IOP Conference Series: Materials Science and Engineering

Substantiation of domestic material and welding technology for improving properties and competitiveness of pyrolysis furnace coils

IOP Conf. Series: Materials Science and Engineering **570** (2019) 012071 doi:10.1088/1757-899X/570/1/012071

Substantiation of domestic material and welding technology for improving properties and competitiveness of pyrolysis furnace coils

F I Murataev[1], E R Galimov[1] and N Ya Galimova[1]

[1]Kazan national research technical university named after A.N. Tupolev, K. Marx street 10, Kazan, 420111, Tatarstan, Russian Federation

kstu-material@mail.ru

Abstract. An alloy of cast pipes produced in the Russian Federation and a welding method for restoring coil sections made of imported pipes damaged by gas corrosion in pyrolysis furnaces are proposed. Substantiation of the alloy choice is carried out according to the research results of composition and structure of the metal of the original pipes and according to the criteria of structural strength using a proven diagram of controlled damageability. Recommendations for optimizing the composition, microalloying, and structure of the proposed alloy of thick-walled cast pipes for the elimination of the deficiencies identified by the research are presented. The alloy advantages by mechanical properties in the temperature range up to 800...890°C are shown on samples of an experimental cast pipe.

1. Introduction

Pyrolysis furnaces coils operate in a wide range of temperatures (400…1125°C) undergoing gas corrosion of the metal with the prevailing reducing medium [1-3]. They can be damaged: in the tube side by C_3+C_4+C_5 hydrocarbons and water vapor at temperatures up to 900°C, in the intertubular space by the NO+NO_2+CO+CH_4+SO_3 flue gases at moderate temperatures in the convection part of the coils and up to 1125°C at the bridge wall (in the radiant section). The coils use imported pipes made of heat-resistant alloy G-X40 NiCrSi 3525. Metal marking in the Russian Federation terminology is 50Cr25Ni35Si2Nb alloy. Damaged areas of the cage (after 10…15 years of operation) are replaced by high-alloy steel cast pipes of domestic production. At the same time, hot cracks occur in the joints of the manual arc welding (MAW) during the formation of a heterogeneous weld [4-6].

2. Body text

The operation of repair sections made of pipes produced in the Russian Federation is only 6…15 months due to their cracking (Fig. 1). This requires the use of new materials functional in tough environments and more efficient welding methods of pipes in the cage during coil repair.

Analysis of pipe fractures indicates that all fractures are brittle, thermal, intercrystalline [1, 2, 4, 6], and from high-temperature gas corrosion. The main part of fractures is across the pipes. Hot cracks from the outer surface resemble in appearance creep cracks [1, 2, 4]. On the inner side of the wall the damages are of the hot cracking nature. Through and non-through cracks of half the wall thickness and more are found on both sides of metallographic sections (Fig. 2).

IOP Conf. Series: Materials Science and Engineering **570** (2019) 012071 doi:10.1088/1757-899X/570/1/012071

