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© Ya. Cheiliakh[1], O. Cheiliakh[2],
K. Shimizu[3], T. Noguchi[4]

APPLICATION OF THERMOCHEMICAL TREATMENT FOR CREATION OF METASTABLE MODIFICATIONS REALIZING THE EFFECT OF SELF-STRENGTHENING AT STEEL WEAR

It was proposed to solve urgent problems of saving scarce and costly high-alloyed and wear resistant steel grades (containing Ni, Mo, V, W, Nb) and increasing wear resistance of metal parts by means of creating surface modifications of metastable phase-structural complexes in inexpensive economical alloys of the similar structural classes. The objective of this work is to investigate the influence of alloying elements upon the formation of the structure, metastability of austenite and properties of chromium-manganese steel grades, undergoing carburizing and manganese steel undergoing decarburizing. In this work the new ways and processes of surface modifications of metastable phase-structural states were developed:

- carburizing Fe-Cr-Mn steels with various contents 2...22 % Cr with subsequent quenching at optimal temperatures of austenitization;

- decarburizing austenitization for a specified depth of high-alloyed wear resistant steel grades (110Mn13 – Hadfield steel, 130Cr12Mo etc.) causing destabilization of austenite and realization deformation induced martensite $\gamma \rightarrow \alpha'$ transformation in the process of wear.

Keywords: *Metastable Austenite; Martensite; Wear-resistant; Steel; Carburizing; Decarburizing.*

Я. Чейлях, А. Чейлях, К. Шимицу, Т. Ногучи. Использование химико-термической обработки для создания метастабильных модификаций, реализующих эффект самоупрочнения при изнашивании стали. *Предложено решение актуальных проблем экономии дефицитных и дорогостоящих высоколегированных и износостойких марок стали (содержащих Ni, Mo, V, W, Nb) и повышение износостойкости металлических деталей путем создания поверхностных модификаций метастабильных фазово-структурных комплексов в недорогих экономичных сплавах подобных структурных классов. Целью данной работы является исследование влияния легирующих элементов на формирование структуры, метастабильность аустенита и свойств хромо-марганцевых марок стали после цементации и марганцевой стали после обезуглероживания. В этой работе были разработаны новые способы и процессы поверхностных модификаций метастабильных фазово-структурных состояний:*

- цементация Fe-Cr- Mn сталей с различным содержанием 2 ... 22 % Cr с последующей закалкой при оптимальных температурах аустенитизации;

- обезуглероживающая аустенитизация на определенную глубину высоколегированных износостойких сталей (110Г13 – сталь Гадфильда, 130Х12М и т.д.) вызывающая дестабилизацию аустенита и реализацию деформационного мартенситного $\gamma \rightarrow \alpha'$ превращения в процессе изнашивания.

Ключевые слова: *метастабильный аустенит; мартенсит; износостойкость; сталь; цементация; обезуглероживание.*

Я. Чейлях, О. Чейлях, К. Шиміцу, Т. Ногучи. Використання хіміко-термічної обробки для створення метастабільних модифікацій, що реалізують ефект са-

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[1] *PhD, Priazovskyi State Technical University, Mariupol*
[2] *DSc. Prof., Priazovskyi State Technical University, Mariupol*
[3] *DSc. Prof., Muroran Institute of Technology, Muroran, Japan*
[4] *DSc. Prof., Muroran Institute of Technology, Muroran, Japan*

мозміцнення при зношуванні сталі. Запропоновано вирішення актуальних проблем економії дефіцитних і дорогих високолегованих і зносостійких марок сталі (вміщаючих Ni, Mo, V, W, Nb та ін.) та підвищення зносостійкості металевих деталей шляхом створення поверхневих модифікацій метастабільних фазово-структурних комплексів в недорогих економічних сплавах подібних структурних класів. Метою даної роботи є дослідження впливу легуючих елементів на формування структури, метастабільність аустеніту і властивостей хромо-марганцевих марок сталі після цементації і марганцевої сталі після зневуглецювання. У цій роботі були розроблені нові способи і процеси поверхневих модифікацій метастабільних фазово-структурних станів:

- цементація Fe - Cr- Mn сталей з різним вмістом 2 ... 22 % Cr з наступним загартуванням при оптимальних температурах аустенітізації;

- зневуглецювання аустениту на певну глибину високолегованих зносостійких сталей (110Г13 - сталь Гадфільда, 130Х12М і т.д.), що призводить до дестабілізації аустеніту і реалізації деформацій мартенситних γ → α ' перетворень в процесі зносу.

Ключові слова: *метастабільний аустеніт; мартенсит; зносостійкість; сталь; цементація; зневуглецювання.*

Statement of the Problem. The problems of saving expensive and scarce alloying components, such as nickel, molybdenum, vanadium, cobalt, etc. when producing steels and alloys and improving their physical-mechanical and operational properties present great interest not only to Ukraine but to many other countries as well. It is actual to solve problems of increasing wear resistance of metal parts by means of creating surface modifications of metastable phase-structural complexes in inexpensive economical alloys of the similar structural classes.

Analysis of recent research and publications. Using the principle of metastable austenite, which was grounded by Bogachev I., Mints R. [1], is a very perspective way of developing special steels with metastable austenite realizing DIMT in the research works of L. Malinov [2], M. Filippov, V. Litvinov, Y. Nemirovskiy [3], G.B. Olson, M.Cohen, Narutani T., [4], V.F. Zackay, E.R. Parker [5], et.al. Regulating the quantity of metastable austenite and the degree of its metastability allowed enhancing of its mechanical and operational properties [2]. It is possible to apply the principle of metastable austenite not only to limited grades of special steels of austenite class, but also for other functional alloys and carburized layers [6-8]. In high manganese cast iron SCI-VMn the work-hardening effects on the material surface happened – reaching 804 HV from the initial hardness of 533 HV owing to austenite – martensite strain-induced transformation [9]. However, in the bulk of them the degree of austenite metastability was not taken into account, as a rule [7], this, as we believe, does not allow to use efficiently the capabilities of its deformation phase transformations in order to increase wear resistant. The influence alloying elements upon structure formation, degree of austenite metastability and the properties of carbonized layers in special steel grades remains unanalyzed, thus limiting the possibilities of thermo-chemical treatment for creation of phase-structural metastable modifications and their efficient surface strengthening.

These modifications, containing heterophase structures: martensite, carbides, carbo-nitrides, ferrite etc. in various combinations must necessarily have metastable austenite of any phase-morphological types. Metastable austenite conditions of any phase-morphological types are realized in the process of wear DIMT, accompanied with emission of carbide (carbon-nitride) particles of expensive phases inside the surface layer. Such transformations cause drastic additional self-strengthening of the surface layer, accompanied with relaxation of micro-stresses, thus ensuring a substantial increase of parts' wear resistance.

