



UDC 669.018.8

DOI 10.17073/0368-0797-2023-1-8-26

<https://fermet.misis.ru/jour/article/view/2474>

Review article

Обзорная статья

CORROSION-RESISTANT STEELS BASED ON Fe – ~13 % Cr: HEAT TREATMENT, CORROSION- AND WEAR RESISTANCE. REVIEW

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Abstract. Martensitic stainless steels with 13 % Cr are widely used in many industries due to their high level of mechanical properties and acceptable corrosion resistance. The paper consolidates information on the guaranteed level of properties and heat treatment conditions required for its implementation. The properties after treatments proposed by researchers are compared with those known for industrial metal. The dependences of the hardness of 13Cr type hardened steels with 0.20 – 0.50 % C on the austenitization temperature and the accompanying changes in structure have been analyzed. The temperatures providing maximum hardening and the temperatures at which the steel ceases to harden have been revealed. The effect of the duration of austenitization, heating and cooling rates on the properties of steels has been considered. The mechanical properties and corrosion resistance after quenching, quenching and tempering in relation to structural-phase states of steels are considered. It is discussed in detail how the type of secondary phases during tempering, their amount, and distribution affect the corrosion resistance of steels with 13 % Cr. It increases with increasing heating temperature during austenitization and decreases with increasing tempering temperature due to the precipitation of Cr₂₃C₆ carbides and depletion of the matrix in chromium to the concentrations below 12 %. The tempering temperature of 500 – 550 °C is recognized as the worst: due to intensive precipitation of carbides the steel is not passive, and the corrosion rate is maximum. Quenching with low tempering is recommended for 20Cr13 steels (to combine high strength, good corrosion resistance and satisfactory plasticity), or, more often, quenching with high tempering is recommended at ~ (650 – 700) °C (good plasticity, satisfactory corrosion resistance). For steels of 40Cr13 type the temperature of ~700 °C is not recommended because of the increased concentration of carbides and insufficient corrosion resistance. Examples of increasing the wear resistance properties of 40Cr13 steels due to surface treatments, from nitriding to laser and plasma surface quenching, are presented.

Keywords: steel, chromium, alloying, carbides, martensite, austenite, quenching, annealing, mechanical properties, corrosion resistance, wear resistance

Acknowledgements: The study was supported by the Russian Science Foundation, grant No. 22-23-01036.

For citation: Kostina M.V., Rigina L.G., Kostina V.S., Kudryashov A.E., Fedortsov R.S. Corrosion-resistant steels based on Fe – ~13 % Cr: Heat treatment, corrosion- and wear resistance. Review. *Izvestiya. Ferrous Metallurgy*. 2023; 66(1): 8–26.

<https://doi.org/10.17073/0368-0797-2023-1-8-26>

ОБЗОР ИССЛЕДОВАНИЙ КОРРОЗИОННОСТОЙКИХ СТАЛЕЙ НА ОСНОВЕ Fe – ~13 % Cr: ТЕРМИЧЕСКАЯ ОБРАБОТКА, КОРРОЗИОННАЯ- И ИЗНОСОСТОЙКОСТЬ

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Аннотация. Мартенситные нержавеющие стали с 13 % Cr широко используются во многих отраслях промышленности благодаря высокому уровню механических свойств и приемлемой коррозионной стойкости. В работе консолидирована информация о гарантированном уровне свойств и условиях термической обработки, необходимых для его реализации. Сопоставлены свойства после предлагаемых

исследователями обработок с известными для промышленного металла. Проанализированы зависимости твердости закаленных сталей типа 13Cr с 0,20 – 0,50 % C от температуры аустенизации и сопутствующих изменений структуры. Выявлены температуры, обеспечивающие максимальное упрочнение и температуры, при которых сталь перестает упрочняться. Рассмотрено влияние длительности аустенизации, скоростей нагрева и охлаждения на свойства сталей. Рассмотрены механические свойства и коррозионная стойкость после закалки, закалки и отпуска во взаимосвязи со структурно-фазовыми состояниями сталей. Подробно рассмотрено, как вид вторичных фаз при отпуске, их количество, распределение влияют на коррозионную стойкость сталей с 13 % Cr. Она повышается с ростом температуры нагрева при аустенизации и снижается с ростом температуры отпуска вследствие выделения карбидов Cr_{23}C_6 и обеднения матрицы хромом до концентраций ниже 12 %. Температура отпуска 500 – 550 °C признана наихудшей: из-за интенсивного выделения карбидов сталь не пассивируется, скорость коррозии максимальна. Для сталей типа 20X13 рекомендуются закалка с низким отпуском (для сочетания высокой прочности, хорошей коррозионной стойкости и удовлетворительной пластичности), либо, чаще, закалка с высоким отпуском при ~ (650 – 700) °C (хорошая пластичность, удовлетворительная коррозионная стойкость). Для сталей типа 40X13 температура ~700 °C не рекомендуется из-за повышенной концентрации карбидов и недостаточной коррозионной стойкости. Приведены примеры повышения износостойкости сталей типа 40X13 за счет поверхностных обработок, от азотирования до лазерной и плазменной поверхностной закалки.

Ключевые слова: сталь, хром, легирование, карбиды, мартенсит, аустенит, закалка, отжиг, механические свойства, коррозионная стойкость

Благодарности: Исследование выполнено при поддержке гранта Российского научного фонда № 22-23-01036.

Для цитирования: Костина М.В., Ригина Л.Г., Костина В.С., Кудряшов А.Э., Федорцов Р.С. Обзор исследований коррозионностойких сталей на основе Fe – ~13 % Cr: термическая обработка, коррозионная- и износостойкость. *Известия вузов. Черная металлургия*. 2023; 66(1): 9–26. <https://doi.org/10.17073/0368-0797-2023-1-8-26>

INTRODUCTION

Medium-carbon high-strength martensitic steels with 0.20 – 0.40 % C and 12 – 14 % Cr are a widely demanded constructional material, which is the most inexpensive among corrosion-resistant steels. They are used in the manufacture of loaded parts, friction pairs and metal seals, pressure vessels, hydraulic units, casings for the oil and gas industry, and steam turbine blades. Although they are not a new material, there are many publications dedicated to them in the scientific literature. These works are aimed at:

- modifying the surface of (20–40)Cr13 steels to increase their strength and wear resistance properties, studying their corrosion resistance;
- forming the structure and phase composition of similar steels, providing high strength while maintaining the process ductility and ensuring corrosion resistance due to variations in the chemical composition and heat treatment modes.

In this review article:

- information on the structure and guaranteed level of properties currently achievable in industrial steels with 0.20 – 0.40 % C and 12 – 14 % Cr is provided;
- the structure and mechanical properties of steels of this type, obtained as a result of modern studies of the effect of different variants for traditional heat treatment of such steels – martensite quenching and different types of tempering (annealing) – are considered;
- information on the results of studies of corrosion resistance of these steels is given.

PROPERTIES OF INDUSTRIAL STEELS

WITH ≤0.20 – 0.40 % C AND 12 – 14 % Cr

When heated above 800 °C, austenite appears in steels with 13 % Cr. The carbon concentration increase con-

tributes to the expansion of the γ -region¹ [1]. Dissolution of carbide phase particles (primary carbides) occurs during high-temperature annealing. Cooling from the austenitic region fixes the martensitic structure in the steel. Depending on the quenching heating temperature and steel composition, some carbide, ferrite or residual austenite particles may be present in it. During the tempering process, depending on the temperature and duration of the process, there may be a return, polygonization, recrystallization, nucleation of secondary dispersed carbides in martensite, their growth and coagulation. In this way, it is possible to obtain a structure consisting of tempered martensite with carbides, or to bring the process to the decomposition of martensite into a ferrite-nitride mixture.

Table 1 provides standard grade chemical compositions of common industrial steel grades with <0.20 – 0.40 % C and 12 – 14 % Cr. In Russia these are steel grades 20Cr13, 30Cr13 and 40Cr13, differing in carbon content only. According to standard GOST RF 5632-2014, they do not contain other metallic alloying elements except chromium (and up to 0.8 % Mn, see Table 1). Such steels are also known to be supplied with up to 0.6 % Ni, up to 0.2 % Ti, and up to 0.3 % Cu². Steel AISI 420 is an analogue of all the mentioned Cr13 grades with 0.2 – 0.4 % C, because its carbon content is limited to the lower limit of 0.15 %, but the upper limit is not specified³ (see Table 1).