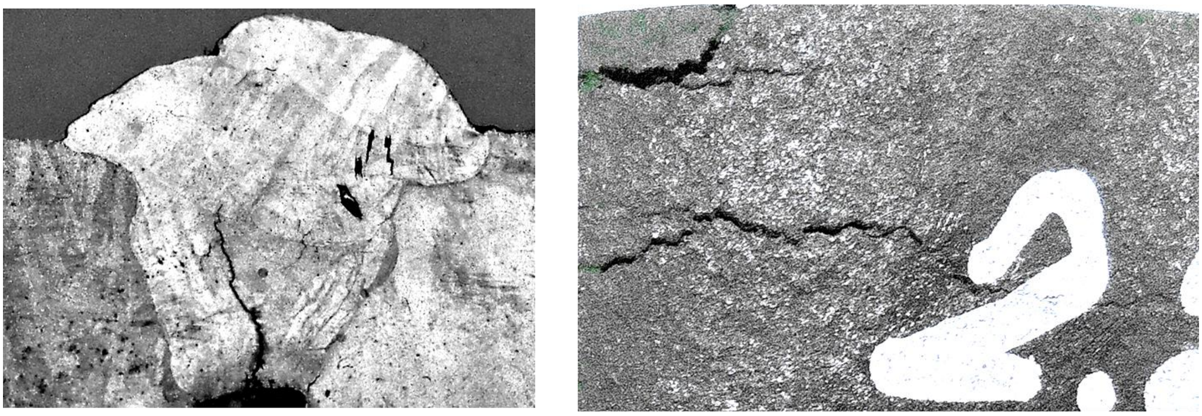


Figure 1. Weld seam damaged under repair and pipe after operation

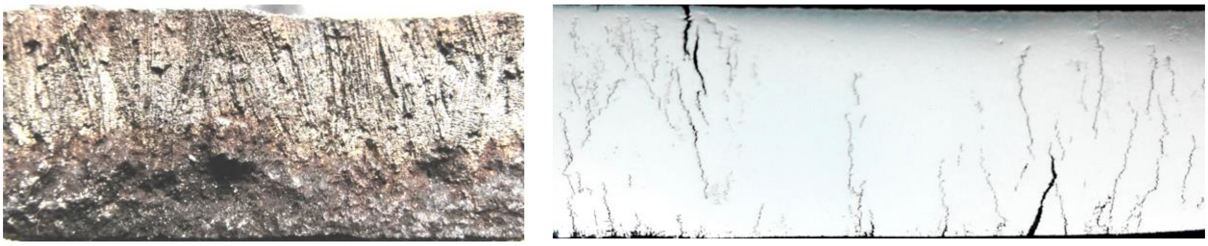


Figure 2. Fracture and cracking of metal of thick-walled cast coil pipes

In order to solve these tasks, integrated studies of the composition of structure and properties of the metal of imported pipes and domestic pipes delivered from Izhevsk and Nizhnekamsk are carried out at higher temperature. The equipment used for the metallography: the METAM-23 research microscope and PS SX150IS (Canon) camera, the X-MET 8000 analyzer, equipment for preparation of metallographic sections: the Remet IPA 30 press, the Remet LSA LS2 polishing pad.

Analysis of the alloys operability according to the composition, technology, and structural state variants was performed based on the characteristics analysis of the stress-deformation diagram [7]: Ilyushin module (1), resistance to tearing-off (2, 3), strain-hardening coefficient (4), condition for normalized metal damageability of metal of cast pipes (5) in the form of expressions:

$$E_K = E_*[1+E/S_K \ln 1/(1-\psi)]^{-1.0}, \quad (1)$$

where: Sк – resistance to tearing-off.

$$S_к = 1233 + 9.27\,\psi \quad (2)$$

or

$$S_к = 75_* m^{(0)} + 955 \quad (3)$$

$$m^{(0)} = 0.75 \ln (S_K/\sigma_{0.2}) \{\ln [l/\sigma_{0.2}/E)\,(S_K/E + \ln l/1-\psi)]\}^{-1.0}. \quad (4)$$

In the absence of data for Ti alloys:

$$m^{(0)} = 0.75 \ln [(1233 + 9.27\,\psi)/\sigma_{0.2}] \{\ln [l/\sigma_{0.2}/E)\,(S_K/E + \ln l/1-\psi)]\}^{-1.0}, \quad (5)$$

or

$$m^{(0)} = (S_к - 955)/75, \quad (6)$$

$$\ln 1/1-\psi = \frac{0.5849 S_к}{E_\mu\left(1.071 - 0.2404\cdot\overline{\sigma}_m - 1\right)}. \quad (7)$$

In the absence of data for Ti alloys:

$$\ln 1/(1-\psi) = 0.585\,(75_* m^{(0)} + 955)/E_\mu\,(1.071 - 0.24\overline{\sigma}_m - 1), \quad (8)$$

$$\ln 1/1-\psi = \frac{0.585\sigma_в\left(1+1.35\psi\right)}{E_\mu\left(1.071 - 0.2404\cdot\overline{\sigma}_m - 1\right)}. \quad (9)$$

IOP Conf. Series: Materials Science and Engineering **570** (2019) 012071 doi:10.1088/1757-899X/570/1/012071

In the absence of data and difficulty of using the expressions (3) – (5), you can use the dependency (6) and the graph presented in figure 3. Analysis of experimental and calculated data as well as the operating experience of equipment parts show the effectiveness of using the above characteristics when substantiating materials and technologies [7-9].

