

ADVANCES IN ELECTROMETALLURGY

1, 2007

Quarterly

English translation of the quarterly «Sovremennaya Elektrometallurgiya» journal published in Russian since January 1985

Founders: E.O. Paton Electric Welding Institute of the NASU
International Association «Welding»

Publisher: International Association «Welding»

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Subscriptions:

4 issue per year;

184\$ — regular, **150\$** — for subscription

agencies, **100\$** — for students;

postage and packaging included.

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NEW TECHNOLOGICAL PROCESS OF PRODUCING SUPER-LARGE STEEL INGOTS BY ESC LM METHOD*

B.E. PATON, L.B. MEDOVAR, V.Ya. SAENKO, A.K. TSYKULENKO, B.B. FEDOROVSKY and V.I. US

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Some possibilities of the new technological process of producing super-large steel ingots using ESC LM method, developed at the E.O. Paton Electric Welding Institute and based on application of single or sequential multiple circumferential electroslag cladding of metal layer of preset composition on a central axial ingot or a forging of similar chemical composition and ensuring satisfactory homogeneous structure in the as-clad ingot, were considered. Main geometric parameters of round ingots of 100 t mass, clad with application of ESC process on the basis of 20 t ESR furnace, depending upon diameter of initial central ingot, were determined. Experimental investigations of model ESC ingots of 170 mm diameter, made from high-alloyed steel of 316L type, which confirmed their high homogeneity and good prospects of new process of enlargement of the section and mass of steel ingots, were carried out.

Keywords: *electroslag remelting, round large-tonnage steel ESR ingots, high-alloyed steels and alloys, spotted segregation, enlargement of ESR ingots, electroslag remelting according to double-circuit power supply scheme, electroslag cladding by liquid metal, multiple circumferential electroslag cladding*

As metallurgical machinery develops and requirements to the power-plant engineering get more stringent, production of large-tonnage ingots from high-alloyed steels and alloys changes and gets new impetus. Different methods of remelting are used for production of the ingots, which include both double vacuum-induction remelting (VIR) + electroslag remelting (ESR) or VIR + vacuum-arc remelting (VAR) and triple VIR + ESR + VAR conversions that is connected with the problem of the spotty segregation

formation as mass and section of the ingots, melted from state-of-the-art high-alloyed steels and alloys, increases [1].

In order to ensure solution of this problem it is necessary to constantly improve technologies of special electrometallurgy, in particular to develop new technological ESR processes for big ingots, made from high-alloyed steels and alloys, inclined to spotty segregation.

Presented in work [2] microstructures of longitudinal sections of big and small ESR ingots (Figure 1) show that the big ingot has a double-zone structure — peripheral area of columnar crystals and central area of equiaxial crystals, while macrostructure of the small ingot completely consists of the columnar crystallites, characterized by a finer structure in comparison with that of the big ingot. For the big ESR ingot, which has a significant section, characteristic are a deeper pool and a higher volume of the molten metal, solidified at each instant of the process of its cladding over the height, in comparison with the ESR ingot of much smaller section. This stipulates more coarse-grained macrostructure of big ingots and creates favorable conditions for development of segregation processes in them.

Developed in PWI new technological double-circuit scheme of electroslag remelting (ESR DS) [3–5] differs from the canonical ESR scheme by the fact that in it does not exist rigid connection between productivity of the process and temperature conditions of the melt, character of heat removal into central part of the ingot, and heat abstraction over its periphery. Application of the ESR DS significantly expands capacity for controlling profile, depth of the molten metal pool and length of the double-phase zone during solidification of the ingots in order to

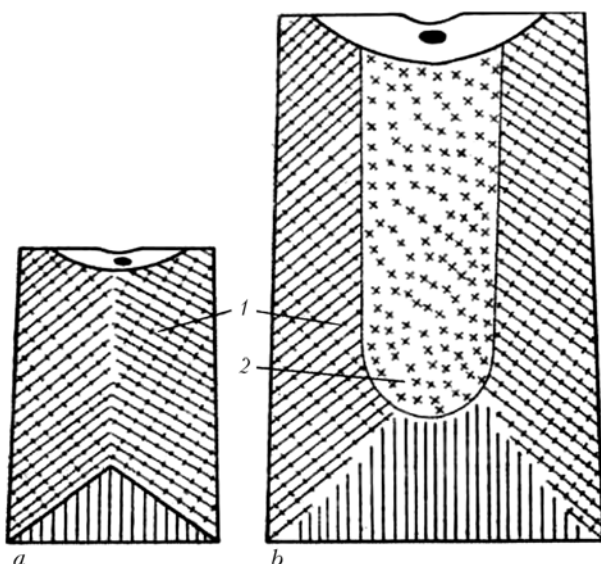


Figure 1. Structural zones of electroslag ingots of small (a) and big (b) section: 1 — columnar; 2 — equiaxial crystals

*In the work also participated employees of PWI Engs. N.T. Shevchenko, V.L. Petrenko, V.V. Zhukov, V.M. Zhuravel, V.A. Zajtsev, R.V. Kozin, A.A. Polishko, A.G. Remizov, and V.M. Yarosh.

