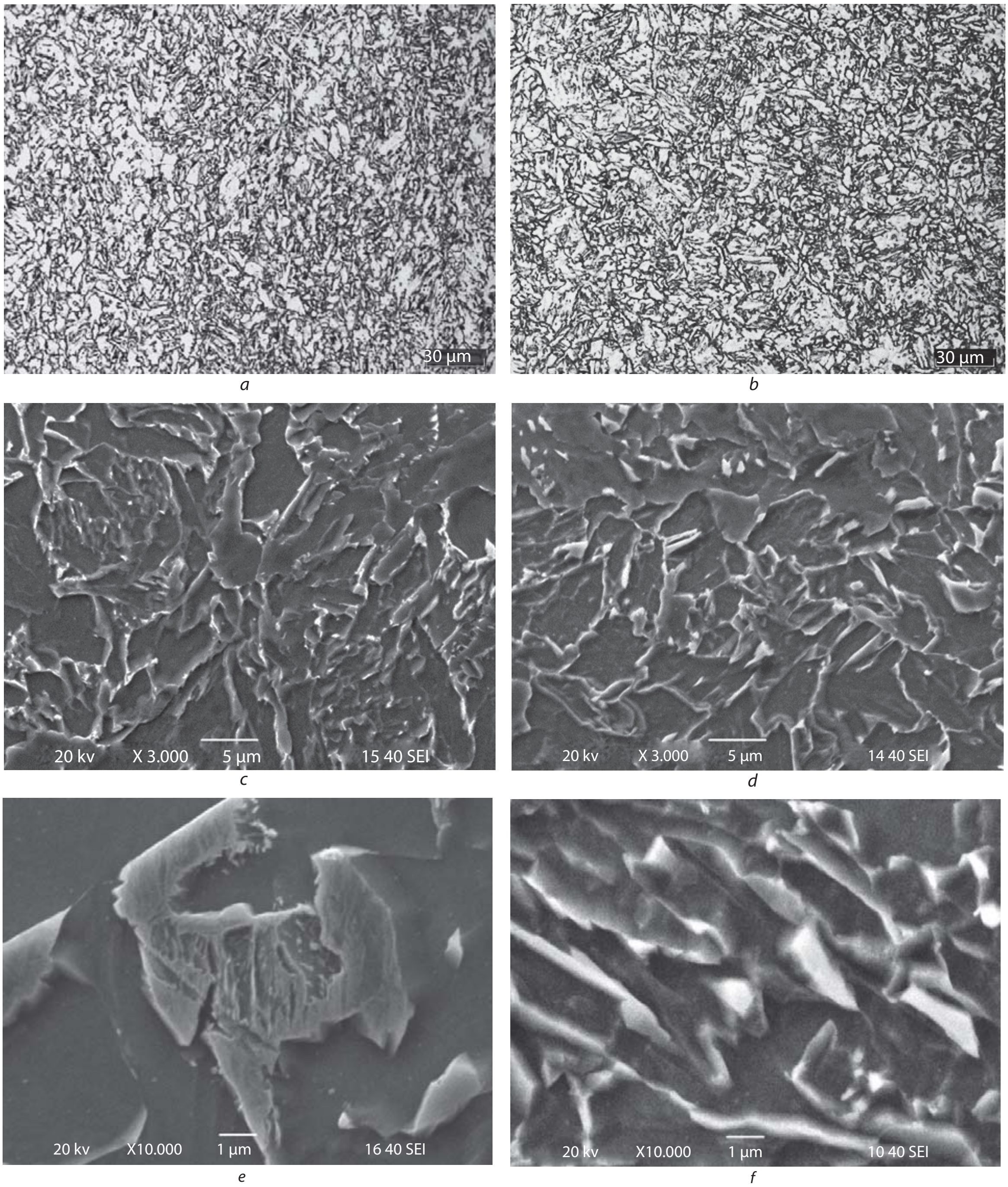
- heating before rolling should be carried out up to the temperature T_{heat} = 1180-1200 °C, for maximally complete dissolution of carbonitrides and transition of alloying elements in solid solution;
- the temperature of deformation termination in the finishing stage and starting of accelerated cooling should be higher than the temperature of $\gamma \rightarrow \alpha$ transformation by 30-40 °C (T_{cr} > 870 °C) to obtain homogenous austenite structure, to provide absence of ferrite-pearlite banding and to prevent forming of polygonal ferrite and origination of bainite banding during accelerated cooling;
- speed of accelerated cooling, which is required for obtaining ferrite-bainite structure, should exceed 10 °C/s;
- the temperature of finishing of controlled accelerated cooling (CAC) should be selected, taking into account the condition of obtaining the required complex of properties: 1) T_{cac}=620-660 °C; 2) T_{cac}=520-540 °C.