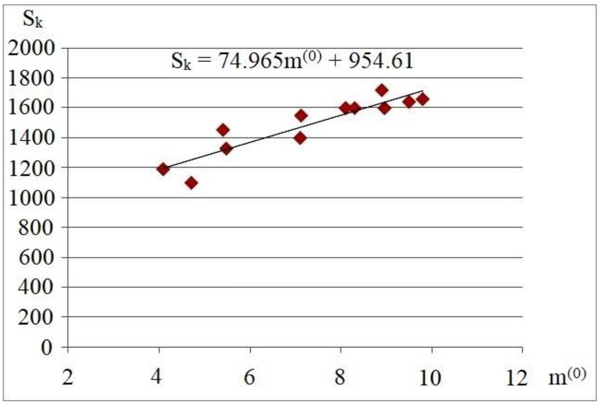


Figure 3. The graph of matching of characteristics resistance to tearing-off (S_k) and strain-hardening coefficient ($m^{(0)}$)

For choosing and substantiating of material with better structural strength characteristics, it is recommended to choose their variants of technology and structure with higher values of ψ, S_K, $m^{(0)}$ and smaller E_K value.

An important but challenging task when substantiating material and technology is finding the optimal ratio of strength and ductility characteristics by searching for a successful structural state. Practically, it is possible to simplify the algorithm of such a solution due to the repeated use of experimentally confirmed dependence (7) in the form of a graph – "a diagram of the limited metal damageability" [7]. Figure 4 illustrates the problem solution of the optimal ratio of ψ and S_K characteristics using the diagram at satisfying the condition when actual properties of the material exceed the values of "the diagram of the limited metal damageability" plotted according to (7) for the conditions of acting stresses ($\overline{\sigma}_m$). That is, it can be seen that when materials represented by the properties are located above the lines, they satisfy the condition (7), and not satisfying materials are located below the lines (solid lines – alloys, dotted ones – steel).

The advantage of imported pipes and pipes produced in Izhevsk, in most cases, is caused by the fundamental difference of the metal compared to the pipes produced in Nizhnekamsk, since they are made of austenitic Fe-Ni alloys 50Cr25Ni35Si2Nb and 45Cr25Ni35NbSi (contain Fe < 37%) and are notable for a large number of the alloying elements Nb and Ni.

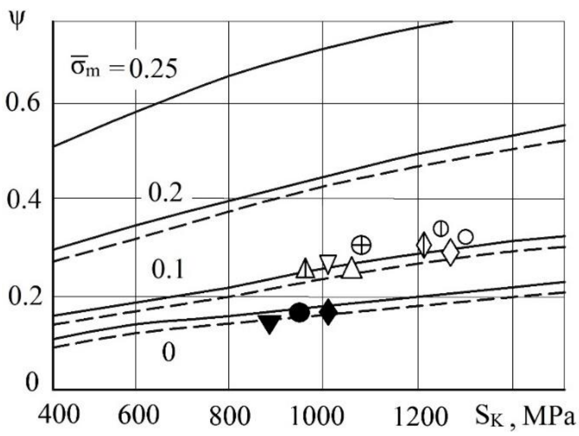
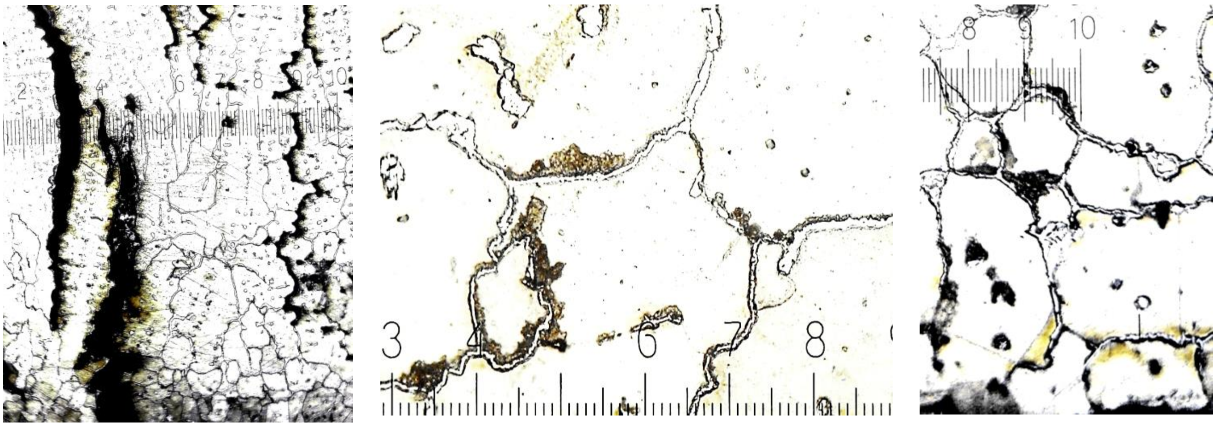