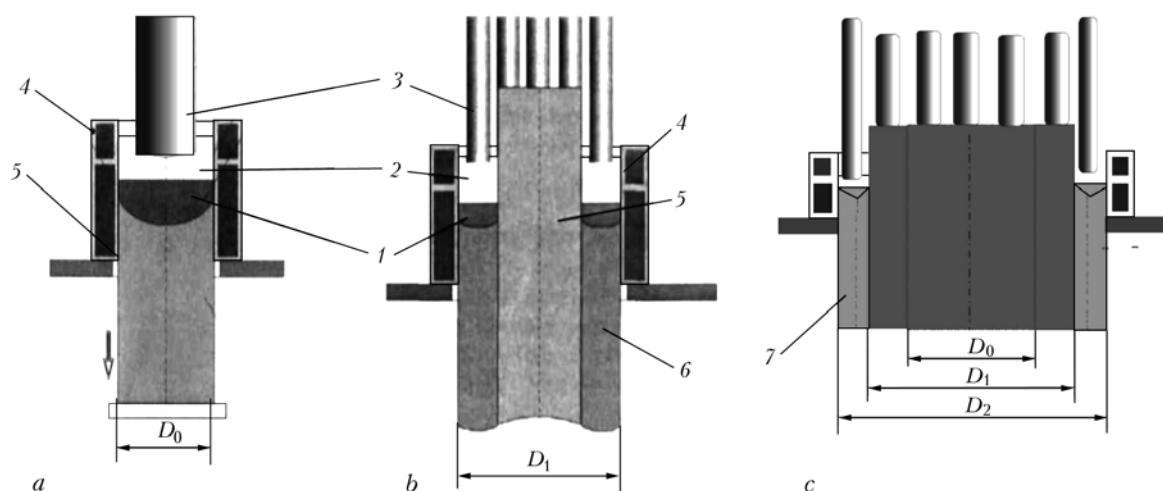


Figure 2. Scheme of round ingot enlargement according to ESC technological scheme with application of consumable electrodes: *a* — melting of initial ingot; *b* — single ESC; *c* — double ESC; 1 — metal pool; 2 — slag pool; 3 — consumable electrodes; 4 — current-conducting mould; 5 — ingot; 6, 7 — metal layers after single and double cladding, respectively

prevent development of undesirable segregation processes in them [3–5]. Nevertheless practical implementation of ESR DS is possible only provided consumable electrodes are used.

Great possibilities in solution of the problem of producing big forging-grade ingots for forgings of rotors and discs of powerful state-of-the-art steam and gas turbines from high-alloyed steels and alloys provides developed in PWI new technological process of electroslag cladding for enlargement of the ingots (ESCe) [6], based on application of a single or a multiple sequential circumferential electroslag cladding of the metal layer of preset composition on the central axial ingot or a forging of similar chemical composition (Figure 2) and ensuring of satisfactory homogeneous structure in the as-clad ingot.

When the ESCe process is used, the metal pool has a minimal volume, and the double-phase zone of liquid-solid state has a minimal length, which allows avoiding formation of defects of segregation character in the clad layer. The ESCe process may be used for producing both super-large homogeneous and heterogeneous ingots and forgings from different steels and alloys [7].

For high-alloyed steels and alloys, inclined to segregation, thickness of a clad layer is determined, on one hand, by technical possibilities of existing equipment for ESR and, on the other hand, by critical size of circumferential section of the metal cladding layer, in case of exceeding of which undesirable segregation processes develop in the metal. That's why if it is necessary to increase a section and a mass of big ingots

Thickness of clad layers of metal in multiple enlargement by ESC LM method of round steel ingots of up to 100 t mass

Initial diameter of ingot D_0 , mm	Height of initial ingot, mm	Diameter of ingot after first cladding D_1 , mm	Thickness of clad layer after first cladding Δ_1 , mm	Diameter of ingot after second cladding D_2 , mm	Thickness of clad layer after second cladding Δ_2 , mm	Diameter of ingot after third cladding D_3 , mm	Thickness of clad layer after third cladding Δ_3 , mm	Diameter of ingot after fourth cladding D_4 , mm	Thickness of clad layer after fourth cladding Δ_4 , mm
600	9000	846.0	123.0	1039	96.5	1200	80.5	1342	71.0
650	7680	916.5	133.0	1126	105.0	1300	87.0	1451	75.5
700	6600	987.0	143.5	1212	112.5	1400	94.0	1565	82.5
750	5800	1058.0	154.0	1300	121.0	1500	100.0	1674	87.0
800	5000	1131.0	165.5	1385	127.0	1600	107.5	1789	94.5
850	4500	1198.5	174.0	1472	137.0	1700	114.0	1900	100.0
900	4000	1269.0	184.5	1559	145.0	1800	120.5	2012	106.5
950	3600	1340.0	195.0	1645	152.5	1900	124.5	2120	110.0
1000	3250	1414.0	207.0	1732	159.0	2000	134.0	2236	118.0
1050	3000	1480.5	215.0	1819	169.0	2100	140.5	2348	124.0
1100	2680	1551.0	225.5	1905	177.0	2200	147.5	2460	130.0
1150	2450	1622.0	236.0	1992	185.0	2300	154.0	2571	135.5
1200	2260	1697.0	248.0	2078	190.5	2400	161.0	2683	141.5
1250	2000	1763.0	256.0	2165	201.0	2500	167.5	2795	147.5

Notes. 1. Designations D_0 , D_1 , D_3 , D_4 and Δ_1 , Δ_2 , Δ_3 , Δ_4 , given in the Table, correspond to designations, given in Figure 3. 2. Mass of clad metal of each layer is the same for all diameters and equals to the mass of initial ingot (20 t).