Using reference resources^{2–8}, the authors summarized the information on industrial steels of Cr13 type (13Cr are foreign grades):

¹ Phase diagram of Fe-Cr-0.2%C. *Wikimedia Commons*. URL: https://upload.wikimedia.org/wikipedia/commons/thumb/3/3c/Phase_diagram_of_Fe-Cr-0.2%25C.svg/1024px-Phase_diagram_of_Fe-Cr-0.2%25C.svg.png

² Steel grades and alloys. *Central Metal Portal*. URL: https://metallicheskiiy-portal.ru/marki_metallov

³ Standard specification for stainless steel bars and shapes. *Cont-ractors Materials Company*. URL: <https://cmcmi.com/wp-content/uploads/ASTM-A276.pdf>

Table 1

Chemical composition, % (wt.), of Russian and foreign steel grades with 0.20 – 0.40 % C and 12 – 14 % Cr (iron is the basis) according to GOST RF 5632-2014 and Contractors Materials Company³

Таблица 1. Химический состав, % (по массе), российских и зарубежных марок сталей с 0,20 – 0,40 % С и 12 – 14 % Cr (железо – основа) согласно ГОСТ РФ 5632-2014 и Contractors Materials Company³

Steel grade	Standard	C	N	Mn	Si	Cr	Mo	Ni	S	P	Other
20Cr13	GOST 5632-2014	0.16 – 0.25	–	<0.8	<0.8	12.0 – 14.0	–	–	<0.025	<0.030	–
30Cr13		0.26 – 0.35	–								
40Cr13		0.36 – 0.45	–								
AISI 420*	ASTM A276	0.15 min	–	<1.0	<1.0	12.0 – 14.0	–	–	<0.030	<0.040	–

* In the USA these are the AISI 420 grades, in Germany – 1.4031, 1.4034, X38Cr13, X39Cr13, X40Cr13, X42Cr13, X46Cr13; in Japan – SUS420J2; in France – X40Cr14, Z33C13, Z38C13M, Z40C13, Z40C14, Z44C14, Z50C14; in the European Union – 1. 4031, 1.4034, X39Cr13, X40Cr13, X41Cr13; and in China – X40Cr14, X41Cr13KU, X46Cr13

– critical points, treatment modes and structure (Table 2);

– impact of the tempering temperature after quenching on their mechanical properties (Table 3);

– mechanical properties of semiproducts from these steels, giving the idea of their guaranteed level of properties, which modern researchers try to surpass (Table 4).

Table 3 shows that high annealing (tempering) at 700 °C causes increased ductility and impact strength, because at this temperature martensite in steel is converted to ferrite and carbides (see Table 2). The yield strength of rods and forgings varies depending on the section and carbon concentration from 440 to 635 MPa, the tensile strength from 510 to 830 MPa, and the ductility from 12 to 16 %. After quenching and low tempering at 200 to 300 °C, these steels have high strength and low ductility (see Table 3). Therefore, for Russian industrial semiproducts after such treatment only hardness values are given (see Table 4), and for semiproducts made of AISI 420 steel the data of tensile tests are also given. Table 4 shows that for semiproducts from Cr13 type steel the main type of heat treatment is quenching from 1000 – 1050 °C and tempering, mainly high, at temperatures in the range of 600 – 770 °C.

⁴ Index of steel. *Lasmet – Laboratory of Special Metallurgy*. URL: <http://www.lasmet.ru/steel>

⁵ Critical points of steel. *HeatTreatment.ru – Equipment and Technologies for Heat Treatment of Metals*. URL: <https://heattreatment.ru/kriticheskie-tochki-stali>

⁶ 40X13. *MarkMet – Education, Profession, Business*. URL: <https://markmet.ru/encyclopedia/40x13>

⁷ Stainless steel 420 grade data sheet. *Atlas Steels – Australia's largest supplier of stainless steel, aluminium and specialty steel products*. URL: <https://atlassteels.com.au/wp-content/uploads/2021/06/Stainless-Steel-420-Grade-Data-Sheet-28-04-21.pdf>

⁸ SS420 grade AISI 420 stainless steel properties, heat treatment, hardness, magnetic. *The World Material*. URL: <https://www.theworldmaterial.com/ss420-astm-aisi-420-stainless-steel-grade/>

STUDIES OF THE IMPACT OF QUENCHING

AND TEMPERING (AGING) PROCESSES ON THE STRUCTURE AND PROPERTIES OF CR13 TYPE STEELS

At the end of this section summary Table 5 is presented with the chemical composition of all steels considered here.

Hardness measurements are most often used to evaluate the mechanical properties of Cr13 type steels, since it correlates with strength. Few tensile and impact bending test results given in the literature are collected in separate summary Table 6 at the end of this section.

Heating temperature for quenching (austenitizing)

It is known that hardening during martensite quenching of steels is caused by several factors and primarily high dislocation density and presence of carbon in the solid solution. The results of studies [2 – 5] on the effect of austenitizing temperatures of Cr13 type steels with 0.14 – 0.45 % C before quenching on their hardness and phase composition are presented in Figure 1. After holding at 800 °C [2] or rolling at 850 °C [4] and quenching in oil, the steel has a structure consisting of ferrite and finely dispersed Cr₂₃C₆ carbides (F + C) and is characterized by minimum hardness. Increasing the heating temperature for quenching to $t \geq 850$ °C causes partial dissolution of carbides and fixation of martensitic structure (M(α)) in the steel during quenching [2]. As the austenitizing temperature increases due to the intensification of carbide dissolution, the hardness of martensite-quenched steel increases. This is due to a significant increase in the degree of tetragonality (c/a) of the martensite crystal lattice, described by dependence [6]

$$c/a = 0.45[C] + 1.00. \quad (1)$$

Table 2

Process parameters and structure of steels 20Cr13, 30Cr13, 40Cr13 (according to ^{2,4,5})

Таблица 2. Технологические параметры и структура сталей 20X13, 30X13, 40X13 (по данным ^{2,4,5})

Feature			20Cr13	30Cr13	40Cr13
Critical points, °C	Temperature of the beginning of austenite formation during heating	Ac ₁	810 ⁵ ; 820 ^{2, 4}	810 ^{2, 5} ; 820 ⁴	800 ² ; 810 ⁵ ; 820 ⁴
	Temperature of the beginning of austenite transformation during cooling	Ar ₁	780 ²	710 ²	780 ²
	Temperature of the end of ferrite dissolution during heating	Ac ₃	900 ⁵ ; 950 ^{2, 4}	860 ^{2, 5} ; 860 – 880 ⁴	860 ⁵
	Temperature at the beginning of ferrite precipitation during cooling	Ar ₃	660 ²	660 ²	–
	Temperature of the beginning of martensite transformation	M _n	320 ⁵	240 ^{2, 5} ; 270 ⁴	240 ⁵ ; 270 ⁴
Deformation temperatures, heating and cooling conditions			1100 – 875 – 950 °C	1100 – 850 °C	
			Heating to deformation is carried out slowly to a temperature of		
			780 °C	830 °C	
			After deformation, slowed cooling in sand or a furnace		
Annealing after deformation			750 – 800 °C, cooling with a furnace to 500 °C	740 – 800 °C, cooling at 25 – 50 °C/h to 600 °C	
Final treatment – quenching and tempering to the required hardness and corrosion resistance			Quenching at 950 – 1000°C with cooling in oil or air + tempering	Quenching at 950 – 1050 °C with cooling in oil or air + tempering. Medical steel: interrupted quenching from 1020 °C to 1040 °C, cooling in alkali at 350 °C	
Microstructure after quenching			Martensite and carbides of $Me_{23}C_6$ type	Martensite, carbides of $Me_{23}C_6$ type have a small amount of residual austenite. Its amount increases as the quenching temperature increases above ≥ 1050 °C	
Microstructure after annealing			Mixture of high-chromium ferrite and carbide of $Me_{23}C_6$ type	Ferrite-carbide mixture	
Effect of tempering temperature			With an increase of $t_{opt} \geq 450$ °C the ductility increases, and the strength and corrosion resistance decrease significantly	In the tempering temperature range of 450 – 550 °C, the secondary hardness effect related to the precipitation of dispersed carbides is observed	

Herewith, in Cr13 steels parameter *c/a* with increasing carbon content increases 2.5 times more intensively than in similar unalloyed steels [2].

The maximum values of HV 540 – 570 for 20Cr13 type steels are achieved after quenching from the temperatures of 1000 – 1050 °C [2 – 4]. For steel with 0.45 % C, the maximum HV level of 696 – 710 is achieved after quenching from 1110 – 1130 °C [5] (see Figure 1). Large-needle martensite is noted in the samples quenched from 1000 °C [2]. When comparing the X-ray diffraction spectra of annealed (α-Fe) and austenitized and martensite-quenched (M(α)) samples, expansion and shifting

of peaks are clearly visible, which is due to the stress state of the martensitic lattice due to its saturation with carbon [3]. Peak shifting increases with increasing quenching temperature, which indicates greater dissociation of chromium carbides with temperature and increased saturation of martensite with carbon.

The noticeable effect of hardness reduction after reaching its maximum during further increase of the heating temperature over 1000 °C, recorded for 20Cr13 steel with 0.08 % N (420U6) [4], 45Cr13 and 50Cr13 steels during heating at 1100 °C and above [5, 7] is explained by the following:

Table 3

Mechanical properties at 20 °C of 20Cr13 and 40Cr13⁶ and AISI 420⁷ steels after quenching and annealing at temperatures from 200 to 700 °C

Таблица 3. Механические свойства при 20 °C сталей 20X13 и 40X13⁶ и стали AISI 420⁷ после закалки и отжига при температурах от 200 до 700 °C

Steel	Tempering temperature, °C	$\sigma_{0.2}$, MPa	σ_v , MPa	δ_5 , %	ψ , %	KCU, J/cm ² (KCV, J)	HRC (HB)
Quenching:	Quenching at 1050 °C, air						
20Cr13 (billet with 14 mm section)	200	1300	1600	13	50	81	46
	300	1270	1460	14	57	98	42
	400	1330	1510	15	57	71	45
	500	1300	1510	19	54	75	46
	600	920	1020	14	60	71	29
	700	650	780	18	64	102	20
Quenching:	Quenching at 1000 °C, oil						
40X13	200	1620	1840	1	2	19	52
	350	1450	1710	11	22	25	50
	500	1390	1680	7	9	19	51
	700	500	780	35	59	71	(217)
Quenching:	Quenching at 980–1035 °C, oil or air ⁷						
AISI 420 (UNS S42000)	Annealed	345	655	25	–	–	(255 max)
	204	1360	1600	12	–	(20)	(444)
	316	1365	1580	14	–	(19)	(444)
	427	1420	1620	10	–	#	(461)
	538	1095	1305	15	–	#	(375)
	593	810	1035	18	–	(22)	(302)
	650	680	895	20	–	(42)	(262)

This steel shall not be quenched in the range from 425 to 600 °C due to induced low impact strength.