Figure 4. Diagram and curves of limited metal damageability

Pipes produced in Nizhnekamsk are cast from heat-resistant austenitic steel 45Cr25Ni20Si2. They are less doped and less resistant to high-temperature gas corrosion. The lower content of harmful S+P impurities in imported fusions (0.025%) attracts attention, and this, apparently, also affects the increases in longevity [4, 5]. An order of magnitude smaller copper content in imported and Izhevsk pipe fusions than that in Nizhnekamsk pipes [4], a lower value of λ_2, deserves the closest attention since it can adversely affect the high-temperature gas corrosion resistance [10-13].

Figures 5 and 6 illustrate the nature of metal pipes damage. The metal degrades along the dendrites boundaries from the surface of the pipes (Fig. 5, a) or from the inside (Fig. 5, b). Arms of dendrite with austenite structure (γ), dendrite boundaries, and interdendritic spaces are formed in the crystallization process of high-alloyed steels. Interstitial phases of MC and eutectic ($MC+\gamma^1$) are formed in steels with active carbide-forming components. In the absence of carbide-forming components: Nb, Ti, Ta, and etc because of the high diffusion activity of carbon along the grain boundaries, $Cr_{23}C_6$ is formed and thereby it weakens the degree of γ–doping with chromium (Fig. 5, b).



a b c

Figure 5. Types of gas corrosion of cast pipes: dendritic and intercrystalline degradation of the structure of domestic steels and imported alloys

Table 1. Characteristics of the metal composition (in %) and structure after operating time of pipes

Pipe material	C	S	P	S+P	Ni	Cu	Nb	λ_2
50Cr25Ni35Si2Nb	0.45-2.2	0.01-0.015	0.018-0.02	0.025	35.0	0.015	0.80	20
45Cr25Ni35Si2Nb	0.41-2.5	0.08-0.015	0.008-0.026	0.041	31.5	0.012	0.85	30
45Cr25Ni20Si2	0.38-0.43	0.011-0.03	0.02-0.026	0.057	19.0	0.15	0.11	60

If a solid carbide network is formed at the boundaries of metal dendrites, then the boundaries are intensely damaged by creep [3, 6] and intercrystalline corrosion (Fig. 6). Eutectic as well as intermittent chains of carbide $M_{23}C_6$ or MC interfere with the process of degradation at gas corrosion (Fig. 6). Figure 7 shows the damage to metal pipes of different delivery.

The main type of metal degradation of imported pipes (for 10-15 years) and pipes delivered from Izhevsk (for up to 1.5 years) is degradation along the grain boundaries in carbides. Steels of Nizhnekamsk pipes (for 6 month) are intensively damaged by gas corrosion along the dendrites boundaries due to a higher content of Cu (~ 10 times) and impurities (S+P).

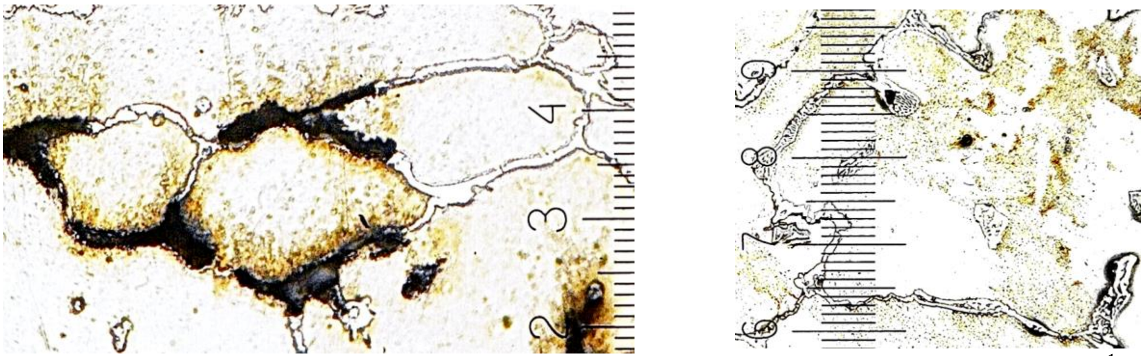
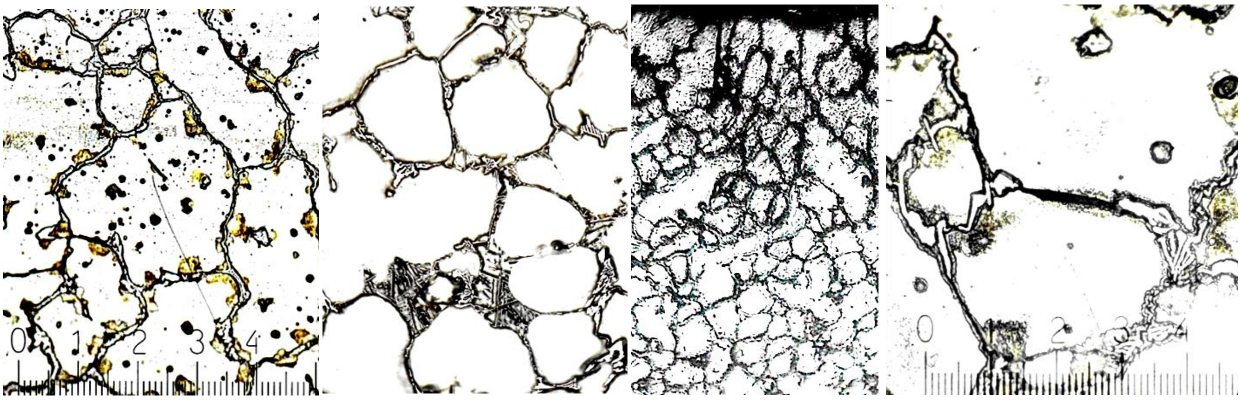