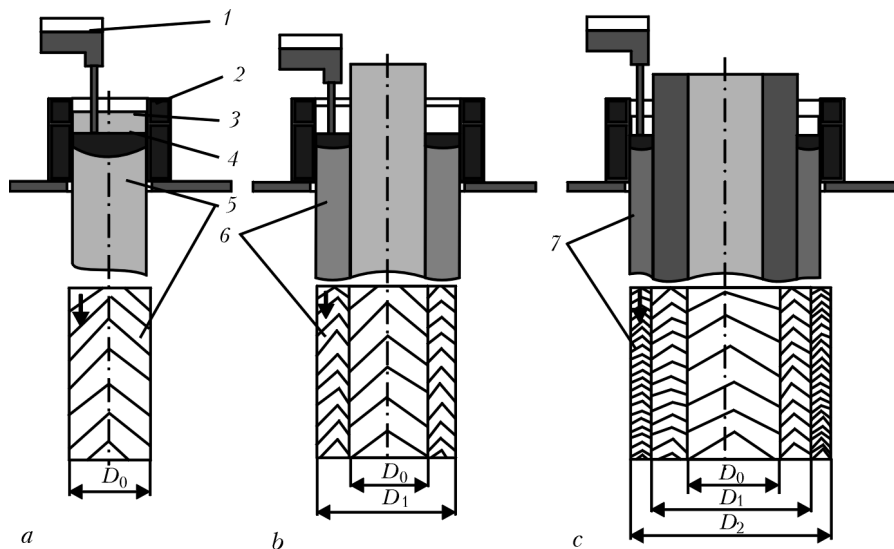


Figure 3. Scheme of round ingot enlargement according to ESCe technological scheme with application of LM (upper row), and schematic view of longitudinal section structure of initial ingot (lower row) (a) after single (b) and double electroslag cladding (c): 1 — pouring device for feeding LM into mould; 2 — current-conducting mould; 3 — slag pool; 4 — metal pool; 5 — central ingot; 6, 7 — metal layers after single and double cladding, respectively

from mentioned materials on the basis of the ESCe process, one should first of all estimate technical possibilities of existing electroslag equipment.

We have carried out calculation (Table) of necessary thickness of the metal layers to be applied by means of multiple sequential circumferential electroslag cladding on initial ingots of different diameters (600–1250 mm), but of the same mass (20 t), for the purpose of producing enlarged ESR ingots of up to 100 t mass by using 20-ton standard ESR furnace, for example EShP-20VG-I2, by which electric furnace shop of MW «Azovstal» is equipped, or a 20-ton furnace of USh-100 type [8]. For the purpose of using main equipment of the 20-ton ESR furnace it was assumed that mass of the clad metal of each layer had to be the same for all diameters and be equal to the mass of the initial ingot (20 t). For fulfillment of the latter condition we proceeded in our calculations from identity of cross-section areas of 20-ton initial ingots of respective diameters and areas of circumferential cross-sections of each clad layer. It allowed using for multiple sequential circumferential cladding of the

layers the same electrical power, not exceeding that of the standard 20-ton ESR furnace.

Analysis of the calculated data (see the Table) showed that while for initial ingots of 600–1250 mm diameter thickness of the circumferential clad layer after first cladding constituted 123–256 mm, after the forth cladding, in which 100-ton ingot was produced, it reduced down to 71.0–147.5 mm.

As far as thickness of the clad layer is determined by size of annular gap between the central ingot surface and forming surface of the ESR mould, cladding of the metal in such small interspace with application of consumable electrodes is possible only according to the ESR scheme, in which counter movement of the as-clad ingot and a short mould with expanded upper (slag) extension is performed.

ESC by liquid metal (ESC LM) in combination with consumable (or non-consumable) electrode, or without the latter, may be used for ESCe (provided a current-conducting mould is used, for which extended upper extension is not needed).

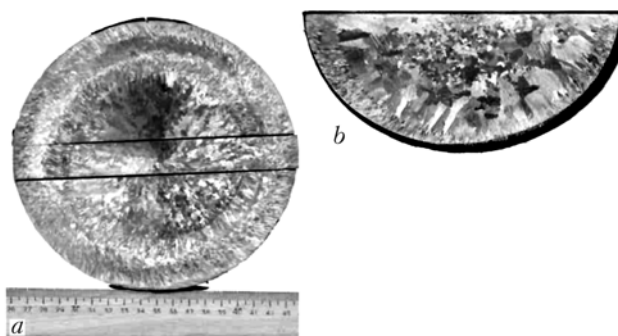


Figure 4. Macrostructure of cross section of ESR ingot from high-alloyed steel of 316L type of 170 mm diameter: a — model ingot produced as a result of single cladding according to ESCe technological scheme (Figure 3, b); b — control ingot of the same diameter produced according to standard technological scheme (Figure 3, a)

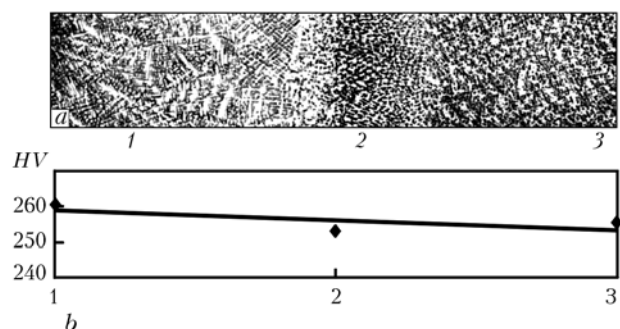


Figure 5. Microstructure (a) and microhardness HV (b) of fusion zone of model ESR ingot of 170 mm diameter from high-alloyed steel of 316L type produced according to ESCe technological scheme (Figure 3, b): 1 — clad layer; 2 — fusion zone; 3 — central ingot (×50)



For implementation of ESC LM it is necessary to additionally equip standard 20-ton ESR furnace with a special unit for producing LM of the required chemical composition and a device for regulated pouring of the latter into the current-conducting mould (Figure 3).

One more problem exists, which has to be solved for implementation of the ESCe process on the 20-ton ESR furnace, in particular, respective strengthening of the mechanisms for installation and holding of the central ingot in the process of multiple cladding, when diameter and mass of the latter gradually increase and achieve limit dimensions (diameter — 2795 mm, mass — 100 t).

It should be also noted that the central ingot plays in sequential ESC of each layer role of the macro-cooler, which exerts positive influence on the shape of the metal pool and structure of the clad metal. As diameter of the central ingot increases with each clad layer, this influence gets more significant.

In Figure 4 fragments of the cross-section macro-structure of the model ingots from high-alloyed steel of 316L type of 170 mm diameter are presented, produced according to the technological scheme (Figure 3, a) and as a result of a single cladding according to the ESCe technological scheme (Figure 3, b). The ESR ingot of 110 mm diameter, made from the same initial metal, was selected as the central ingot for ESC LM.