Application of new generation alloys solves not only the problem of saving expensive and deficit alloying components (Ni, Mo, Nb, W and others) but also increases operational properties of industrial equipment and machine parts. The alloys with metastable structure possess self-organizing capability when loaded during operation. Programmed kinetics of deformation-induced phase transformations (DIPT), such as DIMT, dynamic deformation aging (DDA) in the alloys and surface strengthened layer under the influence of operational conditions allows to achieve a unique combination of extremely high mechanical and operational properties, resulting in efficient alloying and even com-

plete exclusion of expensive components from their composition [10].

The purpose of article. The investigate the influence of alloying elements upon the formation of the structure, metastability of austenite and properties of chromium-manganese steel grades, undergoing carburizing and manganese steel undergoing decarburizing.

The main material. The new economical metastable materials: high-strength and corrosion-resistant (nickel-free) Fe-Cr-Mn steels after carburizing and quenching, Hadfield-steel after decarburizing austenitization were investigated. Various methods and technologies of heat treatment, thermo-chemical treatment, which created metastable states and realized effects of self-organizing and self-strengthening at testing of wear and exploitation owing to application of DIPT are used in this work.

Investigated were chromium-manganese steels: high-strength steels 30Cr(2…8)Mn6Si2V, corrosion-resistant steels 08Cr(14…22)Mn6SiV, its composition is given in Table 1.

Table I

Chemical, phase composition and structural classes of Fe-Cr-Mn steels

Steel grade	Elements content, mass %					Phase content, %			Structural class
	C	Cr	Mn	Si	V	M	F	A	
30Cr2Mn6Si2V	0,28	1,92	6,33	1,64	0,18	81	-	19	M – A
30Cr4Mn6Si2V	0,31	3,25	6,61	1,98	0,20	48	-	52	A – M
30Cr6Mn6Si2V	0,34	5,50	6,57	2,03	0,17	8	-	92	A – M
30Cr8Mn6Si2V	0,35	8,37	6,76	2,05	0,16	2	-	98	A
20Cr14Mn7	0,215	14,4	6,69	0,38	-	7	-	93	A-M
08Cr14Mn6SiV	0,09	14,0	4,99	0,4	0,25	60	-	40	M – A
08Cr18Mn6SiV	0,1	17,69	5,14	0,46	0,22	-	46	54	A – F
08Cr22Mn6SiV	0,08	21,68	6,1	0,50	0,28	-	64	36	F – A
110Mn13	1,26	0,25	11,9	0,28	-	-	-	100	A

Note: M-martensite, A-austenite, F-ferrite; content $S \leq 0,027$ %; $P \leq 0,018$ %.

Steel specimens, 10x10x55 mm in dimensions underwent carburizing inside solid carburizer at temperatures 980-1050 °C within 10…12 hours in shaft furnace. After carburizing quenching was performed at various temperature ranges (850…1150 °C) within 25 min., the cooling was in oil, tempering made in chamber furnace at 250 °C within 1 hour.

Decarburizing austenitization of specimens of cast steel of 110Mn13 grade of standard content was carried out by heating inside an ordinary oxidizing surface atmosphere which contain H_2O; N_2; O_2; CO_2 of an electric furnace at temperature 1150 °C, holding interval being 10…120 min.

In the surface layer of decarburized samples of Hadfield-steel carbon content is determined by X depth the pitch being 0.5mm) by the method of infrared spectral analysis on „Leco CS-244" gas analyzer, and manganese content by KJ photometric. Metallographic method (on optical microscope "Neophot 21") with quantity structural analysis composes, fracture electron microscopy "Jeol JSM-6010LA" with x-ray structural microanalyses of phases, different thermo-metric analyse of critical points were employed in the research. The number of M, F, A phases was determined by metallographic method by relative overall areas of these phases within 30 fields of vision. Hardness (on hardness gauge Rockwell) and micro-hardness (on microhardness gauge "ПМТ-3") tests, were applied, impact energy test on samples 10x10x55 mm with U-notched specimen (on impact testing machine "ИО5003"), as wells as wear tests. Tests of wear-resistance were conducted in two ways: at the dry friction sliding of metal at metal (ε_f) and at impact-abrasive wearing ($\varepsilon_{i.a.}$). Tests at the dry sliding friction were conducted at machine "МИ-1М" on scheme test sample - a roller (the checking body), revolving with constant speed ω_1=500 min^{-1} (peripheral-lineal speed in the friction zone is 1,31 meter per second). The scheme of wear machine "МИ-1М" shown on fig. 1. The time of wear-resistance averaged: quotient – weighting-to-weighting – 3 min, the total time of chafing averaged 24 min. The samples for wearing were 10x10x27 mm. in size. Hardness of the steel roller was HRC 25. Weighting was made within ± 0,0001 gram. range. The load upon the specimen sample was 67 N.

Tests of the samples 10x10x26mm in size at impact-abrasive wearing were conducted on special installation [6] in the environment of molten cast-iron shot (the fractions 0,5…1,5 mm) at the speed of rotation of the samples ω_2=2800 min^{-1}. The scheme of special installation for impact abrasive

wear testing is shown on fig. 2. The total time of wearing averaged 25 min. including the interval 5 min. weight-to-weight. 3 specimen undergo testing simultaneously. The relative wear-resistance under these two types of wearing (ε_f, $\varepsilon_{i.a.}$) was defined by the formula:

Fig. 1 – The scheme of wear machine "МИ-1М" for test of dry sliding: 1 – roller, 2 – sample

$$\varepsilon = \frac{\Delta m_{st}}{\Delta m_s}, \qquad (1)$$

where Δm_{st}, Δm_s a loss of the mass of the standard and sample for same testing time.

An annealed carbon steel 45 (0,45 % C) was used as a standard specimen with hardness 160…180 HB.

In steels and hardened layer it is possible and necessary to reach metastable austenite of any structural and morphological modifications, both independent and combined with any structural components: martensite, carbides, nitrides, ferrite and their combinations. Phase-morphological types of metastable austenite in alloyed cast irons are examined in [9].

In order to develop metastability of austenite it is necessary to employ all known physical-chemical mechanisms and factors of stabilization (or destabilization factors) of austenite and regulation of the degree of its metastability [10]: chemical composition of austenite (across influence on points M_s and M_f) for example, rising carbon in surface layer owing to carburizing or lower carbon content by decarburizing.

1. Carburizing and quenching. Carburizing of Fe-Cr-Mn steels with temperature variation of subsequent quenching for regulation of the amount and degree of austenite metastability is one of the proposed options for realization of surface modification with application of metastable states.

Possessing various chromium content from 2 to 22 %, under the influence of which phase content changed, it embraced different structural classes: martensite (M), martensite-austenite (M-A), austenite-martensite (A-M), austenite (A), austenite-ferrite (A-F) and ferrite-austenite (F-A) (look table I). Steel 30Cr2Mn6Si2V belongs to M-A class. With increase in chromium content from 2 to 8 % in 30Cr(2…8)Mn6Si2V steels the temperature of martensite point M_s drops from 152 ºC to 18 ºC (M_f point is below the room temperature) and the steels pass from martensite-austenite into austenite structural class. Steel 08Cr14Mn6SiV (point M_s=122 ºC) is classified as belonging to martensite-austenite class. With the increase of chromium content from ~14 to 22 % in 08Cr(14…22)Mn6SiV steels martensite component disappears, but δ-ferrite appears, the content of which increases from 46 to 64 %, while austenite content dropping accordingly. (see Table 1).