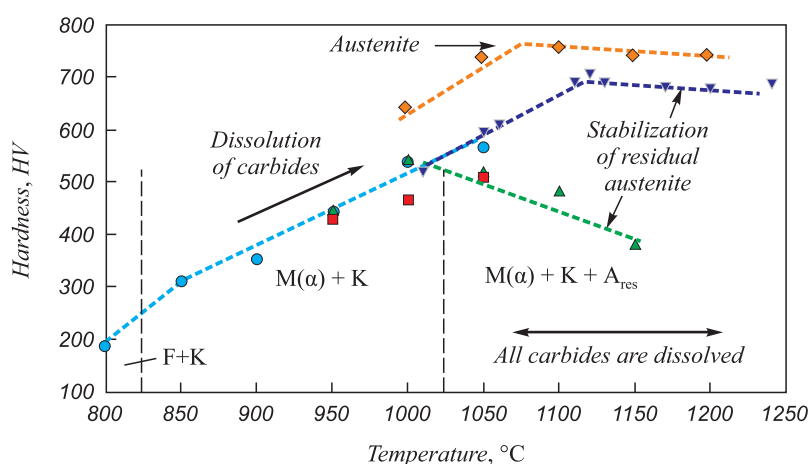


Fig. 1. Effect of austenitization temperature⁹ before quenching on hardness¹⁰ and phase composition of Cr13 steels with 0.14 – 0.45 % C: ● – steel 20Cr13 [2]; ■ – steel 20Cr13 [3]; ▲ – steel 20Cr13 + 0.008 N [4]; ▼ – steel 45Cr13 [5]; ◆ – steel 50Cr13 [7]

Рис. 1. Влияние температуры аустенизации⁹ перед закалкой на твердость¹⁰ и фазовый состав сталей X13 с 0,14 – 0,45 % C: ● – сталь 20X13 [2]; ■ – сталь 20X13 [3]; ▲ – сталь 20X13 + 0,008 N [4]; ▼ – сталь 45X13 [5]; ◆ – сталь 50X13 [7]

⁹ Выдержки при нагреве, охлаждение: [2, 3] – 30 мин, закалка в масло; [5] – 60 с, охлаждение со скоростью 2 °C/с.

¹⁰ Значения измерений в единицах HRC из работ [2, 4] переведены в значения твердости HV по шкале пересчета, приведенной в работе [8].

Table 4

Mechanical properties of semiproducts from 4Cr13 type steels according to the RF standards and AISI 420⁸ steel

Таблица 4. Механические свойства полуфабрикатов из сталей типа 4X13 по стандартам РФ и стали AISI 420⁸

GOST	Type of semiproduct, heat treatment mode	Section, mm	$\sigma_{0.2}$, MPa	σ_v , MPa	δ_5 , %	Ψ , %	KCU, kJ/m ²	HB (HRC ₀ , max)
Mechanical properties of 20Cr13 steel								
GOST 5949-75	Rods. Quenching at 1000 – 1050 °C, air or oil. Tempering at 600 – 700 °C, air or oil	60	635	830	10	50	59	–
	Rods. Quenching at 1000 – 1050 °C, air or oil. Tempering at 660 – 700 °C, air, oil or water	60	440	650	16	55	78	–
GOST 18907-73	Ground rods, machined to the specified strength	1 – 30	–	510 – 780	14	–	–	–
GOST 7350-77	Hot- or cold-rolled sheets. Quenching at 1000 – 1050 °C, air. Tempering at 680 – 780 °C, air or furnace (transverse specimens)	Over 4	372	509	20	–	–	–
GOST 25054-81	Forgings. Quenching at 1000 – 1050 °C, air or oil. Tempering at 660 – 770 °C, air	1000	441	588	14	40	39	–
GOST 4986-79	Cold-rolled strip. Annealing or tempering at 740 – 800 °C	Up 0.2	–	500	8	–	–	–
		0.2 – 2.0	–	500	16	–	–	–
GOST 18143-72	Heat-treated wire	1.0 – 6.0	–	490 – 780	14	–	–	–
Mechanical properties of 30Cr13 steel								
GOST 5949-75	Quenching at 950 – 1020 °C, oil. Tempering at 200 – 300 °C, air or oil	Specimens	–	–	–	–	–	(50)
GOST 18907-73	Ground rods machined to the specified strength	1 – 30	–	530 – 780	12	–	–	–
GOST 25054-81	Forgings. Quenching at 1000 – 1050 °C, oil. Tempering at 700 – 750 °C, air	Up to 1000	588	735	14	40	29	Surfaces 235 – 277
GOST 18143-72	Heat-treated wire	1.0 – 6.0	–	490 – 830	12	–	–	–
GOST 5582-75	Thin sheet, annealing or tempering at 740 – 800 °C	–	–	490	15	–	–	–
Mechanical properties of 40Cr13 steel								
GOST 5949-75	Rods. Quenching at 1000 – 1050 °C, oil. Quenching at 200 – 300 °C, cooling in the air or in oil	Specimens	–	–	–	–	–	(≥52)
GOST 18907-73	Rods:							
	– ground, machined to the specified strength;	1 – 30	–	590 – 810	10	–	–	–
	– annealed	Over 5	–	–	–	–	–	143 – 229
GOST 5582-75	Thin, hot-rolled or cold-rolled sheets. Annealing or tempering at 740 – 800 °C (transverse samples)	Up 3.9	–	550	15	–	–	–
GOST 18143-72	Heat-treated wire	1.0 – 6.0	–	590 – 810	10	–	–	–
Mechanical properties of AISI 420 steel (UNS S42000) ⁸								
ASTM AISI and SAE Standards	Quenching from 1038 °C in oil. Quenching at 316 °C	–	1482	1724	8	25	20 J	(≥52)
	Annealed rod	–	345	655	25	55	–	195
	Annealing, drawing	–	690	760	14	40	–	228

– in the structure of these steels due to the intensification of carbides and carbonitrides dissolution the concentration of austenite-forming elements (carbon [5, 6], carbon and nitrogen [4]) is achieved and increases, contributing to the formation of residual austenite and increasing its quantity after quenching (Fig. 1);

– growth of the austenite grain [7].

It is noteworthy that in the 20Cr13 steel, in the absence of nitrogen in its composition, stabilization of austenite after holding at 1050 °C did not occur [2, 3] in contrast to the 20Cr13 steel with 0.08 % N [4] (Fig. 1). It should be noted that in the 50Cr13 steel, which is on the modified Schaeffler–Delong diagram in the martensite-austenite region near the boundary with the austenite region, the amount of austenite after austenitization at temperatures in the range of 1000 – 1200 °C and quenching increases from 97.5 to 100 % [7].

Grain-boundary carbides not dissolved during thermal soaking inhibit grain growth during heating. Increasing the austenitizing temperature of the 20Cr13 steel with 0.08 % N from 950 to 1100 °C (holding during 30 min) leads to an order decrease in carbide density from ~0.053 to ~0.004 1/μm², and their average diameter decrease from 0.57 to 0.26 μm (Fig. 2, a) [4]. Further increase in the annealing temperature to 1150 °C no longer contributed to significant changes in the particle density and size. Increasing the austenitizing temperature from 950 to 1000 °C did not cause the grain growth during holding for 30 and 60 min at those temperatures, and the grain size remained equal to 15 – 18 μm. Increasing the heating temperatures above 1000 °C led to significant grain growth (Fig. 2, b). Obviously, decrease in the carbide density and increase in the grain size also contribute to the decrease in

hardness of this steel quenched from temperatures above 1000 °C.

Only weak grain growth from 10 to 20 μm was observed for the 45Cr13 steel with higher carbon content [5] in the heating tempering range for quenching of 1000 – 1120 °C; austenitization at 1170 and 1240 °C resulted in the grain growth to 47 and 65 μm respectively. For steel X46Cr13 (1.4034) it was noted [9] that austenitizing at temperatures above 1100 °C causes complete dissolution of carbides in X46Cr13 and optimum distribution of chromium and carbon in the mixed crystal. The elimination of the blocking effect of carbides and the higher diffusion rate lead to significant grain enlargement. Decreasing the austenitizing temperature below 1100 °C leaves mixed chromium and iron carbides in the structure, which reduce hardness and corrosion resistance.