Macrostructure of the ESCe model ingot is characterized by clear presence of the boundary between cast metal of the central ingot and the clad layer. Thickness of the clad layer in cross-section of the model ESCe ingot is practically equal, whereby its structure is characterized by greater fineness, especially metal of the clad layer, in comparison with the control ingot of similar diameter, but produced according to standard technology. Macro- and microanalysis (Figure 5) did not detect any defects (cracks, slag inclusions, flaking, etc.) in the boundary zone. Investigation of distribution of alloying elements (chromium, nickel, molybdenum) and microhardness level in the boundary zone (Figure 6) also prove high homogeneity of the model ESCe ingot metal from high-alloyed steel of 316L type of 170 mm diameter.

CONCLUSIONS

1. Numerical calculations showed principal possibility of producing round steel ingots of up to 100 t mass on the basis of the 20-ton ESR furnace.

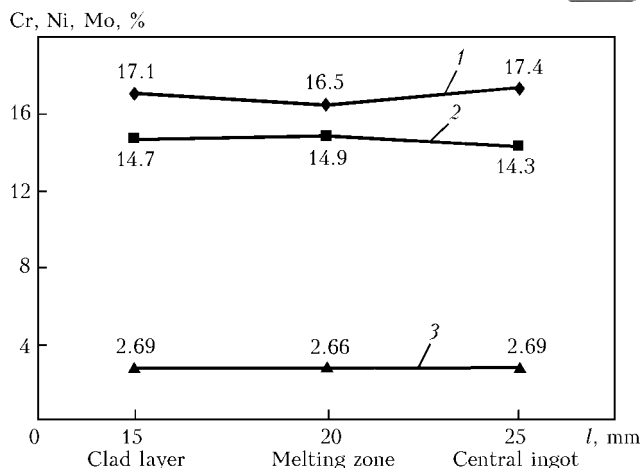


Figure 6. Distribution of chromium (1), nickel (2) and molybdenum (3) in fusion zone of ESR model ingot of 170 mm diameter from high-alloyed steel of 316L type produced according to ESCe technological scheme (Figure 3, b): *l* — length of fusion zone of layers in ESR model ingot

2. Main geometric parameters of the ingots, clad with application of the ESCe process, depending upon diameter of the initial central ingot are determined.

3. Carried out experimental investigations on the ESCe model ingots of 170 mm diameter from high-alloyed steel of 316L type confirmed high level of homogeneity of the ESCe ingots, which proves good prospects of using new ESCe process for solving problems of increasing cross-section and mass of big ingots from high-alloyed steels and alloys, inclined to spotty segregation, on the basis, as one of the options, of state-of-the-art 20-ton ESR furnaces.

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INVESTIGATION OF A NUMBER OF REGULARITIES OF ELECTRON BEAM EVAPORATION AND CONDENSATION OF CARBON

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Regularities of carbon evaporation and condensation in its electron beam evaporation through the tungsten melt are investigated, which allows significant increasing rate of carbon evaporation. Dependencies of the carbon evaporation rate and tungsten impurity content in the condensate upon heating power and angle of vapor flow incidence are obtained.

Key words: electron beam evaporation, tungsten melt, carbon evaporation and condensation, rate of carbon evaporation, content of tungsten impurity, heating power, angle of vapor flow incidence

Rather wide use of electron beam evaporation and deposition of substances in vacuum is stipulated, first of all, by high productivity of these processes [1]. Corrosion-, heat-resistant and heat-shielding coatings on components of turbine engines are examples of practical application of electron beam technology.

In recent time attention of the researchers to carbon-base condensed materials and coatings has significantly increased. However, methods of direct evaporation are connected with certain difficulties. In electron beam heating of graphite surfaces intensive outburst of the tiny flakes occurs, which makes impossible production of quality coatings [2]. This is stipulated by sublimation of carbon without formation of a molten pool.

Significant increase of the rate of electron beam evaporation of carbon and production of a homogeneous vapor flow of material may be achieved by change of the evaporation conditions. This is achieved due to carbon evaporation from the liquid phase, for example from the melt. Such process is performed after placement on the graphite surface being evaporated of a molten pool, consisting of a substance with a lower than in carbon vapor pressure (for example, tungsten or rhenium) [2]. Due to difference of the

vapor pressure values mainly carbon evaporates from the pool.

A shortcoming of mentioned method for production of carbon-containing materials is presence in the condensate of small amounts of the refractory metal. Weight share of tungsten in the condensate in case of carbon evaporation through the tungsten melt may constitute from 2.5 to, approximately, 10 % [2].

The goal of this work consists in investigation of certain regularities of carbon evaporation and condensation in its electron beam evaporation from the pool of molten tungsten.

The experiments were carried out on electron beam installation UE-150. Internal diameter of the crucible was 50 mm. Distance from the melt surface to the substrates was 250 mm. Vacuum in the work chamber was $1.33 \cdot 10^{-2}$ Pa. The rod being evaporated, having diameter 48.5 mm and height 200 mm, was made of fine-grain graphite of the MG-1 grade. On consumable end of the graphite rod a washer, made of the VCh-grade tungsten, having diameter 48.5 mm and mass 125 g, was placed. Vapor flow of carbon according to two diagrams was investigated (Figure 1). Steel strip, bent over 250 mm radius and having width 100 mm, on which discrete substrates from the stainless steel net and narrow strips from sheet metal for collection of condensate were fixed, was used as substrates according to the scheme shown in Figure 1, a, and according to the scheme shown in Figure 1, b,