After carburizing and heat treatment carbide phases were formed in the surface layer, with different composition, depending on chromium content in steel. In steels, containing 2…6 % of Cr, carbides of mainly cementite type were formed (Fe,Cr)$_3$C, while in steels, containing 8…22 % of Cr - special carbides of chromium were formed like (Fe,Cr)$_{23}$C$_6$ and (Fe,Cr)$_7$C$_3$,
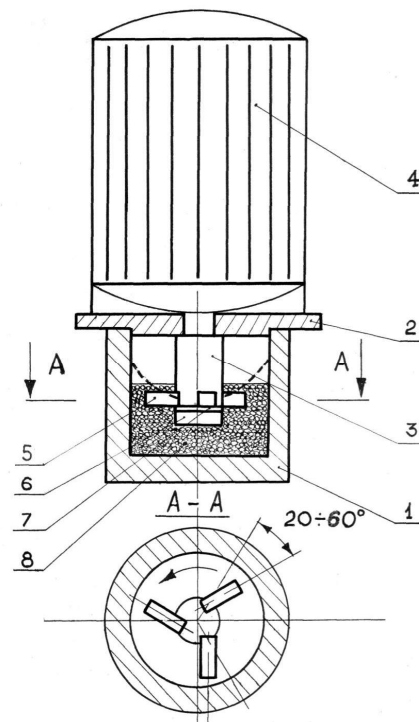

Fig. 2 – The scheme of wearing machine for impact abrasive wear: 1 – work's box; 2 – cover; 3 – shaft-holder; 4 – motor; 5 – samples (3 piece); 6 – pinching screw; 7 – washer; 8 – cast-iron shot

some vanadium carbides (VC) were also traced.

The correlation between the main phase components of steels' microstructure was regulated by heat temperature for quenching. Microstructure of steels 30Cr6Mn6Si2V and 20Cr14Mn7 after carburizing 1050 °C (12 h) and quenching at various temperature is represented in Fig. 3. At relatively low heat temperature for quenching (850 °C) the surface layer of specimens of 30Cr(2…8)Mn6Si2V presents a mixture of carbides, martensite and residual austenite, an increased value of micro-hardness of this mixture well corresponding to it 560…650 HV (Fig. 4). As the distance from the surface becomes bigger the structure of 30Cr6Mn6Si2V steels becomes big grain austenite (90…150 μm), micro-hardness reducing to 470…500 HV, then follows M-A structure with fine grain (15…35 μm), dispersed with vanadium (VC) and chromium (($Cr,Fe)_{23}C_6$) carbides.
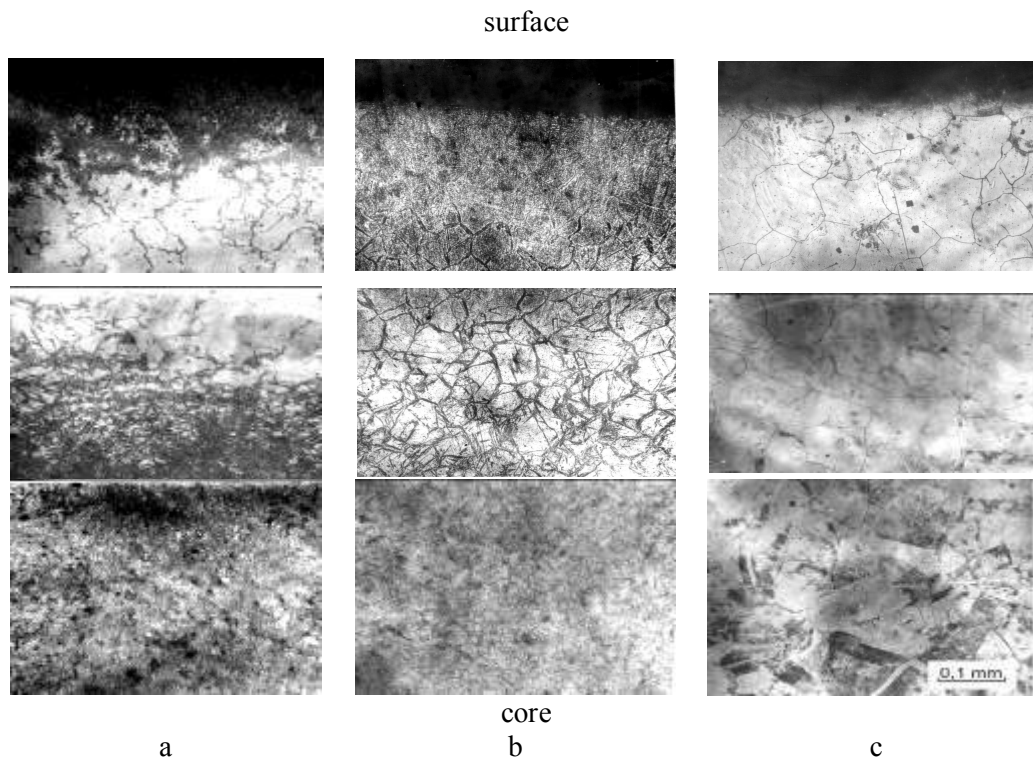
surface

core

a b c

Fig. 3 – Microstructure of steels 30Cr6Mn6Si2V (a) and 20Cr14Mn7 (b, c) after carburizing 1050 °C (12 h) and quenching at various temperature: a – 850 °C; b – 1050 °C; c – 1150 °C

As the temperature of heating for quenching of carburized steels 30Cr(2…8)Mn6Si2V is increased from 850 to 1150 °C carbide content is reduced due to their solution in austenite, while the amount of austenite is raised. Here, greater chromium content in steel, the bigger is the amount of austenite, formed in the surface layer, after quenching.

Microstructure of 20Cr14Mn7 grade is characterized by more developed carbide reticulation alongside grain boundaries, due to greater content of carbide forming chromium (see Fig. 3 b, c). In big grains of austenite of carburized layer after quenching at 850-1050 ºC temperatures formation of big-lamellar high-carbon martensite is observed. Its amount decreases alongside with increase of heating temperature, this is explained by reduction in M_s martensite point, due to solution of carbides and saturation of austenite with carbon. After quenching of carburized steel 20Cr14Mn7 with increased temperature 1150 ºC carbides $Cr_{23}C_6$ inside the surface layer completely dissolve in austenite. Along the layer's depth, gradually, austenite structure is transformed into austenite-martensite. As the result the character of changing of micro-hardness along th depth of carburized layer basically remains the same, its absolute values, however, decreasing.