Metallographic investigations displayed that the steel 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti is characterized by forming of dispersive and homogenous (along cross section) microstructure after controlled rolling and accelerated cooling (CRaAC) according to the selected procedures. This microstructure consists mainly of bainite (80 %) and small amount of quasi-polygonal ferrite (20 %) (**Fig. 4**, *a* and *b*). At the same time, the researches, which were conducted via SEM, showed that bainite component presents granular bainite in the form of α-phase with “islands” of martensite-austenite component (when subjected to processing via the following procedure: T_{cr} > 870 °C and T_{cac} = 620-660 °C) (Fig. 4, *c* and *e*). When another technological procedure was applied (T_{cr} > 870 °C and T_{cac} = 520-540 °C), there lathe bainite was also identified in bainite component. Lathe bainite consists of elongated α-phase lathes, which are organized in packages, and of areas with residual austenite, which are enriched by carbon or martensite (M/A), on lathe boundaries (Fig. 4, *d* and *f*), what is explained by lower final temperature of accelerated cooling.

The results of mechanical testing of laboratorial samples of the examined hot-rolled coiled steel, which were processed according to the above-mentioned procedures, are presented in the **Table 1**.

The suggested CRaAC procedures for the steel 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti guarantee high cold resistance at the testing temperatures down to minus 70 °C, at the same time PTC KCV-50 in fracture makes 100 %. At the same time, high corrosion resistance of steel is provided (**Table 2**); corrosion rate in carbon dioxide and hydrogen sulfide environments does not exceed 0.1 and 0.3 mm/year respectively. Additionally, the positive results were obtained during testing for hydrogen cracking resistance (CLR=0; CTR=0; CSR=0) and sulfide cracking corrosion resistance under stress, according to the NACE TM0177 standard (method A: for $\sigma_в$ 80 % of $\sigma_{0,2}$) and ASTM G-39 standard (four-point bending).

Thus, the steel 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti after CRaAC meets the requirements in mechanical properties of the most often used strength classes of pipe products for the noted procedures.



a *b*

c *d*

e *f*

Fig. 4. Steel microstructure after CRaAC via the procedures:
1) $T_{cr} > 870$ °C and $T_{cac} = 620\text{-}660$ °C (*a*, *c*, *e*) and 2) $T_{cr} > 870$ °C and $T_{cac} = 520\text{-}540$ °C (*b*, *d*, *f*)

Conclusion

Phase and structural transformations for the new steel with 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti alloying system were examined, structural diagram and thermokinetic decomposition diagram for undercooled austenite were built.

It was established that steel microstructure presents homogeneous dispersive ferrite-bainite structure after controlled rolling and accelerated cooling via the following procedures: 1) T_{cac}=620-660 °C; 2) T_{cac}=520-540 °C. Volumetric part of quasi-polygonal ferrite in the structure does not exceed 20 % in both cases. For the first procedure, bainite component in steel makes mainly granular bainite, while for the second procedure, the structure contains granular and lathe bainite approximately in equal correlation.