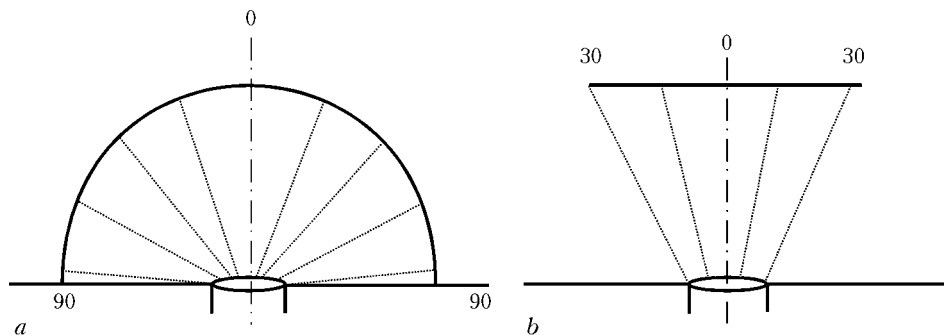


Figure 1. Scheme of electron beam evaporation and condensation of carbon in investigation of vapor flow within angle ranges of its incidence of 180° (a) and 60° (b)

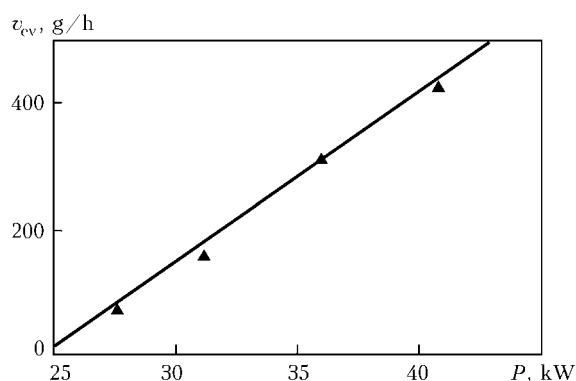


Figure 2. Dependence of graphite evaporation rate v_{ev} upon power P of tungsten melt heating

plates, made of molybdenum, having size $250 \times 250 \times 1$ mm, were used as substrates.

Graphite evaporation was performed at various values of the electron beam power within the range 27–42 kW at fixed value of accelerating voltage, which equaled 24 kV. According to scheme in Figure 1, *a*, current of the beam equaled 1.15 and 1.50 A, according to scheme in Figure 1, *b* — 1.15, 1.30, 1.50 and 1.70 A. Mass of the tungsten shot was maintained at the constant level.

In Figure 2 dependence of the graphite evaporation rate upon heating power of the tungsten melt pool is shown. The graphite evaporation rate was determined proceeding from difference of the graphite rod mass before and after evaporation and duration of the process. After cooling the tungsten shot easily separated from the rod for checking its mass.

Investigation of dependence of the tungsten content in the carbon condensate upon power of heating

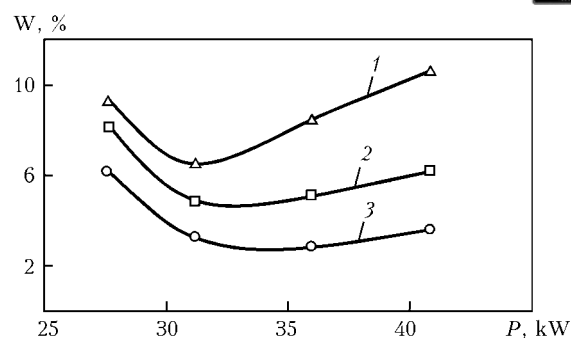


Figure 3. Dependence of tungsten content in condensate upon power of heating at following values of angle of vapor flow incidence, deg: 1 — 0; 2 — ± 15 ; 3 — ± 30

(Figure 1, *b*) was carried out with selection of samples for analysis within the range of angles of vapor flow incidence 0, ± 15 and $\pm 30^\circ$ (Figure 3).

General character of dependence of the tungsten content in carbon condensate upon power of heating, presented in Figure 3, proves that at low power of the melt heating (27.6–31.2 kW) quantity of tungsten in the carbon condensate decreases, while as the power grows (31.2–40.8 kW) it increases only in center of the substrate.

Process of reduction of the tungsten weight share at low power of heating is connected, in our opinion, with the carbon quantity increase in the tungsten melt due to its dissolution and delivery on the reaction surface by convection flows, taking into account increase of the tungsten pool volume and area of the melt contact with solid carbon. Increase of the heating power up to 31.2 kW causes saturation of the melt with carbon due to stabilization of the pool size and

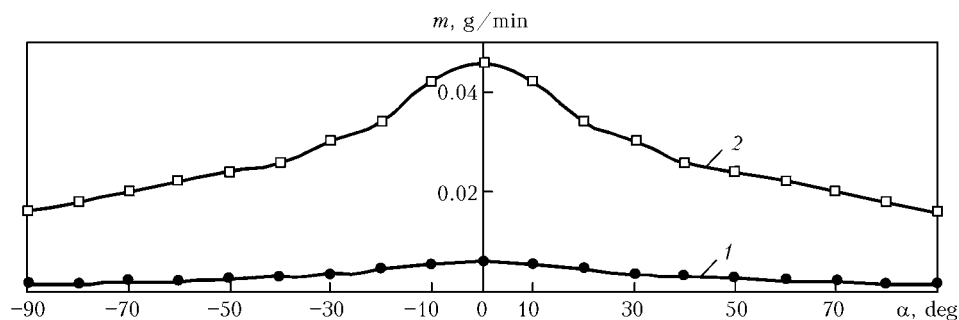


Figure 4. Condensation rate m of carbon flow depending upon angle of its incidence α at following values of current, A: 1 — 1.15; 2 — 1.5