Figure 6. The development of metal corrosion in carbide edging and blocking by eutectic ($MC+\gamma^1$)



a b c d

Figure 7. Condition of pipes' metal after operation: from Japan (a-c), pipes delivered from Izhevsk (d)

The following materials were proposed to ensure the required service properties: steel 30Cr23Ni7Si and alloys 35Cr24Ni24Nb, 20Cr25Ni25TiAl. The conformity assessment of the test pipes' metal was performed by their properties in the range of operating temperatures. The results are shown in table 2. The advantage of the 35Cr24Ni24Nb alloy in characteristics of high-temperature strength at temperatures of 800°C can be seen.

Table 2. Tensile tests results of metal samples of cast pipes (D85 mm) at temperatures 800-890°C

No.	Steel grade	Temperature, °C	$P_{0,2}$	P_B	$\sigma^t_{0.2}$	σ^t_B	δ^t	Ψ^t	$\sigma^t_{B1}/\sigma^t_{Bi}$
			kilogram-force		MPa		%		
1	35Cr24Ni24Nb	800	925	995	311	334	22	30	1
2	30Cr23Ni7Si	890	370	375	127	128	21	54	2.61
3	20Cr25Ni25TiAl	865	-	490	-	165	36	67	2.02
4	45Cr25Ni20Si2	880	625	675	217	234	18	31	1.43
5	50Cr25Ni35Si2Nb	860*	-	680	-	225	22	23	1.48

This advantage is caused by the presence of niobium [12-15] which forms a more resistant to gas corrosion eutectics [(Nb, Cr, Ni) $C+\gamma^I$] (Fig. 8).

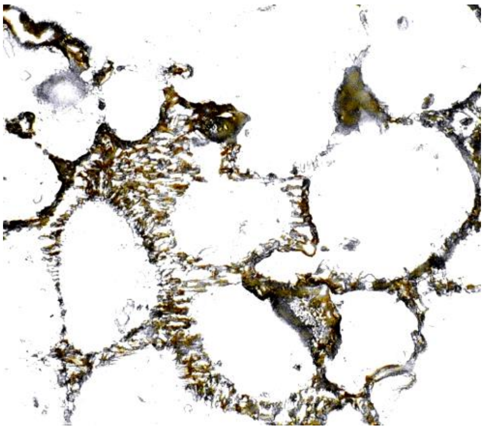


Figure 8. Microstructure of 35Cr24Ni24Nb alloy of pipe's experimental fusion

Eutectic is contaminated with impurities (P+S+Cu); microalloying and refining will allow pipes made of the 35Cr24Ni24Nb alloy to provide better functionality. In addition, it is more resistant to heat and does not burn out at welding, increasing the stability of the welding seam structure in operation [2, 5]. Welding of test joints of pipes delivered from Nizhnekamsk with pipes made of original G-X40 NiCrSi 3525 (50Cr25Ni35Si2Nb) alloy after operation using the method of manual argon-arc welding showed better weldability compared to the standard manual arc welding.