With subsequent increase of chromium content 18…22 % in 08Cr (18…22)Mn6SiV steels micro-hardness of the surface layer is substantially higher (730…960 HV) than in steels with lesser

chromium content (see Fig. 4b). It may be explained by increased volume of carbide phases inside the carburized layer of specimens and also by limitation of carbon solubility in ferrite. Carbide phase content inside the surface layer in high chromium steels reached 30…40 % like in alloyed white cast irons [10, 11]. This leads to increased carbon content ~ 2,7 – 4,5 % and chromium over equilibrium level inside steels carburized layer. This can be explained by the effect of reactive diffusion and the mechanism of internal carburization [11].
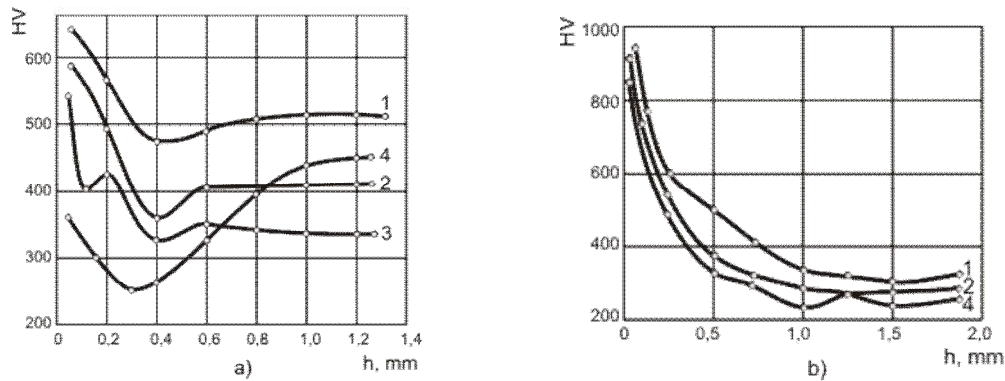

Fig. 4 – Changes in micro-hardness alongside depth of carburized layer of steels 30Cr6Mn6Si2V (a) and 08Cr18Mn6SiV (b), at heating temperatures for quenching: 1 – 850 °C; 2 – 950 °C; 3 – 1050 °C; 4 – 1150 °C

Microstructure of 20Cr14Mn7 and 08Cr22Mn6SiV steels after carburizing and quenching at 1150 ºC is shown in Fig. 5. A part of chromium carbides is dissolved in austenite, the remaining part, left not dissolved inside $(Cr,Fe,V,Mn)_7C_3$ are arranged as broken along the grain boundaries of austenite (see Fig. 5 a). In 08Cr22Mn6SiV steel of ferrite-austenite class a multitude of carbide particles of $(Cr,Fe)_{23}C_6$ content is likely to be observed, this testifying to the presence of carbon diffusion at carburising through the ferrite phase with formation of carbides, because the solubility of carbon in ferrite is low. Chromium, manganese, vanadium and silicon in phases of 08Cr22Mn6SiV steel are distributed unevenly and more ferrite forming elements – Cr, V, Si, are dissolved in ferrite grains, as compared to austenite, where there is greater content of ferrite-forming manganese (see Fig. 5 c, d).

The content of carbide particles of predominantly spherical shape, which are found in austenite grains reveals a complicated character on the basis of chromium carbide $(Cr,Fe,V,Mn)_xC_y$. Chromium content in it is ~64 %.

The character of fracture of carburized and quenched specimen of the investigated steels differs essentially. Fractograms of fractures are summarized in Fig. 6. In 30Cr2Mn6Si2V carburized steel of martensite-austenite class after quenching at 850 ºC the fracture in the core part has a mixed brittle-tough structure, the share of tough part being ~30 % (see Fig. 6 a).The structure of fracture of carburized layer is characterized by a great share of tough component ~ 50…55 % (Fig. 6 b), despite substantially greater carbon content. This is explained by greater content of more tough austenite inside the structure of the surface layer, as compared to the core, which favours the increase in impact strength of the specimen in general (KCU=13 J/sm^2). The fracture of the core part of 20Cr14Mn7 carburized steel of austenite-martensite class after quenching at 850 ºC possesses mainly tough cup-shaped structure (Fig. 6 d). The character of destruction of the carburized layer of this steel is entirely different – "quasi"-brittle with the multitude of small facets of the "quasi"-brittle chip. Though the signs of a substantial micro-plastic deformation are observed in them, thus showing the satisfactory impact strength (KCU=10J/sm^2). Such character of the broken carburized layer can be attributed to formation in the layer saturated with carbon of the multitude of chromium carbides (up to 35…38 %, like in high-chromium wear resistant cast irons).

Dependence of hardness and relative impact-abrasive wear resistance upon chromium content and heating temperature for quenching for two groups Fe-Cr-Mn steels from 2…8 % Cr and 14…22 % Cr are summarized in Fig 7 and 8. For carburized steels 30Cr(2…8)Mn6Si2V with increased chromium content at each heating temperature for quenching hardness increases (see Fig. 7a). It can be