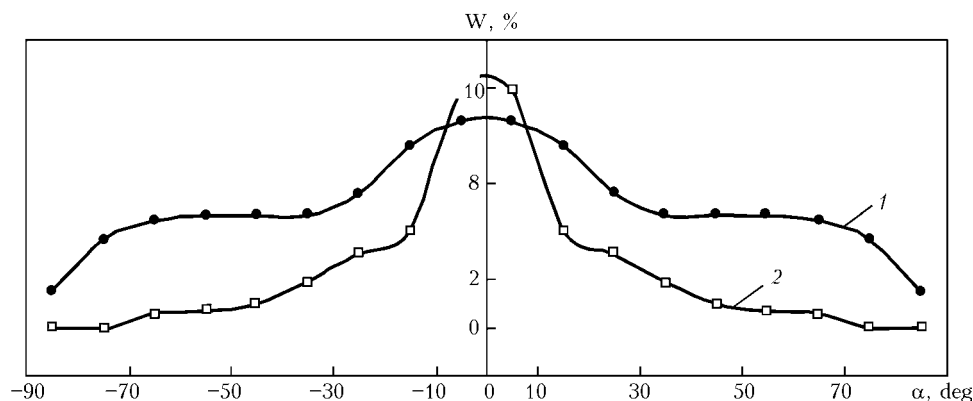


Figure 5. Tungsten content in carbon condensate depending upon angle of vapor flow incidence at following values of current, A: 1 — 1.15; 2 — 1.5

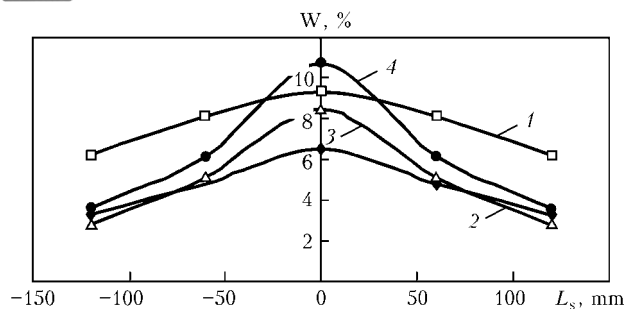


Figure 6. Dependence of tungsten content in carbon condensate over substrate surface L_s upon power of heating, kW: 1 — 27.6; 2 — 31.2; 3 — 36.0; 4 — 40.8

establishment of constant area of the molten tungsten contact with solid carbon, owing to which forms a certain equilibrium content of tungsten according to the constitutional diagram of W-C (2.2–3.6 %) [2].

As power increases up to 40.8 kW, process of tungsten content reduction in the condensate stops (Figure 3, peripheral areas of the substrate $\pm 30^\circ$) and increases only in center of the substrate (0°).

Investigation of dependence of the carbon condensation rate and tungsten content in the condensate upon angle of the vapor flow incidence (see Figure 1, a) was carried out by taking samples for analysis through each 10° (Figures 4, 5). Investigation of the vapor flow characteristics showed that while at the point 1.15 A rate of graphite evaporation is practically constant within the range 180° , except insignificant increase within 60° range, under intensive conditions (current 1.5 A) rate of carbon evaporation smoothly increases to the center due to increase of the melt surface temperature and only within 60° range its sharp increase is noted (Figure 4).

Data of Figure 5 prove influence of more intensive conditions of evaporation and, therefore, temperature on content of tungsten in the condensate. While at uniform rate of evaporation (close to the Langmuir one) the condensate contains constant quantity of tungsten ($\approx 5\%$), except insignificant increase in the central area, under conditions of intensive evaporation, when rate of carbon evaporation increases together with the melt temperature growth (see Figure 4), content of tungsten in carbon condensate at the periphery reduces to zero, while in central zone it significantly increases and localizes with maximum at 11 %.

Basic mass of vapor flow deposits on the substrates, located within range of angles $\pm 30^\circ$, and constitutes, approximately, 60 % of mass of total vapor flow (see Figure 1, b). Content of tungsten in carbon condensate at different distances from center of the substrate ($0, \pm 60, \pm 120$ mm, which corresponds to the angles of the flow incidence $0, \pm 15$ and $\pm 30^\circ$) in evaporation at different powers is shown in Figure 6.

At low power of the melt heating (27.6 kW) content of tungsten over the whole surface of the substrate changes smoothly with a small difference to the center

from the edge (3 %). As power of heating increases (31.2–40.8 kW), weight share of tungsten in carbon condensate, similar to the investigation carried out according to the scheme in Figure 1, a, increases in the central zone (maximum equals 11 %). Difference in amount of tungsten in center of the substrate and at its periphery constitutes 6–7 %.

Increase of the surface temperature enables not just increase of the evaporation intensity, but also change of the evaporation mechanisms and movement of vapor from the evaporation surface [3]. In weak evaporation vapor molecules freely leave the surface without colliding with each other. In case of intensive evaporation Knudsen layer occurs near the phase interface, the length of which equals several free path lengths, where primary collisions of molecules, which leave the surface, take place, and formation of the vapor flow starts. As a result of a great number of collisions a certain portion of molecules gets back on the evaporation surface.

Further, behind Knudsen layer, a gas-dynamic area is located, in which vapor flow moves perpendicular to the surface at transonic speed. When moving from the surface, vapor flow starts to expand into vacuum, which is substantiated by its own pressure, whereby vapor expansion occurs not just perpendicular to the surface, but also in lateral directions, due to which a vapor jet is formed. Lateral expansion of the vapor flow gets significant at distances from the evaporation surface equal, approximately, to its linear size, for example in case of electron beam melting, to the crucible diameter.

Flow lines, over which moves the vapor, bend, and centrifugal force occurs, which exerts stronger effect on heavy molecules than on light ones. This invokes increase of the rate of diffusion of heavy molecules to center of the jet, which causes separation of components in the jet [3–5].

It should be also taken into account that in intensive evaporation, caused by increase of the electron beam density, pressure of the beam in center of the pool increases. Shape of the pool surface changes, a concavity appears, and the vapor flow gets narrower [6].

So, presented results allow optimizing technological process of evaporation and condensation in production of different carbon-base materials.

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COMMERCIAL ELECTRON BEAM INSTALLATION UE-5812

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Design peculiarities and technical characteristics of new commercial electron beam installation UE-5812 are presented. The need of wide introduction of the installations of this class into titanium metallurgy is substantiated. Economic efficiency of this installation due to technical and technological advantages, in particular possibility of melting non-crushed blocks of spongy titanium, is shown.