3. Conclusions

1. Substantiation of the alloy grade of the pyrolysis furnace pipes should be agreed with the actual temperature level of the outer and inner wall surface including the furnace specific zone.

2. The most useful alloying elements in relation to operating requirements of pipes are Nb and Ta, which will provide (because of the dispersed arrangement of the MC and the eutectic ($MC+\gamma^1$) at the boundaries of the twisted and cellular configuration of dendrites) long –term heat resistance with low λ_2.

3. When repairing the cages of coils the detailed control and analysis of elements (C, O, N, H) in the pipes after the operation is required.

4. It is necessary to limit the content of impurities (Sn+As+Pb+Sb+Vi+Zn)
< 0.015%, S < 0.01%, P < 0.012%, severely limit the Cu impurity and maintain the ratio Nb/C = 2.5…3.8 to increase high-temperature plasticity and improve weldability.

5. It is proposed to replace standard manual arc welding with manual argon-arc welding when repairing damaged pipes sections of cages.

6. The choice of heat-resistant steels and alloys is substantiated by the diagram of the limited metal damageability ($\psi = f\ [S_K]$), lower structural damageability, and dependencies of the properties of structural strength (1), (4), (7) with higher values of ψ, S_K, $m^{(0)}$ and smaller E_K value.

7. An economically alloyed casting heat-resistant alloy 35Cr24Ni24Nb with greater high-temperature strength is proposed.

References

[1] Goritskiy V M 2004 *Metal diagnostics* (Moscow: publishing house Metallurgizdat) 408 p
[2] Murataev F I 2013 Typical and degradation features of welded joints microstructure of structural and special steels *Vestnik of KSTU* number 3 Issue 2 pp 84-89
[3] Pakhomov V S and Shevchenko A A 2009 Chemical resistance of materials and corrosion protection (Moscow: publishing house Khimiya. Kolos-S) 444 p
[4] Murataev F I and Murataev A F 2015 Adaptation of the composition, structure, properties of the metal and welded joints of heat exchangers to the resistance of high-temperature gas corrosion *Vestnik of KSTU* number 3 pp 119-125

[5] Wegst Z V 1993 *Key to steels. Reference book* (Krasnogorsk: publishing house NovoIM) 581 p
[6] Murataev F I, Klabukov M A and Murataev A F 2016 Degradation of composition and structure of steels and welded joints of vaporization coils in conditions of chemical and electrochemical corrosion *Vestnik of KSTU* number 4 pp 44-49
[7] Murataev F I and Shkanov I N 1999 Substantiation of processing technology of compressor disks according to characteristics of static and cyclic deformation *Izv. VUZ. Aviatsionnaya Tekhnika* number 1 pp 43-47
[8] Shkanov I N, Braude N Z and Murataev F I 1982 Model of optimization of basic mechanical properties with respect to static and fatigue strength criteria in complex stress state conditions *Soviet Aeronautics* vol 25 Issue 1 pp 79-84
[9] Murataev F I and Khakimov S Sh 2014 Substantiation of microstructure and properties relationships of titanium alloys for prediction problems of fatigue resistance *Vestnik of KSTU* number 3 pp 110-113
[10] Sims C T, Stoloff N S and Hagel W C 1995 *Superalloys II. Translation Superalloys II: High-temperature materials for aerospace and industrial power* (Moscow: Metallurgiya) 384 p.
[11] Murataev F I and Murataev A F 2015 Influence of composition and morphology of intermetallic phase of IN-738LC alloy on damageability of gas turbine blades *Vestnik of KSTU* number 3 pp 43-48
[12] Tarasenko L V 2005 *Heat-resistant cast nickel alloys of equiaxed crystallization* (Moscow: Herald of the Bauman Moscow State Technical University) pp 50
[13] Murataev F I and Murataev A F 2016 Structure and properties of structural steel after long-term overheating *Vestnik of KSTU* number 3 pp 82-86
[14] Murataev F I, Saitkulov V G, Khusnutdinov Sh N and Trifonov A A 2014 Regularities of composition, structure, and damageability of turbine blades metal after bench-test and operating time *Vestnik of KSTU* number 2 pp 74-78
[15] Murataev F I and Klabukov M A 2014 Study of influence of structure characteristics on fatigue damageability of cast blades made of IN-738LC alloy *Vestnik of KSTU* number 3 pp 107-109