Duration of heating during austenitization (during heating for quenching)

The effect of duration of annealing (~950 – 1200 °C, 30, 60 and 120 min) of the 20Cr13 steel with 0.08 % N on the structure and hardness has been studied [4]. It is shown that the longer the holding time at a given temperature, the coarser the grain size, and this effect is more significant the higher the heating temperature (Fig. 2, b). At low temperatures (960 and 1000 °C), the holding time had little effect and the grain growth from the 15 – 20 μm level was practically not registered. At 1200 °C such holding led to the grain growth up to 87 – 142 μm. With all holding times, the hardness maximum was observed when the austenitization temperature increased to 1000 °C, and

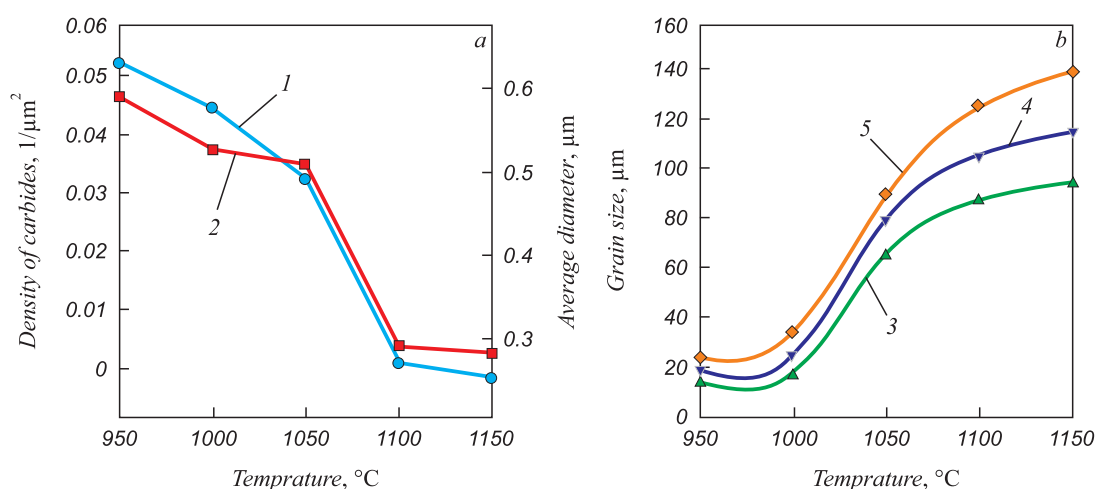


Fig. 2. Effect of austenitization temperature of 20Cr13 steel with 0.08 % N on density (1) and average size of carbide particles (2) during holding for 30 min (a) and martensite grain size (b) during soaking for: 3 – 30 min; 4 – 60 min; 5 – 120 min [4]

Рис. 2. Влияние температуры аустенитизации стали 20Х13 с 0,08 % N на плотность (1) и средний размер карбидных частиц (2) при выдержке 30 мин (a) и размер зерна мартенсита (b) при выдержке: 3 – 30 мин; 4 – 60 мин; 5 – 120 мин [4]

Table 5

Chemical composition of 13Cr steels under study

Таблица 5. Химический состав рассмотренных сталей 13Cr

Source	C	N	Mn	Si	Cr	Mo	Ni	S	P	Other components
[2]	0.16 – 0.25	–	≤0.800	≤0.800	12.00 – 14.00	–	≤0.600	≤0.025	≤0.0300	Cu ≤0.3, Ti ≤0.2
[3]	0.17	–	0.700	0.500	12.20	–	–	0.030	0.2300	–
[4]	0.14	0.085	0.590	0.380	13.78	–	–	0.006	0.0270	–
[5]	0.45	–	0.440	0.320	13.00	–	0.380	0.016	0.0300	–
[9]	0.42	–	0.530	0.400	13.92	0.030	0.310	–	–	Cu = 0.15
[10]	0.45	–	0.440	0.320	13.00	–	0.380	0.016	0.0300	–
[11]	0.43	–	0.600	0.560	13.00	–	–	–	–	–
	0.19	–	0.640	–	12.77	–	–	–	–	–
[12]	<0.2	<0.020	0.500	0.310	12.78	<0.050	0.130	0.016	0.0010	Nb + V + Ti = 0.064, Cu <1.0
¹¹	0.26 – 0.35	–	≤1.500	≤1.000	12.00 – 14.00	–	–	≤0.030	≤0.0400	Cu ≤0.3, Ti ≤0.2
[13]	0.15	–	1.160	1.060	12.08	0.131	0.952	0.030	0.0400	–
[16]	0.38	–	0.600	0.900	13.60	–	–	–	–	V = 0.30
[17]	0.18	–	0.850	0.300	12.90	–	–	0.002	0.0200	–
[18]	0.347	–	0.332	0.422	14.11	–	–	0.030	0.0156	–

then it decreased with increasing temperature. The longer the holding time in the range of 1050 – 1150 °C, the more residual austenite was in the steel and the lower the hardness was achieved during subsequent quenching. Treatment at 1000 °C for 30 min was chosen as optimal, as it provided maximum hardness while maintaining a relatively fine grain size.

Thus, the maximum effective temperature of austenitization before quenching, which provides high hardness, is 1000 – 1020 °C for steel type 20Cr13 and 1100 – 1120 °C for steel type 45Cr13.

Heating rate during austenitization and cooling rate during quenching

When quenching carbon-containing steels, martensitic transformation occurs in a shear manner. However, this does not exclude the possibility of diffusive redistribution of carbon in austenite during cooling to the temperature of the beginning of martensitic transformation (M_n) and further in the formed martensite when cooling from M_n to the room temperature [6].

The study [10] conducted on steel with 0.45 % C and 13Cr (45Cr13) showed that the temperature required to achieve complete dissolution of $Me_{23}C_6$ carbides in the austenitic phase increases with the increasing heating rate from 0.05 to 10 K/s, changing from 1353

to 1448 K (1080 – 1175 °C). For a given heating rate and holding time (60 s), the amount of carbide in the quenched microstructure of this steel decreases with increasing temperature. Carbide precipitation was found during quenching from 1393 K (1120 °C) and slower cooling rates than 20 K/s. For these cooling rates, the amount of carbide precipitation increased with the decreasing cooling rate. With continuous cooling at any quenching rate from 1333 K (1060 °C) no significant carbide precipitation is observed. After annealing at optimum temperatures, starting from the cooling rate of 1 °C/s, the hardness of martensite microstructures is very close to the maximum. The hardness obtained by quenching from their respective optimum temperatures reaches the values between 700 and 710 HV₅ when cooling at 1 °C/s. For X45Cr13 steel heated to 1120 °C, the percentage of the carbide area in the final microstructure after quenching at a cooling rate of 1 °C/s is 3.2 %, whereas when quenched from 1060 °C at a cooling rate of more than 25 °C/s it is 6 % [10].

High-rate heating (50 °C/s) by the method of current transmission through the specimen was carried out on steel 20Cr13 specimens (length of 100 mm, diameter of 10 mm), after which they were quenched in oil [2]. The obtained properties were compared with the results of metal heated in the furnace and similarly quenched metal. The maximum value of the tensile strength of 1530 MPa when heated in the furnace was achieved after quenching from 950 °C, and the relative elongation did not exceed 4.7 %. During high-rate heating the same strength was obtained after quenching from a temperature of 1020 °C, and the relative elongation in this case did not

¹¹ X30Cr13 – Nr. 1.4028. Rodacciai. URL: https://www.rodacciai.com/UPLOAD/datasheets/420B_X30Cr13-Nr.1.4028-ENG.pdf

Table 6

Mechanical properties of 13Cr steels after various heat treatments

Таблица 6. Механические свойства сталей 13 Cr после различных термических обработок

Source	% C in steel	Heat treatment (temperature in °C)	Treatment number	$\sigma_{0.2}$, MPa	σ_v , MPa	δ_5 , %	Ψ , %	Hardness	Impact energy, J
[13]	0.15	Quenching from 1000 + tempering for 2 h at temperatures:	200 + 200	780	1720	–	–	HRC	52
			450 + 450	736	1605	–	–		51
[17]	0.18	Quenching from 980	3	570	712	20	64		212
		Quenching from 1040	4	640	780	26	66	BHN	232
		Quenching from 1040 + 980	5	620	752	27	66		227
[11]	0.19	Quenching at 1050, 240 s + tempering for 375, 375 s	6	–	1515	7.5	–	–	–
[2]	0.16 – 0.25	Quenching	800	–	579	29	–		14
			950	–	1530	4.7	–		45
		Quenching from 850 + tempering for 2 h at temperatures:	500	–	–	–	–		34
			600	–	–	–	–		17
			700	–	–	–	–	HRC	12
			500	990	1010	1	4		43
		Quenching from 1000 + tempering for 2 h at temperatures:	600	730	855	16	55		33
			650	–	–	10	30		–
			700	560	700	17	57		19
			850	265	530	14	–		200
[18]	0.347	Annealing for 15 min, cooling with a furnace	200	755	989	15	–		310
		Annealing at 850 + quenching from 1000, 15 min, air cooling + tempering at temperatures	500	630	880	19	–	HV	400
		Annealing + quenching + cryogenic treatment + tempering at temperatures	200	440	664	15	–		250
			500	650	933	40	–		260
[11]	0.43	Quenching at 1100, 300 s + tempering for 400, 300 s	21	–	1800	11	–	–	–

* Charpy samples, tests at –10 °C

exceed 6.5 %. After a series of experiments in [2] it was concluded that high-rate heating leads to a shift of hardening curves by 40 – 60 °C up the temperature scale compared to the curves obtained during furnace heating.