explained by the fact that the influence hard-solution mechanism upon steel strengthening is raised. Generally, for each carburized steel hardness is reduced with the increase of heating temperature for quenching, owing to solution of chromium carbide in austenite, increase of austenite content and its stability.
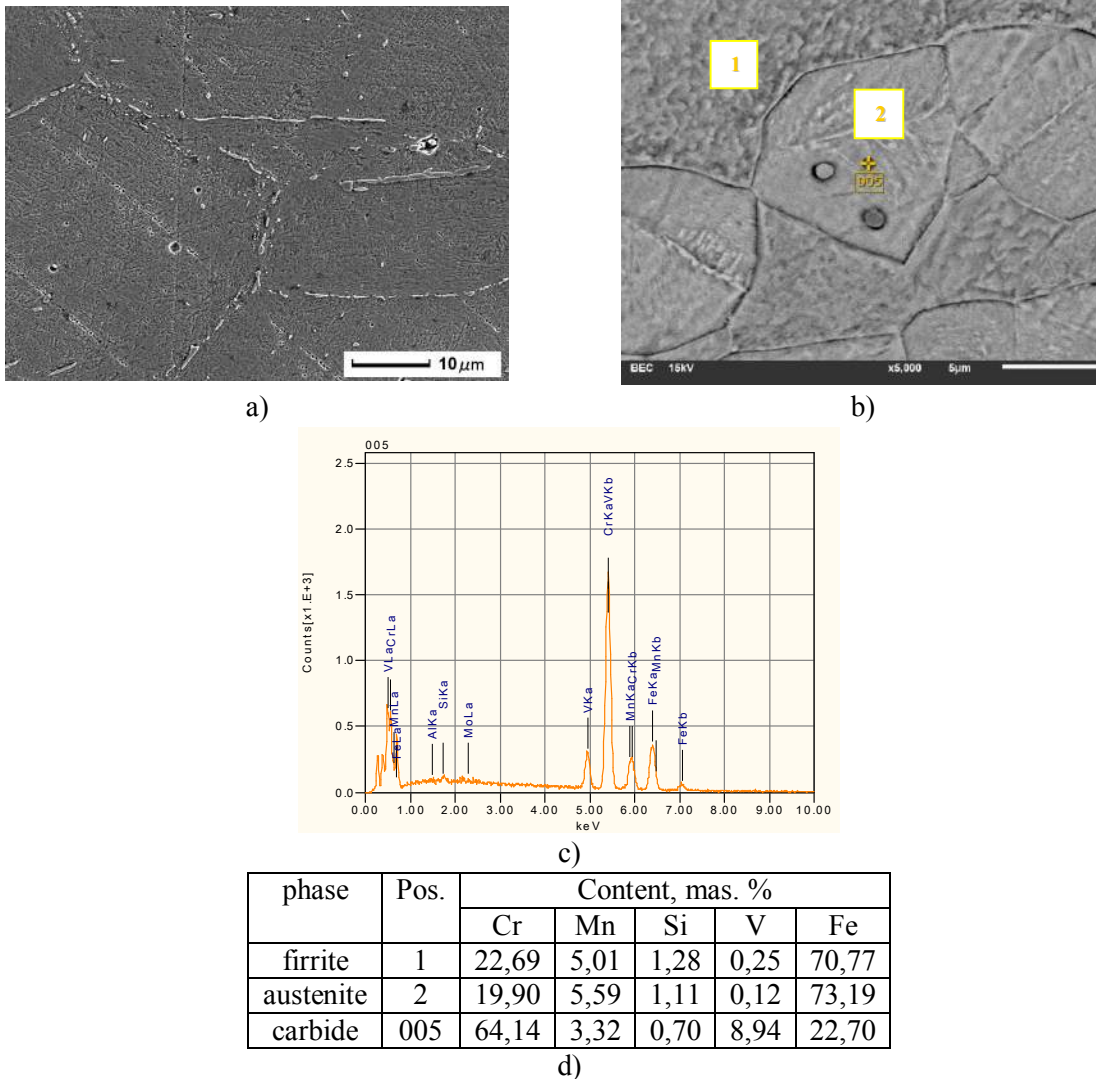

a)

b)

c)

phase	Pos.	Content, mas. %				
		Cr	Mn	Si	V	Fe
firrite	1	22,69	5,01	1,28	0,25	70,77
austenite	2	19,90	5,59	1,11	0,12	73,19
carbide	005	64,14	3,32	0,70	8,94	22,70

d)

Fig. 5 – Microstructure of steels, diffraction pattern and chemical composition of phases in steel 08Cr22Mn6SiV after carburizing and quenching at 1150 ºC: a) – 20Cr14Mn7 steel; b) – 08Cr22Mn6SiV steel; c) – diffraction pattern with carbide (pos. 005); d) – chemical composition of phases steel 08Cr22Mn6SiV

Relative impact-abrasive wear resistance (in cast iron shot media) ($\varepsilon_{i.a.}$) of the investigated steels does not show such clear dependence on chromium content and quenching temperature. Thus, for the highest value of hardness of 30Cr8Mn6Si2V steel, after quenching from 850 °C (49 HRC) corresponds relatively low wear resistance ($\varepsilon_{i.a.}$=3.8), whilst its highest value ($\varepsilon_{i.a.}$=6.4) is found after quenching from 1050 °C, the value of hardness being just 37 HRC.

Completely different picture of changes in properties under the influence of chromium and heat treatment is revealed for corrosion-resistant steels with increased chromium content (14…22 %). For each quenching temperature within 850…1150 °C range, as chromium content is raised from 14 to 22 % hardness of cemented steels drops (see Fig. 8), while for 30Cr(2…8)Mn6Si2V it was increased, the conditions of treatment being the same (see Fig. 7 a).

Unlike changes of hardness of carburized steels, as chromium content is raised and quenching temperature is increased, impact-abrasive resistance ($\varepsilon_{i.a.}$) is raised (see Fig. 8) Here, after quenching,

the highest value of wear resistance ($\varepsilon_{i.a.}$=5.2…5.5) corresponds to relatively low hardness (~20 HRC) of steel 08Cr22Mn6SiV of F-A class. It can be explained by an extremely important contribution of $\gamma\to\alpha'$ DIMT and dynamic deformation aging (DDA) into development of the process of self-strengthening at wear, resulting in improved wear resistance of carburized steels.
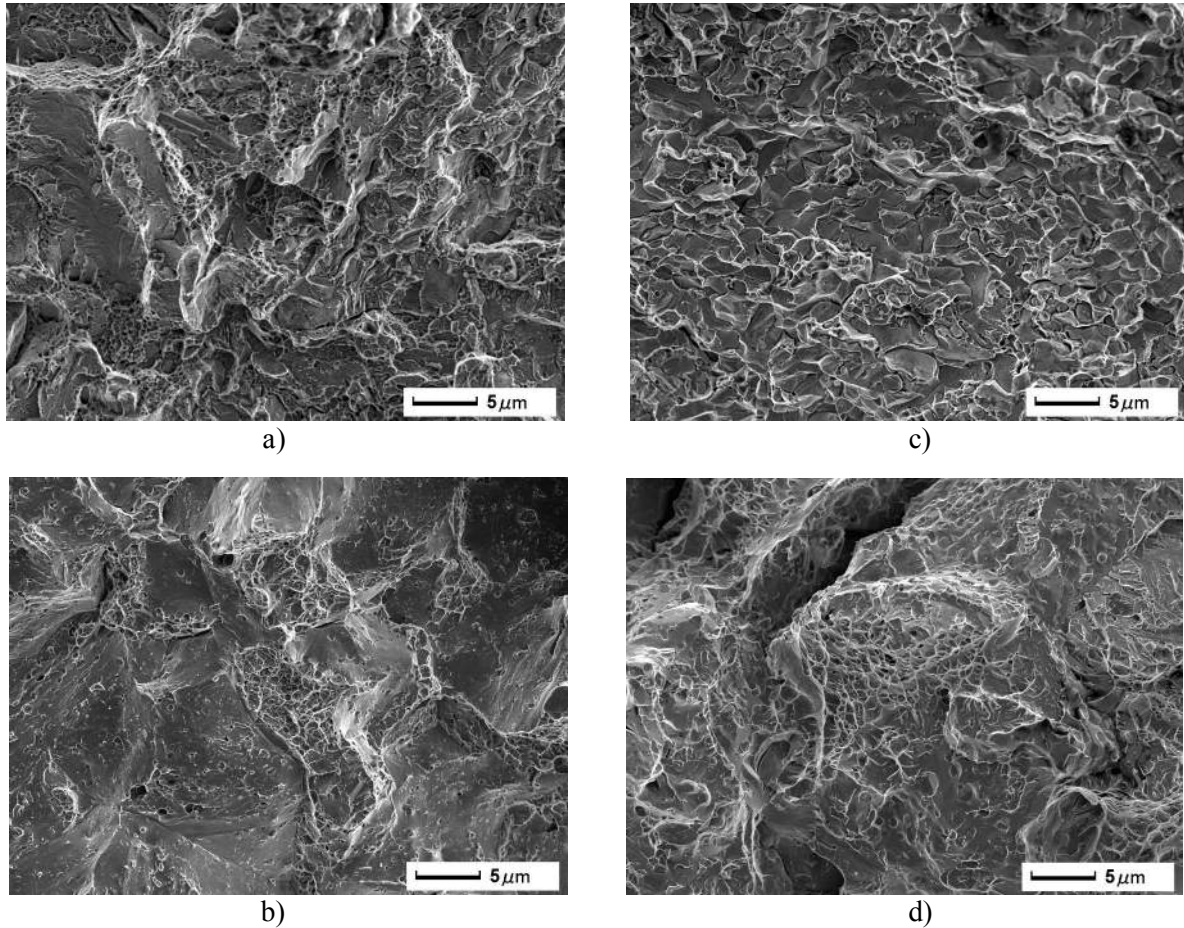