Key words: electron beam remelting, installation, intermediate unit, axial gun, melting of metals and alloys

Electron beam melting [1] significantly expands technological possibilities of the process due to the presence of an independent concentrated source of heating — the electron beam. The next 10–15 years it may offer serious competition to the vacuum arc melting (VAM) [2] in the area of production of the titanium alloy ingots due to such higher technological possibilities and quality of the metal as expansion of the nomenclature of the charge being remelted, (scrap, non-pressed sponge, and spongy titanium blocks) [3] (Figure 1); separation of the metal melting processes, its refining (including from inclusions of high and low density), and solidification of the ingot in space and time by using the intermediate unit [1]; possibility of producing ingots of not just round, but also of rectangular section, used as a tape cast billet for manufacturing a rolled sheet [4]; complete removal of non-metallic inclusions of high density and significant refining and removal of inclusions of low density in the intermediate unit, and increase due to this of the ingot metal quality [5]; increase of the efficient metal yield due to reduction of the number of remelting operations (1 instead of 2–3) and melting of the ingot surface layer instead of the surface machining (increase of the efficient metal yield by 10–15 %) [6].

By now the newest technologies of melting of ingots of different metals and alloys by the EBCHM method have been developed [1, 4]. For achieving maximum effect from implementation of these technologies new high-productivity installations of commercial type are needed. During development of a new installation UE-5812 (Figure 2) experience of designing and operating electron beam installations UE-185M [1] and UE-121 [7] was used.

Design of UE-5812 differs from the earlier developed and operated in the industry of Ukraine installations mainly by the fact that rod mechanisms for the feedstock feeding and extraction of ingots are replaced for the chain mechanisms. This allowed increasing mass of the molten ingots 2 times. In addition,

the installation is characterized by high adaptability to manufacture in different melting processes, achieved by means of a rather simple replacement of one fitting-out for the other one that allows manufacturing ingots of round section from 100 to 600 mm and ingots of rectangular section, having size from 80×400 to 200×1250 mm and length up to 4 m.

Electron beam installation UE-5812 structurally consists of a melting chamber and loading and ingot chambers. All elements of the structure have hollow walls, in which circulates water for forced cooling in the process of melting and cooling of the ingot. In the melting chamber a technological fitting-out and mechanisms for feeding and extraction of the ingot are located and attached to it. The installation is equipped with electron beam guns, power supply sources, control and beam current stabilization systems, and a vacuum system.



Figure 1. Melting of ingot from spongy titanium briquettes



Figure 2. Appearance of electron beam installation UE-5812

**Technical characteristics
of electron beam installation UE-5812**

Installed power, kV·A	1500
Acceleration voltage, kV	30
Number of guns, pcs	5
Maximal dimensions of billet, m:	
length	5.3
section	1.0×1.0
Maximal dimensions of ingot, m:	
length	4.0
diameter	0.6
for rectangular section	1.1×0.3
Overall dimensions of installation, m	$14 \times 8 \times 5$

Melting chamber is central part of the installation, in which melting process is performed. It represents a vertically located cylinder, limited from above by the vacuum-tight cover with mounted on it electron beam guns (5 pcs) and equipped from below with a technological hole for connection of the ingot chamber. Inside of the chamber a technological fitting-out, consisting of the mould and the intermediate unit, is located.

A movement system is used for lifting and displacing the upper cover with electron beam guns outside the melting chamber limits. Convenience of this system consists in simplification of removal of the ready ingot by means of the workshop crane and cleaning of the internal surfaces from sublimation substances outside of the melting chamber.

Cooling water is fed through the pipe connections, located on the upper cover, into the mould through a system of pipes, and to the intermediate unit — from the loading chamber side. On side wall of the chamber the operator's inspection system of stroboscopic type and connecting pipes for installation of high-vacuum lamps are installed.

To the left from the operator connecting pipes of 630 mm diameter are located in the chamber wall, through which the melting chamber is connected with a pumping-out system by means of vacuum gates. To the right from the operator a vacuum-tight technological door with located on it inspection system is located, which is used by the process engineer for monitoring the melting process. Opposite the operator the melting chamber connects with the loading chamber.

The loading chamber represents a hollow cylinder with a cooling jacket. On the side of the cylinder a

vacuum-tight technological door is located, which is designed for convenience of performing various technological operations during maintenance of the installation.

During loading of the charge mentioned parts of the chamber are detached after release of the clamps, located over the sealing perimeter, then rear detachable part of the loading chamber moves back by means of the electric drive.

In the loading chamber a charge feeding mechanism is located (a pair of parallel guides, along which a pusher mechanism moves by means of a chain drive), which moves back together with the detachable part. The feeding mechanism allows feeding a single-piece billet, a consumable box with the charge materials, the lumpy charge, the bulk materials (for example, spongy titanium), and non-crushed blocks of spongy titanium, having mass up to 1 t.

In two first cases a roller table, over which a pusher mechanism feeds a billet into the melting zone, is installed on the guides. In case of the divided charge a non-consumable box is installed on the guides, the width of which does not exceed width of rear wall of the intermediate unit, and the pushing mechanism uniformly pushes charge materials into the intermediate unit. Possibility of the loading chamber disengagement allows operative loading of the charge by means of the workshop crane.

The ingot chamber represents a water-cooled cylinder, attached to the lower cover of the melting chamber through a flange. The basis for building up an ingot is a copper water-cooled plate, which moves relative the ingot chamber by means of a cross-piece, brought into motion by the chain mechanism. «Embedded parts», manufactured from material of the ingot to be melted, are fixed on the plate before beginning of the melting.

In lower part of the ingot chamber a technological manhole is located, by means of which access to internal parts of the extraction mechanism is ensured. Through mentioned technological manhole installation of «embedded parts» before melting and release of a ready ingot from the attachment after its melting before its extraction from the installation are performed.