The effect of different cooling rates (from 3 to 100 K/s) during hot forging of X46Cr13 steel on the hardness, strength and ductility of steel after quenching (1100 °C, 300 s) and after additional tempering (1100 °C, 300 s) was studied [11]. This factor was shown to have no effect on hardness: it is at a level of about 700 HV₁₀ after quenching and 580 HV₁₀ after tempering. During the study of the effect on strength and ductility, the steel sheets were cooled to the room temperature at a rate of 3 to 140 K/s, caused by different surface pressures in the tool and outside the cooling medium. No significant effect on the tensile strength was found, whereas the relative tensile elongation could decrease from 11 to 6 % with the increasing cooling rate. The best properties (strength of 1800 MPa and relative elongation of 11 %) were obtained after a low surface pressure of 1 MPa and a cooling rate of 30 K/s.

Effect of tempering modes after quenching from different temperatures

Tempering of quenched laboratory steels 20Cr13 [2], AISI 420 with 0.17 % C [3] and <0.20 % C [12] causes their hardness reduction especially significant in the temperature range from 400 to 780 °C (Fig. 3, a). In the tempering temperature range up to ~600 °C higher hardness values are inherent in steels quenched from higher temperatures, which have higher supersaturation of austenite with carbon during quenching (this shows a significant difference in hardness values for the same tempering temperature obtained in different studies). The results of the study of properties after quenching and tempering over the widest temperature range are given for the X30Cr13 steel (1.4028) with a grade content of 0.26 – 0.35 % C and up to 1 % Si (Fig. 3, b)¹¹.

The annealing temperature range of 710 – 780 °C was studied in [12] due to the fact that the 13Cr steel casings are used in the condition after quenching and tempering at 680 – 780 °C (API-5CT). After quenching from 975 °C, the steel was characterized by the presence of lath martensite and hardness of 525 HV. Holding of such martensite for 20 min at 710, 730, 750, 770, 780 °C showed that tempering at ~(710 – 730) °C leads to martensite enlargement. It becomes equiaxial, and in its structure there are Cr₂₃C₆ carbides in the form of spheres/rods and needle Cr₇C₃ carbides (~100 nm). Tempering at 770 °C causes dissolution of Cr₇C₃ carbides and enlargement of spherical Cr₂₃C₆ carbides, and recrystallization occurs. Hardness at such high tempering decreases (Fig. 3, a).

Hardness of the X30Cr13 steel weakly decreases in the temperature range up to 300 °C, then a plateau is observed up to 500 °C, after which, in the range

of 500 – 600 °C, there is a sharp decrease in hardness (Fig. 3, b). The strength properties change in a similar way, including the ultimate strength decreasing from 1600 to 900 MPa for anneals between 500 and 700 °C. The ductility and impact strength change mirror-like, and when annealed at temperatures above 500 °C they increase significantly. The manufacturer recommends¹¹ the following temperatures for this steel: 900 – 1100 °C for hot deformation, 745 – 825 °C for annealing with cooling in the air, 950 – 1050 °C for quenching in oil or air, and 625 – 675 °C for annealing (after quenching from 850 °C).

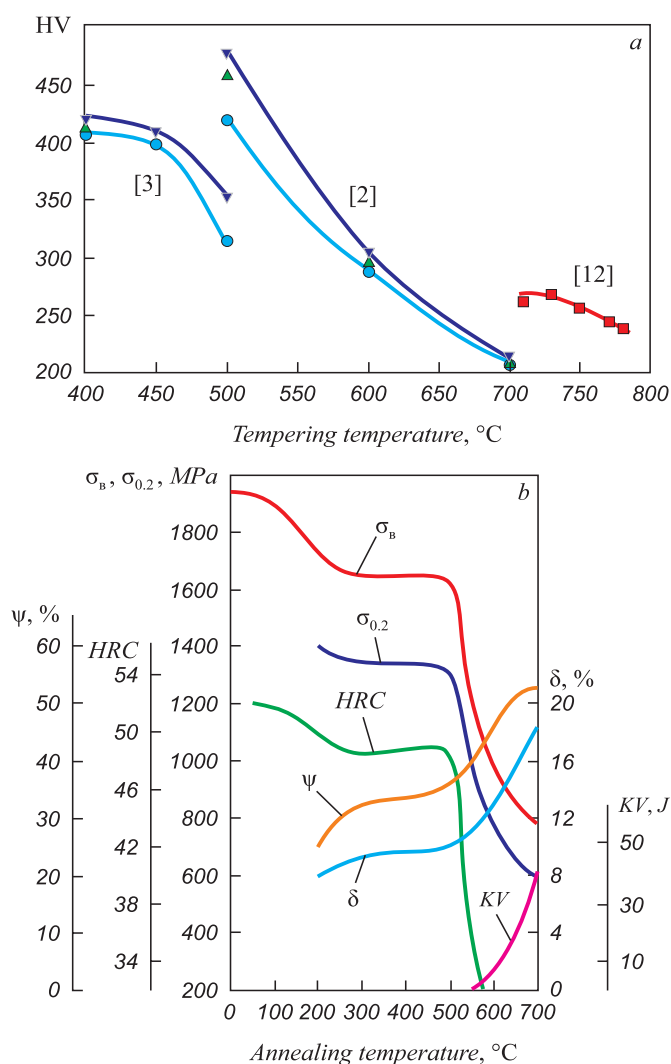


Fig. 3. Effect of annealing temperature:
a – on hardness of laboratory steels of 20Cr13 type after quenching from different temperatures [2, 3, 12] (● – 950, ■ – 975, ▲ – 1000 and ▼ – 1050 °C);
b – on hardness, strength, ductility and impact energy of industrial steel X30Cr13 – Nr. 1.4028 (30Kh13)¹¹

Рис. 3. Влияние температуры отжига:
а – на твердость лабораторных сталей типа 20X13 после закалки от разных температур [2, 3, 12] (● – 950, ■ – 975, ▲ – 1000 и ▼ – 1050 °C);
б – на твердость, прочность, пластичность и энергию ударного разрушения промышленной стали X30Cr13 – Nr. 1.4028 (30X13)¹¹

The effect of isothermal holding of steel quenched from 975 °C at 750 °C for 5 – 60 min on the carbide formation processes was studied [12]. After isothermal treatment for 5 min, Cr_{23}C_6 carbides were formed mainly at the grain and lath boundaries, and Cr_7C_3 carbides were formed inside the laths. Further increase in the time of isothermal annealing led to dissolution of Cr_7C_3 carbides and enlargement of Cr_{23}C_6 carbides. Accordingly, after holding for 5 and 15 min, the return processes were observed, and after longer holding recrystallization and grain growth processes took place. The return and recrystallization during tempering reduce the hardness of steels up to 250 HV. Minimum hardness at 750 °C is achieved during 15 min holding, at which time it decreases from 550 to 275 HV. Further heating at 750 °C (up to 60 min) does not lead to changes in hardness. In this case, the average particle size increases from ~45 to ~130 nm, and their density decreases compared to the maximum one by a factor of 3. The density of the particles is maximum after holding for 5 min; and during this time about 50 % of the total amount of the carbide phase is precipitated for 60 min, estimated by the “area fraction, %” parameter.

In [11] the heating temperatures for quenching of the X20Cr13 steel varied from 950 to 1150 °C and the tempering temperatures were 225, 375 and 525 °C. The holding times during such treatments were 240 and 480 s. The strength of the steel in this case ranged from 1310 to 1660 MPa, and the ductility varied from 3.5 to 7.5 %. The best combination of these characteristics, 1515 MPa strength and 7.5 % elongation, was achieved after quenching from 1050 °C (240 s) and tempering at 375 °C (420 s).

In this section only the effect of tempering on the structure and mechanical properties of steels is considered; below, in a separate section, attention is paid to the effect of this treatment on the corrosion resistance of steels with 13 % Cr.

Use of complex heat treatments:

repeated austenitization, double annealing, cooldown

The effect of double annealing on the structure, hardness, strength and impact strength of AISI 410 steel was studied [13]. In the initial state the steel had a structure consisting of ferrite and chromium-rich carbides Me_{23}C_6 after annealing at 750 °C for 2 h followed by slow cooling inside the furnace to a temperature of 25 °C for 20 h in order to obtain maximum softness for molding [13, 14]. Such samples were heated in the range of 900 and 1100 °C (30 min) and quenched in oil, followed by double annealing at temperatures between 200 and 700 °C (steel was cooled after annealing and then annealed again at the same temperature). The purpose of repeated annealing was to promote the transformation of residual aus-

tenite into martensite, since, according to [15], residual austenite is almost completely transformed as a result of double tempering at high temperature.

It was shown [13] that chromium carbides Me_{23}C_6 dissolve in the temperature range from 950 °C. Varying the tempering temperature of steel samples austenitized at 900 °C does not effectively change the microstructure or cause hardening (Fig. 4, a), as Me_{23}C_6 carbides are not precipitated, martensite and ferrite become softer and ductility increases. The structure after this treatment is ferrite in a matrix of lath-tempered martensite with Me_{23}C_6 chromium carbide particles (primary and small particles of secondary). The highest values of hardness as well as the yield strength and tensile strength are achieved after quenching from higher $T_A = 1050$ °C and tempering at 200 °C (Fig. 4, a – c).