Fig. 6 – Fracture carburized steels after quenching at 850 ºC: a) – surface, b) – center of sample steel 30Cr2Mn6Si2V; c) – surface, d) – center of sample steel 20Cr14Mn7
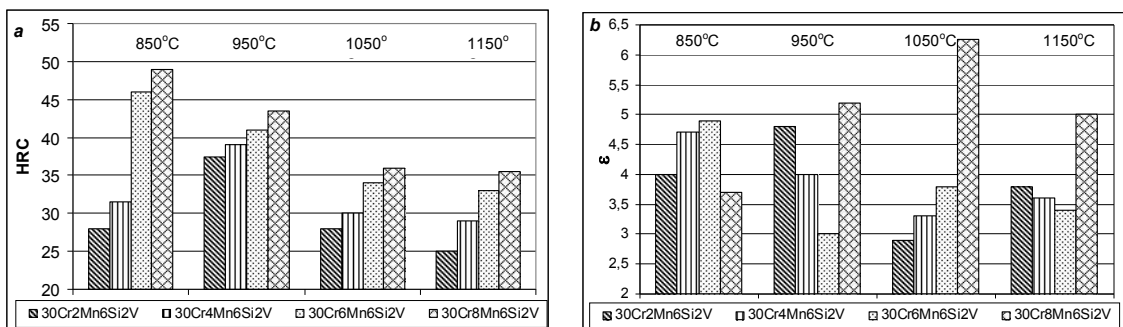
Fig.7 – Influence of chromium and heating temperature for quenching for hardness (a) and relative impact-abrasive wear resistance (b) carburized high strength steels 30Cr(2…8)Mn6Si2V

2. Decarburizing austenitization at quenching. The possibility of austenite destabilization for initiating $\gamma\to\varepsilon'$ and then $\gamma\to\alpha'$ DIMT can be realized inside the surface layer of parts, made, for example, of Hadfield steel, by application of high temperature decarburizing austenitization at quench-

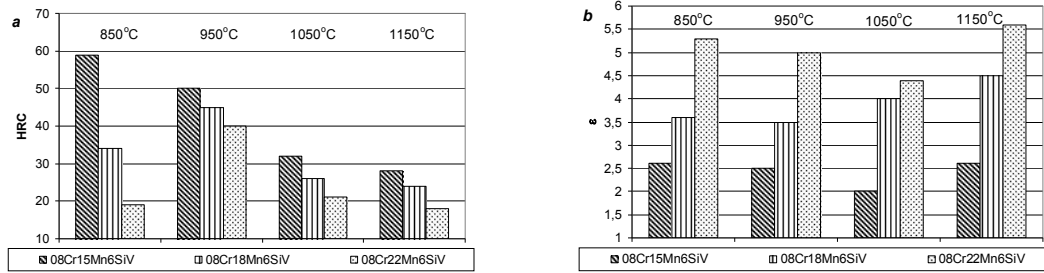ing. It should be noted that decarburization of alloys is not used for these purposes at present.

Fig. 8 – Influence of chromium and heating temperature for quenching for hardness (a) and relative impact-abrasive wear resistance (b) carburized corrosion resistant steels 08Cr(15…22)Mn6SiV

Such atmosphere acting upon metal (in fact, absence of parts protection from decarburization) causes reactions of chemical interaction between carbon and γ-solid solution on the samples surface, the leading of which, as the data of [10] testify is:

$$H_2O + C_{s.s.} \leftrightarrow CO + H_2 \tag{2}$$

Decrease in carbon concentration on the surface of the samples ($C_{s.s.}$ – carbon concentration in γ-solid solution) as the result of such reaction causes carbon diffusion in γ-solid solution from the core to the surface at certain depth. The average chemical composition of the surface of steel 110Mn13 samples, depending upon the time of decarburizing is summarized in Table 2.

Table 2

Content of carbon and manganese in surface layer steel 110Mn13
after decarburizing austenitization at 1150 °C with different holding

time, min.	Content elements, mass. %		
	C	Mn	Depth layer X, mm
10	1,26	11,9	< 0,1
30	0,58	11,45	0,7 – 0,9
60	0,43	11,20	1,1 – 1,3
90	0,38	11,40	1,4 – 1,6
120	0,34	11,45	1,8 – 2,3

As the interval of holding was raised at 1150 °C carbon content inside the surface layer was reduced from 1.26 to 0.34 %, while manganese content dropped but slightly by 0.45…0.70 %. The depth of decarburized layer (x) is raised.

The problem of carbon distribution along depth from (x) surface in time of decarburization (t) can be solved by means of the following equation:

$$C(X,t) = C_S + (C_o - C_S)erf\left(\frac{x}{2\sqrt{D\tau}}\right), \tag{3}$$

where C_o and C_s – are initial and the ultimate (on the surface) carbon concentration $erf\left(\frac{x}{2\sqrt{D\tau}}\right)$ – errors function from the value of $\left(\frac{x}{2\sqrt{D\tau}}\right)$ is determined by means of special tables; D – coefficient of carbon diffusion in γ-iron, could be determined for the applicable temperature of decarburizing austenitization with regard to mutual influence of alloying elements upon thermo dynamical activity of carbon [12].

The values of dependence of carbon distribution along the depth of decarburized steel layer 110Mn13 for different austenitization times are summarized in Fig. 9.