It is shown, that the complex of properties ($\sigma_{0.2}$=520-560 N/mm^2, $\sigma_в$=600-673 N/mm^2; δ_5=26-23.5 %; HBW 207-229) is provided in the steel 0.08C-1.50Mn-1.20Cr-0.06Nb-0.04Ti after CRaAC via the noted procedures. This complex of properties corresponds to the most required different strength classes of pipe steels and guarantees high cold resistance down to -70 °C (KCV^{-70}=252-245 J/cm^2)

Table 1. **Results of mechanical testing**

No.	Temperature procedures CRaAC			Mechanical properties							
	T_{heat}·, °C	T_{cr}, °C	T_{cac}, °C	$\sigma_{0.2}$, N/mm^2	$\sigma_{\text{в}}$, N/mm^2	δ_5, %	$\sigma_{0.2}/\sigma_{\text{в}}$	KCV^{-70}, J/cm^2	KCU^{-60}, J/cm^2	PTC KCV^{-50}, %	HB
1	1200	>870	620-660	520	600	26	0.87	252	330	100	207
2	1200	>870	520-540	554	673	23.5	0.82	245	295	100	229

*PTC – Part of tough component

Table 2. **Results of corrosion testing**

No.	T_{heat}, °C	T_{cr}, °C	T_{cac}, °C	BP (HIC), %			Total corrosion rate, mm/year		CKPH (SSC), %	
				CLR	CTR	CSR	CO_2	H_2S	Method A	Method of 4 point bending. ASTM G39
1	1200	>870	620-660	0	0	0	0.078	0.260	720 h 80 % of 415	720 h without cracks
2	1200	>870	520-540	0	0	0	0.081	0.212	720 h 80 % of 415	720 h without cracks

and increased corrosion resistance in carbon dioxide and hydrogen sulfide environments.

Providing of such favourable combination of strength, increased corrosion and cold resistance at the temperatures down to -70 °C makes it possible to use the new steel for manufacture of pipes of different strength classes in oil and gas industry, for operation in the Far North regions.

The research was carried out under financial support of RF Ministry of Education and Science within the framework of realization of the complex project for development of high-tech production, which was conducted with participation of the higher education institution (Agreement No. 075-11-2021-063 dated 25.06.2021)