The microstructure after tempering at 200 – 650 °C consists of ferrite islands and small spheroidal particles of secondary chromium carbide Me_{23}C_6 in a matrix of coarse-grained lath-tempered martensite. Tempering at $t \geq 550$ °C leads to an increase in the number of precipitations along grain boundaries. A satisfactory combination of hardness, strength and impact energy is achieved by double tempering of steel at 200 and 450 °C after quenching from 1050 °C (Fig. 4, Table 6) [22]. In general, double tempering did not result in a significant change in mechanical properties for any of the tested specimens; the microstructure after it still contained a significant amount of residual austenite. During conventional austenitizing treatment, carbide dissolution and grain size growth intensified with increasing austenitizing temperature, while double tempering treatment promoted carbide formation with a slight increase in the grain size. For comparison, in the 40Cr13 type steel (with 0.38 % C and 0.3 % V, i.e., in which the number of carbide particles must be much larger) the precipitations in the samples after single tempering at 300, 500 and 650 °C are nanosized $\epsilon\text{-Me}_3\text{C}$ carbides, chromium-rich nanosized Me_{23}C_6 carbides and micron or submicron Me_{23}C_6 carbides, respectively [16].

The effect of treatment with double quenching and double annealing (710 °C + 680 °C) on the microstructure, hardness, and mechanical properties of 13Cr hot-rolled steel with 0.2 % C was studied [17]. Austenitizing followed by quenching (duration of 3 h 15 min) was carried out according to the following modes: 980 °C, quenching + 1040 °C, quenching; 1040 °C, quenching + 980 °C, quenching. Cooling during quenching and after tempering was carried out in oil. Both in the case of single quenching at 980 °C and double quenching (1040 °C + 980 °C), there was no delta-ferrite in the tempered martensite microstructure. After single heat treatment, the structure contained carbides along the grain boundaries, and very fine distribution of ferrite was observed. During single quenching, continuous carbide chains along the grain boundaries of the former austenite contributed

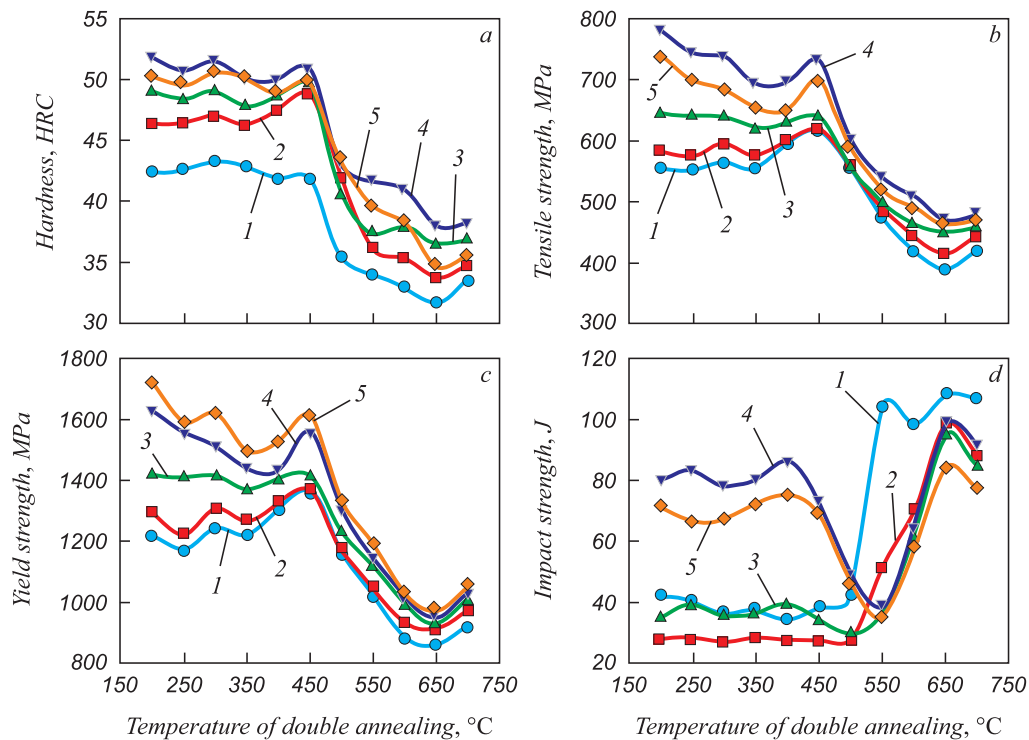


Fig. 4. Effect of double annealing temperature on hardness (a), yield strength (b), tensile strength (c), impact strength (d) of AISI 410 steel after quenching from austenitization temperatures (T_A), °C [13]:
1 – 900; 2 – 950; 3 – 1000; 4 – 1050; 5 – 1100

Рис. 4. Влияние температуры двойного отжига на твердость (a), предел текучести (b), предел прочности (c) и ударную вязкость (d) стали AISI 410 после закалки от температур аустенизации (T_A), °C [13]:
1 – 900; 2 – 950; 3 – 1000; 4 – 1050; 5 – 1100

to the reduction of the impact strength, and its values did not meet the specification requirements. When this steel with the initial martensite microstructure obtained during the first quench from 1040 °C was subjected to secondary austenitizing at 980 °C, recrystallization of the grain structure from the defective matrix of martensitic laths obtained during the first quench occurred. The modified heat treatment with double quenching at 1040 °C + 980 °C provided a finer grain size along with a higher degree of carbon dissolution in the austenitic matrix. During tempering, very fine carbides (having a much smaller size compared to the single heat treatment process) formed in small numbers at low-angle and high-angle boundaries. This resulted in the increased strength and impact strength after tempering, compared to single quenching from 980 °C (Table 2).

In [18] the effect of conventional heat treatment and cryogenic treatment on the mechanical properties of AISI 420 steel was compared. Cryogenic treatment was carried out by a gradual decrease in temperature to avoid the thermal shock: –20 °C, 4 h; –70 °C, 5 h; –196 °C, 24 h. Subsequent heating occurred in the reverse sequence. In the initial state (annealing at 850 °C and cooling with a furnace) the steel had a ferrite-carbide structure with low mechanical properties. Quenching to martensite from 1000 °C followed by tempering at 200 °C provided

a martensite structure with residual austenite and undissolved dispersed carbides, and a combination of strength of 989 MPa with ductility of 15 %. Increasing the tempering temperature to 500 °C resulted in coarsening of Me_7C_3 carbides and partial transformation to $Me_{23}C_6$ carbides, some reduction in strength and increase in ductility. Conducting a stepwise cryogenic treatment before tempering at 500 °C increased the strength properties to 933 MPa and the relative elongation to 40 % (Table 6) due to the precipitation of finely dispersed carbides. The combination of strength and plastic properties thus obtained for this steel is a good result, but the disadvantage of such treatment is the complexity of cryogenic treatment using long periods of holding in a refrigerator, dry ice and liquid nitrogen and subsequent heating in the reverse sequence.

Suggested heat treatment options and mechanical properties

Data on the chemical composition of 13Cr type steels discussed above are given in Table 5. The mechanical properties obtained by researchers for 13Cr steels when varying both conventional quenching and tempering modes and dual heat treatments are given in Table 6. Comparison of the properties of treatments No. 1 – 21 from

Table 6 with the properties of industrial steels of the 13Cr group (Table 3) shows that treatments No. 1 and 2 for 20Cr13 type steels and treatment No. 21 for the 40Cr13 steel achieved a higher level of strength than that specified in the known reference materials for these steels. After treatments No. 4 and 5, the 20Cr13 type steel had a level of strength close to that of this steel after tempering at 700 °C in Table 3, but a higher ductility was achieved in this case. The results of treatments No. 16 – 20 are new, and in the reference literature there is no such data for the 30Cr13 steel.

The publications dedicated to the study of corrosion resistance and the possibilities to increase the wear resistance of steels of the Cr13 group are considered below.

STUDIES OF WEAR RESISTANCE OF STEELS WITH 13 % Cr

In the Russian scientific segment, a number of publications have been found that consider the prospect of increasing the wear resistance of 40Cr13 steel due to surface treatments. In addition, a significant place is given to the surface layer saturation with nitrogen during the following treatments:

- nitrocementation [19];
- ion-plasma nitriding [20, 21], including thermal-cycle [20];
- nitriding combined with heat treatment [22].

It is demonstrated that diffusion layers on the cutting surfaces of 40Cr13 steel, saturated with large amounts of carbonitrides during nitrocementation, provide high cutting ability, self-sharpening and wear resistance [19]. Ion-plasma thermal-cycle nitriding made it possible to obtain hardened wear-resistant surfaces, which have a complex of specific physical, mechanical and operational properties [20]. It has been established that during high-frequency nitriding of 40Cr13 steel in inductively coupled plasma of the argon, hydrogen and nitrogen mixture a three-layer structure is formed in the near-surface layer. Its wear rate is the lower the higher the amplitude of the displacement potential [21]. A study of the wear mechanism of ion-modified nitrogen in 40Cr13 steel subjected to various modes of pretreatment has shown that the nitrated layer is an α -Fe matrix phase with chromium nitrides CrN. In the process of friction of nitrogen-modified 40Cr13 steel, accelerated wear of the nitrided layer is registered as its thickness decreases to a certain critical value. As the hardness of the substrate increases, the critical thickness of the nitrided layer decreases from 11 – 12 to 9 – 10 μm [22].