These dependencies allow to forecast formation of the phase content and the degree of austenite metastability inside the surface layer upon the time of decarburizing. Thus, after decarburizing for 30…60 minutes at 1150 °C, when carbon content in the surface layer decreases to 0,43…0,6 %, its structure remains largely austenite. Austenite, however, becomes deformation-metastable, capable of phase $\gamma \rightarrow \varepsilon'$ and $\gamma \rightarrow \varepsilon' \rightarrow \alpha'$ DIMT. Increase of holding time at 1150 °C up to 90…120 min. with carbon content decrease to 0,38…0,34 %, promotes formation of ε- and α-quenching martensite in the surface layer.
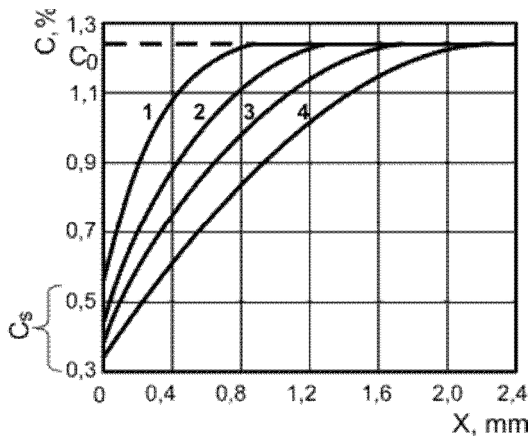

Fig. 9 – Dependences of carbon concentration upon the surface distance for different times of decarburizing austenitization of 110Mn13 steel (Hadfield steel), at 1150 °C (min.): 1 – 30; 2 – 60; 3 – 90; 4 – 120

Microstructure[5] along depth of the decarburized layer of 110Mn13 steel is pictured in Fig. 10. Signs of ε- and α-martensite and metastable austenite can be observed in the microstructure of decarburized layer of 110Mn13 steel. Microstructure of ε–martensite is characterized by the system of straight sliding lines, crossing at the angle ~60 °, whilst α-martensite possesses lath (package) structure. The greater is the time of decarburization, the greater is the depth of martensite zone, it could be explained by reduction of carbon content and elevation of M_s point above the room temperature. It can't be excluded that after a series of short holdings, lasting for 15…30 min. formation of the surface deformation martensite is possible already in the process of microfliff preparation. After extended holdings (90…120 мин.) quenching martensite at cooling from 1150 °C to the room temperature is most likely to have been formed.

Micro-hardness distribution, shown in Fig. 11 witnesses such character of changes in microstructure along depth of the decarburized layer. Macro-hardness has the biggest values – HV420…450, near the surface of the decarburized layer, which corresponds to the structure of ε- and α-martensite. Along the depth of the layer it is reduced to HV230…300, which corresponds to transition into austenite structure. The bigger is holding time at 1150 ºC, then micro-hardness is reduced at a bigger depth, at holding time 30…60 min. at depth 0,2…0,3 mm., while at holding time equal to 120 min. – at depth 2,4 mm. Combining of this dependence with phase diagram of Fe-Mn steels with 12 % Mn, represented in [13], allows to predict formation of phase composition and the degree of metastability of phases inside the surface layer against the time of decarburization. As the holding time and consequently the degree of decarburization at 1150°C is increased, hardness of 110Mn13 steel is slightly decreased at the beginning (Fig. 12), owing to the drop in austenite strength, but then it is raised, due to its destabilization and capability of strengthening by means of DIMT. Impact energy of steel is reduced here, it may be explained by growth of austenite grains and also by formation of some amount of ε´- and α´- phases at quenching. Relative wear resistance under conditions of dry sliding friction of metal against metal (ε_f) after decarburization is changed in the view of a curved line with two peaks (Fig. 13). The first peak corresponds to the holding time 10 minutes, when decarburization is still relatively small is explained by the classical mechanism of strengthening of steels of 110Mn13 grade, due to twinning process, formation of packing defects and dislocations. The second one, bigger in value ε_f at holding time equal to 90 min, when there are about 0,4 % of carbon in the surface layer and austenite is quite unstable is explained by dynamic twinning and realization of strengthening mechanisms $\gamma \rightarrow \varepsilon´$ or $\gamma \rightarrow \alpha´$ DIMT at optimal kinetics. Decrease in ε_f after 120 minutes of holding can be explained by formation of some amount of ε´- and α´- martensite of quenching and excess depletion of austenite by carbon, lessening the effect of self-strengthening.

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[5] *In the research take part Yu. Kutsomelya*
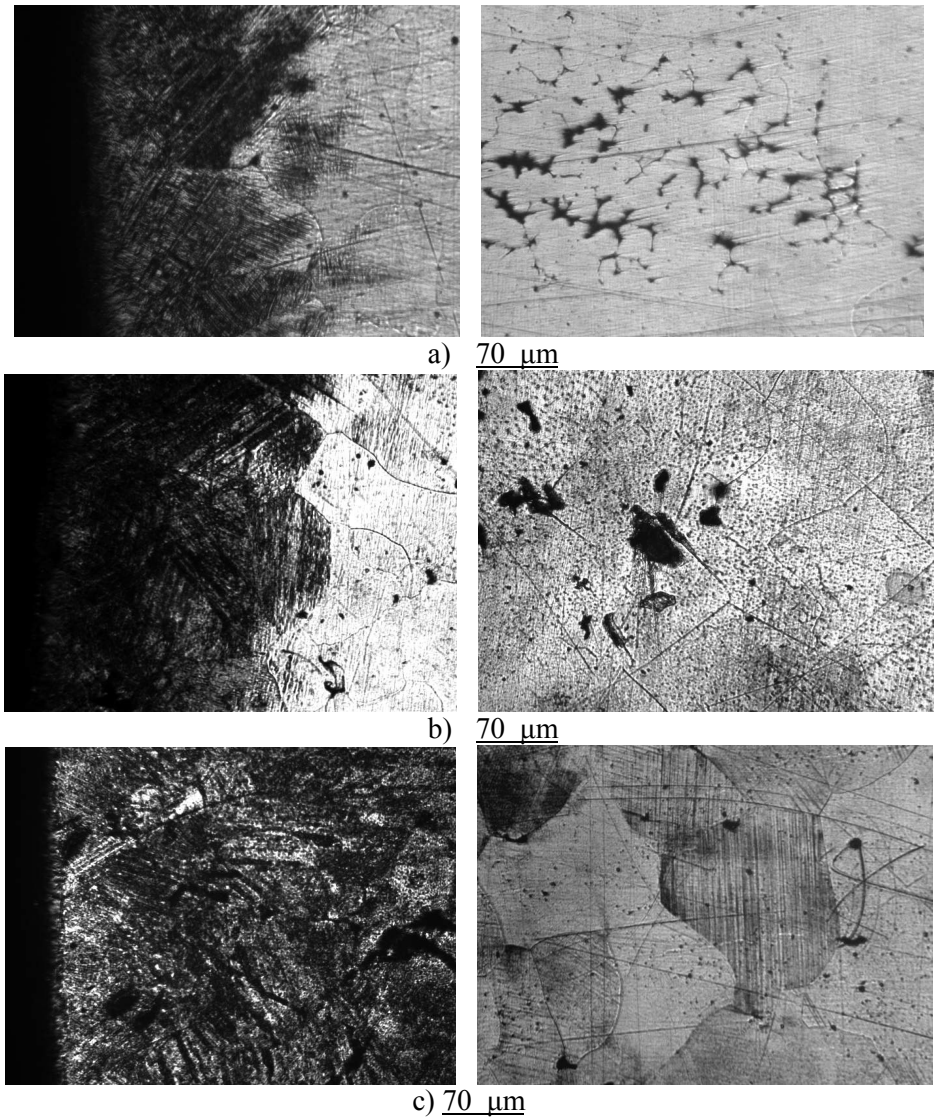
a) <u>70 μm</u>