REFERENCES

1. Poletskov P. P., Gulin A. E., Emaleeva D. G., Kuznetsova A. S., Alekseev D. Yu., Kukhta Yu. B. Analysis of actual directions of researches in the field of production of multifunctional materials for extremal operating conditions. *Vestnik Magnitogorskogo gosudarstvennogo tekhnicheskogo universiteta im. G. I. Nosova*. 2021. Vol. 19. No. 3. pp. 109–114.
2. Chukin M. V., Poletskov P. P., Gushchina M. S., Kuznetsova A. S., Nikitenko O. A., Alekseev D. Yu. Development of the import-substituting technology for rolled sheet production from high-strength structural steel for Arctic application. *Proizvodstvo prokata*. 2019. No. 4. pp. 5-11.
3. Poletskov P. P., Nikitenko O. A., Kuznetsova A. S., Alekseev D. Y. Development of Heat Treatment Modes for Novel Structural Sparingly Alloyed High-Strength Steel for Arctic and Far North Applications. *Metal Science and Heat Treatment*. 2021. Vol. 63. No. 3-4. pp. 171-177.
4. Nice P. I., Takabe H., Ueda M. The development and implementation of a new alloyed steel for oil and gas production wells. *«Corrosion 2000»*. 2000. p. 154.
5. Tikhontseva N. T. Development of chemical compositions and heat treatment procedures for high-strength pipes with resistance to hydrogen sulfide effect. Dissertation...of a Candidate of Technical Sciences.Ural State Technical University. Ekaterinburg. 2007.
6. Erekhinskiy B. A., Chernukhin V. I., Arabey A. B. et al. Development of domestic high-strength pipes of oil grade and dimension range, resistant in hydrogen sulfide containing environments. *Transport i khranenie nefteproduktov i uglevodorodnogo syrya*. 2016. No. 4. pp. 40-46.
7. Bhadeshia H. Prevention of hydrogen embrittlement in steels. *Mater. Sci. Metallurgy*. 2016. Vol. 56 (1). pp. 24-36.
8. Pumpyanskiy D. A., Pyshmintsev I. Yu., Khatkevich V. M. Et al. Hydrogen brittleness of pipe steels. *Metally*. 2023. No. 3. pp. 36-46.
9. Rodionova I. G., Amezhnov A. V., Papshev A. A. et al. Effect of nanosized phase precip-itates on the corrosion resistance of cold-rolled high-strength low-carbon niobium microalloyed steels. *Metallurgist*. 2022. Vol. 65. No. 9-10. pp. 968-978.
10. Rodionova I. G., Naumenko V. V., Amezhnov A. V. et al. Study of resistance against CO_2-corrosion of pipe steels in oilfield engineering environment of different composition. Part 2. *Stal*. 2022. No. 9. pp. 37-43.
11. Tkachuk M. A., Golovin S. V., Efron L. I. et al. Effect of alloying with molybdenum and chromium on low-carbon pipe steel structure and properties. *Metallurgist*. 2020. Vol. 63. No. 9-10. pp. 1043-1053.
12. Matrosov Yu. I. Comparison of influence of Nb, Ti, V microadditives on the processes of microstructure forming in a low carbon, low alloy steel. *Metallovedenie i termicheskaya obrabotka metallov*. 2023. No. 3 (813). pp. 25-31.
13. Ouchi C., Sampei T., Okita T., Kozasu I. Microstructural changes of austenite during hot rolling and their effects on transformation kinetic. *Conference on hot deformation kinetics of austetite, New York,* 1977, pp. 68—85.
14. Carneiro R. A., Ratnapuli R. C. The influence of chemical composition and microstruc-ture of API linepipe steels on hydrogen induced cracking and sulfide stress corrosion cracking. *Materials Science and Engineering*. A357. 2003. pp. 104—110.
15. Nayak S. S., Misra R. D. K., Hartmann J. Microstructure and properties of low manga-nese and niobium containing HIC pipeline steel. *Materials Science and Engineering*. A494. 2008. pp. 456—463.
16. Hara T., Asahi H., Ogawa H. Conditions of Hydrogen-induced Corrosion Occurrence of X65 Grade Line Pipe Steels in Sour Environments. *Corrosion*. 2004. Vol. 60. No. 12. pp. 1113—1121.
17. Matrosov Yu. I., Kholodnyi A. A., Matrosov M. Yu. et al. Influence of accelerated cooling parameters on microstructure and resistance to hydrogen cracking (HIC) for low-allow pipe steels. *Metallurg*. 2015. No. 1. pp. 68—75.
18. Kazakov A. A., Kiselev D. V., Sych O. V., Khlusova E. I. Quantitative assessment of structural inhomogeneity in cold-resistant low-alloy steel sheets for interpretation of technological features of their manufacturing. *Chernye metally*. 2020. No. 11. pp. 4-14.
19. Zikeev V. N., Kornyushenkova Yu. V., Konnova I. Yu. Structural parameters of structural steel, which determine resistance to hydrogen cracking. *Metallovedenie i termicheskaya obrabotka metallov*. 1991. No. 11. pp. 19-20.
20. Charbonnier J. C., Margot-Marette H., Moussy F. et al. Influence of metallurgical parameters on HIC and SSC behavior of linepipe steel. *NACE conference corrosion 1987. San Francisco*. 1988. 85. pp. 91-105.
21. Hof W. M., Graf M.K., Hillenbrand H.G., et al. New high strength large diameter pipe steels. *Journal of Materials Engineering*. 1987. Vol. 9. pp. 191-198.