The possibilities of hardening the 40Cr13 steel by surface laser and plasma quenching have been studied [23, 24]. The possibility of effective surface hardening of products using laser heating is also considered.

The influence of arising thermal stresses on the temperature interval of austenitic transformation is taken into account, and the dependences of hardness on density, power and treatment rate are analyzed. The work showed that high hardness is achieved when heating to a temperature of 150 – 200 K below the melting temperature [23]. The technology of plasma surface hardening of products made of high-alloy corrosion-resistant steel 40Cr13 allows obtaining a hardened martensitic layer more than 4 mm deep on its surface [24]. The feature of the technology is the microhardness values evenly distributed over the section, the absence of changes in the geometric shape and structure of the 40Cr13 steel part core. In the hardening zone from the solid phase a spectrum of structures is observed – from the martensitic type structure on the boundary with the melting zone with the transition to the martensitic type structure with carbides precipitation (both in the grain body and on the grain boundaries). In the transition zone (thermal impact zone) the structure has the form of a ferrite-carbide mixture of sorbitic type of different dispersion. Such a distribution of microstructures in zones is characteristic of the traditional hardening of 40Cr13 steel products for maximum hardness with preservation of corrosion resistance properties.

Complex treatment of the 40Cr13 steel consisting of heat and mechanical treatments, high-vacuum annealing and diffusion siliconizing has been proposed [25]. It provides the possibility of hardening to a depth of 4.2 mm. Tests of fracture and wear resistance, evaluation of the hardness and microgeometry of the surface layer of samples showed that this treatment can increase the durability of parts.

The use of the 40Cr13 steel as a coating on steel 45 to increase the wear resistance of the material is of interest [26]. Gas-thermal coating of 40Cr13 wire steel was applied to steel 45 plates by high-speed metallization. Additionally, the coating was treated with nitrogen ions. Ion-beam treatment increases the microhardness of coatings to the values of 1000 – 1450 $\text{HV}_{0.025}$ and their wear resistance under friction in the I-20 lubricant medium by 1.7 times. Based on the results obtained, the temperature mode of ion-beam nitriding with the highest tribotechnical properties has been selected.

STUDIES OF CORROSION RESISTANCE OF STEELS WITH 13 % Cr

It is known that heat treatment is an important factor influencing the tendency of alloys to corrosion. Stainless steels are most resistant to corrosion effects in the state of treatment for a solid solution. Tempering in the temperature range of excess phases (carbides, carbonitrides, nitrides) reduces the resistance of steel to intergranular and pitting corrosion. This is due to the emergence around the carbides of zones depleted in chromium, with reduced

corrosion resistance. The less (negative) the pitting corrosion potential of an alloy, the greater its tendency to pitting. The value of the pitting potential is a measure of the tendency of metals to pitting.

The works [7, 9, 16, 27 – 31] are dedicated to the studies of the effect of heat treatment on corrosion resistance of steels with 13 % Cr.

In [7] the object of the studies was steel with 13.7 % Cr with increased carbon content (0.497 %), high-purity due to vacuum melting. The effect of microstructure changes at different austenitizing (T_A) temperatures on various corrosion mechanisms was studied. Polarization scanning was carried out in the 0.1 M NaCl + 0.1 M phosphate buffer solution ($pH = 7.5$). It is demonstrated that the resistance against general corrosion increases with increasing T_A up to 1100 °C due to dissolution of carbides and the associated increase in the chromium content of the alloy matrix. This also leads to better passivation and a thicker internal passive layer rich in chromium. A further increase in T_A does not increase the chromium content and resistance to general corrosion, since all carbides are dissolved. On the other hand, with increasing T_A up to 1100 °C, the carbon content increases, which increases the internal lattice stress and leads to a more defective passive layer, causing a decrease in the resistance to pitting. A further increase in T_A , without affecting the carbon content, increases the grain size. The density of lattice defects in the bulk material decreases, reducing the defectiveness of the passive layer and increasing the resistance to pitting. In contrast, the critical potential shows a contradictory course, increasing up to 1100 °C and decreasing at lower temperatures. A higher pitting potential means less susceptibility to pitting, while a higher critical pitting potential means slower pitting, if any. The authors of [7] note that:

- the research can show that there is not one corrosion resistance, but several different corrosion mechanisms, which are influenced by different microstructure properties;

- the amount of carbon is a critical factor for the pitting corrosion potential;

- alloys with a lower carbon content exhibit different pitting behavior and, given this, the seemingly contradictory results simply refer to different phenomena and are not a contradiction.

A similar study to evaluate the effect of austenitizing temperature and cooling rate (water/air) on corrosion resistance was also conducted on high carbon steel with 13.92 % Cr, 0.42 % C (X46Cr13 (1.4034)) under potentiodynamic polarization in 0.1 M H_2SO_4 [9]. Heating followed by cooling in water was performed at temperatures: 850 °C (72 h), 900 °C (9 h), 950 °C (90 min), 1000 °C (30 min), 1050, 1100, 1150 °C (15 min), and 1200 °C

(10 min). Heating followed by air cooling was performed at 1000 °C (30 min), 1050 and 1100 °C (15 min). It was also noted, as in [7], that austenitization at temperatures of 1100 °C and above leads to a complete dissolution of carbides. The optimal distribution of chromium and carbon in the mixed crystal is ensured. The elimination of the blocking effect of carbides and the higher diffusion rate lead to significant grain enlargement. Decreasing the austenitizing temperature below 1100 °C leaves mixed chromium and iron carbides in the structure, which reduce hardness and corrosion resistance. Temperature-dependent diffusion processes occur during slow air cooling. New carbides form during cooling at the grain boundaries or in the grains themselves and locally remove chromium from the matrix. Second, iron is precipitated from the remaining mixed chromium and iron carbides as solubility drops sharply with temperature. Both processes lead to chromium depletion during air cooling, which is localized mainly on carbides at 1100 °C and on carbides and grain boundaries at 1000 and 1050 °C. Depletion of the chromium content locally worsens the stability of the passive layer, and the resistance to pitting decreases significantly.

In works [16, 27 – 29] the effect of tempering modes on electrochemical corrosion in aqueous NaCl solutions of 13Cr steels with different carbon content was studied.

Experiments on the potentiodynamic polarization in the 3.5 % aqueous NaCl solution of low carbon steel with 0.03 % C and 12.8 % Cr (AISI 410) were performed after quenching from the temperatures in the range from 950 to 1100 °C and quenching from 1050 °C with tempering at 300 – 700 °C [27]. The corrosion rate of AISI 410 steel decreases as the austenitizing temperature increases. The microstructure after austenitizing and tempering is represented by tempered martensite, residual austenite and carbides. The lowest corrosion current density was obtained after tempering at 300 and 400 °C, and the lowest corrosion rate after austenitizing at 1050 °C, quenching and tempering at 600 °C.

The effect of heat treatment on the corrosion behavior of AISI 420 steel (12.10 % Cr, 0.23 % C) in 0.5 M NaCl with $pH = 6.26$ and electrical conductivity of 49.9 mS/cm was studied on samples in four structural states [28]. In the initial state (*A*), a continuously cast calibrated rod was considered. Treatment *B* was annealing at 770 °C for 20 min and cooling with a furnace. Treatment *C* was 1000 °C, 30 min, martensite quenching in water. Treatment *D* was tempering at 700 °C, 60 min, cooling in air. The order of samples by corrosion resistance value from higher to lower was established: $B > C > D > A$. Sample AISI 420 (*B*) is the most resistant to corrosion, and sample *A* is the most susceptible to corrosion. Sample *C* also showed high polarization resistance.

The results of studies [16, 29] of steels close in the chemical composition of the studied steels, heat treatment modes and conclusions made are summarized in Table 7.

The peculiarity of research [30] is that the evolution of microstructure and corrosion behavior of martensitic stainless steel of type 420 with increased carbon content (13.7 % Cr, 0.46 % C, 0.47 % Si, 0.39 % Mn) was studied, tempering of which after austenitizing (950 °C, 1 h, water) was carried out not only at 550 and 700 °C, but also at lower temperatures of 250 and 400 °C (1 h, air), and the potentiodynamic polarization test was conducted not in salt solution, but in the 0.1 M HCl solution at 20 °C. After austenitization and quenching, the metal had a martensitic structure and most of the $Cr_{23}C_6$ carbides dissolved. After tempering at 250 °C some amount of $Cr_{23}C_6$ carbides was found on the grain boundaries. After tempering at 400 °C they were larger and more abundant, and after tempering at 550 °C precipitation of CrC, Cr_7C_3 and an even greater number of $Cr_{23}C_6$ particles, also at the grain boundaries, were found. After tempering at 700 °C only $Cr_{23}C_6$ carbides were observed, with local corrosion and nucleation of pits near carbides. After all tempering temperatures, pitting corrosion was observed, with the specimen tempered at 250 °C having the highest corrosion resistance and a hardness value of well above 500 HV, and after treatment at 550 °C, general and intergranular corrosion was also observed. The concentration of chromium in the solid solution after different treatments was: 200, 400 °C – >12 %, 550 °C – 10.5 %, 700 °C – ≈11.5 %, i.e. after the last two treatments it was below the critical level. Thus, in contrast to works [16, 29] (see Table 7), a different order of carbide occurrence during tempering can be noted for the studied steel. The temperature of 250 °C is specified as the best choice of tempering temperature, which provides the highest corrosion resistance (high kinetics E_{pit} and low pit growth kinetics). Tempering modes at 550 and 700 °C should be avoided because corrosion resistance reduced due to a large amount of large-size chromium carbides formed at these tempering temperatures.