b) <u>70 μm</u>

c) <u>70 μm</u>

Fig. 10 – Microstructure of 110Mn13 steel after quenching with decarburizing austeniza-tion at 1150 ºC with different holding time: a) – 30 min.; b) – 60 min.; c) – 120 min. To the left – the surface layer to the right – the core of the specimen
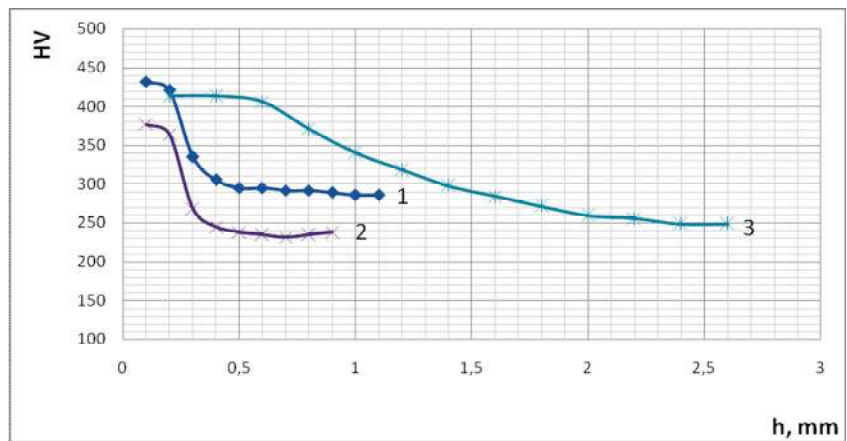

Fig. 11 – Influence of the time of holding at decarburizing austenization 1150 ºC upon changes in micro-hardness along the depth of decarburized layer of 110Mn13 steel: 1 – 30 min.; 2 – 60 min.; 3 – 120 min.
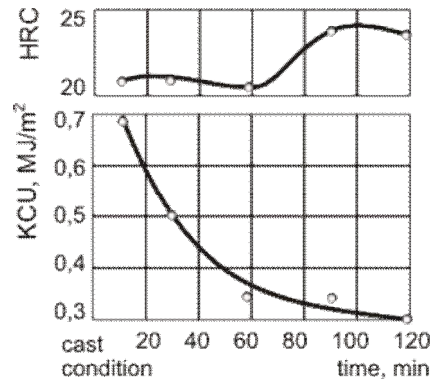
Fig. 12 – Influence of time of decarburizing austenitization at 1150 °C upon mechanical properties of 110Mn13 steel (Hadfield steel)
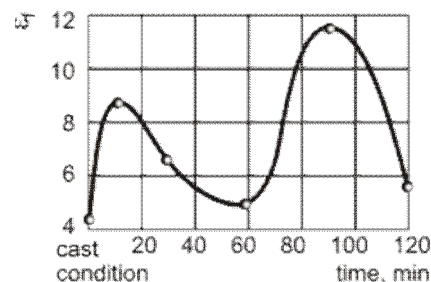

Fig. 13 – Influence of time of decarburizing austenitization at 1150 ºC upon relative wear resistant of friction sliding metal by metal of 110Mn13 steel (Hadfield steel)

Conclusions

1. Application of carburizing of chromium-manganese steels with various chromium content from 2 to 22 % and subsequent quenching from different temperatures allows to regulate within wide range phase content and microstructure as well as create various metastable-austenite phase-structure modifications of surface layers and control their properties efficiently.

2. With increase of chromium content in chromium-manganese steel grades $(08…30)X(2…22)\Gamma 6Si(1…2)V$ from ~ 2 % to ~ 14…22 % micro-hardness of the surface (Austenite-carbide) zone increases constantly up to 860…970 HV, the amount of chromium carbides ($Cr_{23}C_6$ and Cr_7C_{23}) reaches 32…40 % as the result of reactive (uprising) diffusion of chromium.

3. The highest value of impact-abrasive wear resistance is reached in steels from 6…8 % Cr after carburizing and quenching from relatively not high temperatures 850-1050 ºC, and in steels with 18…22 % Cr after carburizing and quenching at increased temperatures 1150 ºC and when austenite–carbide structure of the surface area of the carburized layer underwent $\gamma \to \alpha'$ DIMT and DDA.

4. Increased impact-abrasive wear resistance of Fe-Cr-Mn steels after carburizing and quenching is explained by high content of carbides, transformation of metastable austenite into martensite with formation of high-dispersed carbides, causing the effect of deformation self-strengthening during the process of wear.

5. The method of surface strengthening with application of proposed by us decarburizing austenitization at quenching ensures substantial increase of wear resistance of 110Mn13 steel, due to realization of deformation induced $\gamma \to \varepsilon'$ and $\gamma \to \varepsilon' \to \alpha'$ martensite transformations mechanism inside the surface layer at the process of wear.

6. As time of holding is increased from 10 to 120 min. at increased temperatures (1150 ºC) carbon content is decreased, due to decarburization in the oxidizing atmosphere of the surface layer of 110Mn steel. This causes destabilization of austenite, the degree of which depends upon the depth of decarburization in accordance with the law of carbon content distribution.

7. Both methods – carburizing and quenching treatment, as well as decarburizing treatment on high Mn-steels are quite effective and seem to be an economical way of getting high wear resistant steels, using standard commercial steels.

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© Дан Л.А.[1], Олейник И.М.[2], Трофимова Л.А.[3], Дан Е.Л.[4]

СВОЙСТВА ЗАЩИТНЫХ ПОКРЫТИЙ НА ОСНОВЕ ОТХОДОВ ПЕНОПОЛИСТИРОЛА

Исследованы пленкообразующие материалы на основе растворов пенополистирола в скипидаре. Показано, что 30% раствор обеспечивает наилучшее сочетание свойств и может быть предложен в качестве основы для приготовления защитных красок и покрытий.
Ключевые слова: *пенополистирол, скипидар, пленка, защитное покрытие.*

Дан Л.О., Олійник І.М., Трофімова Л.О., Дан О.Л. Властивості захисних покриттів на основі розчинів пінополістиролу. *Досліджені плівкоутворюючі матеріали на основі розчинів пінополістиролу у скипидарі. Показано, що 30% розчин за-*

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[1] канд. техн. наук, доцент, ГВУЗ «Приазовский государственный технический университет», г. Мариуполь
[2] канд. техн. наук, доцент, ГВУЗ «Приазовский государственный технический университет», г. Мариуполь
[3] канд. техн. наук, доцент, ГВУЗ «Приазовский государственный технический университет», г. Мариуполь
[4] студент, ГВУЗ «Приазовский государственный технический университет», г. Мариуполь