Since the AISI 420 martensitic stainless steel is quenched and tempered or double tempered at temperatures up to 250 °C for tableware applications, corrosion resistance was also compared for steel with 12.1 % Cr and 0.19 % C after single and double tempering at 180 °C (2 h, air) after austenitizing at 1050 °C (5 min, air) [31]. The potentiodynamic polarization test was performed in aerated 3.5 % NaCl (pH = 6.0). Single tempering showed a hardness close to air quenching and did not degrade the pitting corrosion resistance. Double tempering did not improve the resistance to pitting corrosion, and hardness decreased afterwards. Only single tempering is recommended.

CONCLUSIONS

The properties of steels with 12 – 14 % Cr and $0.2 \leq \% C \leq 0.4$: industrial steels produced with heat treatment according to the standards and known from reference literature, as well as metal properties of laboratory melts treated by various modes of austenitizing and tempering are considered.

In these steels initially annealed at ~800 °C with the formation of the ferrite-carbide structure, with their heating from 800 to 1240 °C, the dissolution of carbides of $Me_{23}C_6$ type occurs, which causes the formation of austenite at 810 – 820 °C with the fixation during quenching of the martensite-carbide structure. Depending on the concentration of carbon in these steels, carbide dissolution in them ends at 950 – 1050 °C. Dissolution of carbides is accompanied by the growth of the austenite grain and preservation of residual austenite after quenching in the structure. Therefore, as the austenitization temperature increases, the quenched steels first show a linear increase in martensite hardness due to carbide hardening ($c/a = 0.45[C] + 1.00$). And then, when the maximum degree of carbide dissolution is achieved, the steels hardness decreases with further heating, which is associated with the formation of residual austenite and growth of the austenite grain. The maximum effective austenitizing temperature before quenching, which provides high hardness, is 1000 – 1020 °C (HV ~550) for 20Cr13 steels and 1100 – 1120 °C (HV 700 – 750) for 45Cr13 steels.

The grain size during austenitization is the coarser the longer the holding time at a given temperature, and this effect is the more significant the higher the heating temperature. The longer the holding time in the temperature range above the maximum effective austenitizing temperature, the greater the residual austenite in the steel and the lower the hardness after hardening.

The temperature required to achieve complete dissolution of $Me_{23}C_6$ carbides in the austenitic phase increases with the increasing heating rate. High-rate heating leads to a shift of hardening curves after quenching by 40 – 60 °C up the temperature scale compared to the curves obtained during furnace heating.

Quenching not in water at slower cooling rates than 20 K/s (including air) causes precipitation of some carbides.

Hardened steels 20Cr13 – 40Cr13 are characterized by high strength, hardness, and low ductility, especially high-carbon steels. Tempering of hardened laboratory steels in the range up to 400 °C causes a slight decrease in martensite hardness and strength (a small amount of carbides precipitates in martensite, and it becomes unstable). In the interval of 400 – 500 °C a slight increase in hardness and strength due to the effect of dispersion hardening is possible. Then, in the range of 500 – 780 °C, there

Table 7

**Effect of tempering at 300, 500–550 and 650 – 700 °C on corrosion resistance of steels
with 13 % Cr and 0.31 – 0.38 % C**

**Таблица 7. Влияние отпуска при 300, 500 – 550 и 650 – 700 °C на коррозионную стойкость сталей
с 13 % Cr и 0,31– 0,38 % C**

Main provisions of the paper	Source [29]	Source [16]
Steel	13.3 % Cr, 0.31 % C, 0.04 % V, 0.48 % Cu	13 % Cr, 0.38 % C, 0.3 % V
Quenching mode	1020 °C (30 min, quenching in oil)	1030 °C (45 min, quenching in oil)
Tempering mode	300, 550 and 700 °C (2.5 h, cooling in air)	300, 500 °C and 650 °C (2 h, cooling in air)
Type of tests	Potentiostatic polarization tests	
Test medium	0.1 M NaCl solution	3.5 % NaCl aqueous solution
Precipitation in steels during tempering	300 °C – nanosized ϵ - Me_3C carbides; 500 – 550 °C – nanosized $Me_{23}C_6$ carbides; 650 – 700 °C – micron or submicron $Me_{23}C_6$ carbides	
Structure after austenitizing	Austenitizing at 1020 – 1030 °C did not lead to the complete dissolution of carbides	
	Fine-lath martensite with residual austenite interlayers at the lath boundaries, $Cr_{23}C_6$ carbides	Martensite and $Cr_{23}C_6$ carbides
	The share of residual austenite decreases with tempering temperature, and after tempering at 550 and 700 °C residual austenite is not observed	Residual austenite is observed only after tempering at 300 °C, and there is no residual austenite after tempering at 500 and 650 °C
Effect of austenitizing and tempering at 300 °C on corrosion resistance	In the austenitized state a passive film enriched with chromium is formed. The sample austenitized and tempered at 300 °C shows less current transients, and no sustained pitting corrosion is observed in the 3 h test	Pitting corrosion potential of hardened steel is higher than that of tempered steel and decreases with increasing tempering temperature. Relatively low-temperature tempering (300 °C) slightly reduced corrosion resistance compared to steel after quenching
Corrosion after tempering at 500 – 550 °C	Tempering reduced the pitting potential and increased the metastable pitting. Tempering at 550 °C made the steel highly prone to pitting. Pitting occurred at the carbide-matrix interface due to the presence of chromium depletion areas associated with the massive precipitation of chromium-rich carbide. The passive film formed at corrosion potential was enriched with iron particles. It was less protective than the film after austenitization and increased the corrosion current density at corrosion potential and showed no passivity in the 0.1 M NaCl solution above the corrosion potential	The sample after tempering at 500 °C exhibits active corrosion behavior without passivation. This is explained by the precipitation of a large number of chromium-rich nanosized $Me_{23}C_6$ carbides. The large carbide/matrix interface, as pitting occurred, prevented the formation of a protective passive film on the steel surface due to the small distance between the carbides
Comparison of the corrosion behavior after tempering at 500 – 550 and 660 – 700 °C and final conclusion	The Epit value is higher for the sample tempered at 700 °C compared to the sample tempered at 550 °C. A possible reason is the repeated diffusion of Cr from the matrix into the depleted regions, which minimizes the discontinuity of the interfacial regions. The above results confirm the assumption that tempering of steel with 13 % Cr should be carried out at 700 °C because it also provides resistance to pitting.	The sample 1030-650 showed better corrosion resistance than sample 1030-500, even though the Cr content of the matrix was slightly lower than that of sample 1030-500. The tempering temperature for the 13 % Cr steels should be much lower or higher than 500 °C to avoid the massive precipitation of nanosized $Me_{23}C_6$ carbides. Steels with 13 % Cr, tempered at 300 °C, show a combination of high relative hardness and high corrosion resistance.

is a significant decline in these characteristics (intensive precipitation of carbides → decomposition of martensite into ferrite and carbides → coagulation of carbides and their partial dissolution, recrystallization). The plasticity and impact strength increase symmetrically.

The heat treatment with double quenching at 1040 °C + 980 °C provided a finer grain size along with a higher degree of carbon dissolution in the austenitic matrix. During tempering (double at 710 °C + 680 °C), very fine carbides (having a much smaller size compared to the single heat treatment process) formed in small numbers at low-angle and high-angle boundaries. This resulted in increased strength and impact strength after tempering, compared to single quenching from 980 °C.

Corrosion resistance increases with increasing austenitizing heating temperature and decreases with increasing tempering temperature, at which pitting and intergranular corrosion are added to general corrosion, which is associated with the precipitation of Cr₂₃C₆ carbides and depletion of the matrix in chromium to the concentrations below 12 %. The recommended heat treatments for 20Cr13 steels are quenching with low tempering at 200 – 300 °C (combination of high strength, good corrosion resistance and satisfactory plasticity), or quenching with high tempering at ~700 °C (good plasticity, satisfactory corrosion resistance). For steels of 40Cr13 type the temperature of ~700 °C is not recommended. The worst tempering temperature is 500 – 550 °C because of the maximum precipitation of ultradispersed carbides.

The possibility of ensuring increased wear resistance of 40Cr13 steels by saturating the surface layer with nitrogen (nitrocementation, ion-plasma nitriding, nitriding and heat treatment), surface laser and plasma quenching, a combination of heat and mechanical treatments, high-vacuum annealing and diffusion siliconizing is demonstrated.

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V. S. Kostina – search for literary data on corrosion resistance, translation, participation in writing a section on corrosion.

A. E. Kudryashov – search and translation of literary data on wear resistance, participation in writing a section on wear resistance.

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Received 11.11.2022

Revised 05.12.2022

Accepted 26.12.2022

Поступила в редакцию 11.11.2022

После доработки 05.12.2022

Принята к публикации 26.12.2022