The technological fitting-out consists of the intermediate unit and the mould [1, 5]. The former one represents a copper water-cooled surface, limited by walls, in one of which an aperture is made for pouring liquid metal. Into it the charge, fed from the loading chamber, is molten. The intermediate unit serves for averaging chemical composition and refining the melt from impurities and inclusions [1].

In the process of melting skull forms on bottom of the intermediate unit, which protects its walls and bottom against interaction with the molten metal that pours from the intermediate unit into the mould (a hollow close water-cooled circuit, internal part of which, contacting with the ingot metal, is made of copper). The mould and the intermediate unit are



fixed on the loading chamber frame, and when the chamber recoils they move together with it. This allows performing operative maintenance of all units. Cooling of the fitting-out is performed by the cooling liquid, supplied over a system of pipes.

Installation UE-5812 is equipped with electron guns of axial type «Paton-300» (Figure 3), located on upper cover of the melting chamber [1]. Each gun consists of the cathode unit with a tungsten electrode, installed on a high-voltage insulator of the anode water-cooled unit, a magnetic lens, and a deflection system, and it is equipped with an individual pumping-out system, which allows stabilizing operation of the gun under conditions of intensive gas release in the process of melting of primary charge materials.

Technical characteristics of gun «Paton-300»

Rated power, kW	300
Maximum scanning frequency, Hz	1000
Maximum current, A	15
Angle of beam deflection from gun axis, deg	0–35

Design location of electron guns above the melting zone and possibility of operative changing of both established zones of heating and put into them thermal power allow active influencing on the process of electron beam melting.

Electric power supply of the guns is performed by means of high-voltage 30 kV direct voltage sources, consisting of the switching start-protective equipment, thyristor keys, chokes, transformers, rectifiers, and cathode calefaction sources of the guns. Each gun is equipped with its own source of voltage, which allows increasing reliability of operation of the heating system as a whole.

Vacuum system of installation UE-5812 includes vacuum manifolds, gates, and pumps (mechanical, steam-jet, and diffusion ones). The manifolds consist of steel pipes, connecting the pumps between each other, with the melting chamber and the guns and ensure necessary passage sections for maximum use of productivity of the pumps. Degassing of internal cavities of the installation chambers from the atmospheric pressure level is performed by a mechanical pump RVN-6. For degassing of the installation and removing gases and metal vapors in the process of melting the following vacuum pumps are used: NVZ-300 (2 pcs); 2DVN1500 (2 pcs); a steam-jet pump 2NVBM630 (2 pcs); a diffusion pump N-160 / 700 (5 pcs).

Vacuum system of installation UE-5812 allows creating vacuum within the melting chamber volume ($1 \cdot 10^{-2}$ Pa) and in the guns ($1 \cdot 10^{-3}$ Pa), which ensures uninterrupted operation of the guns and necessary degree of refining of the metal being remelted during the whole technological process.



Figure 3. Electron guns «Paton-300»

CONCLUSIONS

1. It is shown that commercial installation UE-5812 is a highly productive unit for electron beam cold hearth melting of metals and alloys. This model differs from other electron beam installations by a higher level of technical and economic characteristics. So, replacement of the rod mechanisms for the chain ones allows two-fold reducing of overall dimensions of the charge loading and ingot extraction chambers, which makes it possible to reduce necessary mounting space and the volume being pumped out.

2. It is demonstrated that the main advantage of the installation is possibility of remelting non-crushed blocks of spongy titanium, which enables exclusion of labor-consuming operations of crushing and sorting the sponge and involvement into remelting of low-grade layers of the sponge that significantly reduces cost of EBCHM of titanium alloys. Due to possibility of operative replacement of the technological fitting-out it is possible to melt ingots of both round and rectangular sections from iron-, nickel-, titanium- and refractory metal-base alloys.

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MORPHOLOGY OF CARBIDES AND MICROSTRUCTURE OF STEEL R6M5 OF ELECTRON BEAM REMELTING

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Results of investigation of structure, chemical and phase compositions of high speed steel R6M5, produced by the method of electron beam remelting, in structure of which eutectic of two morphological types: prevailing laminar one (on the basis of metastable carbide M_2C) and skeleton one (on the basis of M_6C) are presented. Reduction of chemical inhomogeneity, high dispersion and uniformity of carbide distribution in EBR ingots are noted.

Key words: electron beam remelting, high speed steel, ingot, microstructure, grain, carbides, eutectic, heat treatment, heat resistance

Accelerated controllable cooling in solidification of high speed steel ingots, produced by the methods of special electrometallurgy, in particular EBCHR, causes phase and structural changes, which exert significant influence on properties of the ingot metal. This opens wide possibilities for producing quality ingots with assigned complex of mechanical and operation properties by variation of controllable parameters of the technological remelting process and subsequent processing [1–4].

Data on control of structure formation of high speed steel ingots in EBCHR are practically absent in the literature. In this connection peculiarities of structure formation, morphology of eutectic, phase and chemical compositions of high speed steel R6M5 of electron beam remelting are investigated in this work.

Methodology of investigation. Cylindrical ingots of 70, 100 and 130 mm diameter and 140×160 mm slabs from high speed steel R6M5, produced by EBCHR method from industrial waste of tool production according to developed by RPE «Gekont» technology, were used as investigation objects [5]. Specimens for the investigation were cut out from head, medium and bottom parts of ingots along and across the axis. Microstructure of the specimens was investigated on optical microscope «Leica» DM4000M, equipped with digital camera «Leica» DFC 150 with magnification power 100, 200, 500 and 1200, and on the JEOL scanning microscope Superprobe-733. Chemical composition of the metal was determined using X-ray microspectral analysis on spectrometer «Spectroscan». X-ray phase analysis was performed on the «Philips» diffractometer X'pert with automatic registration of the diffraction pattern. The results obtained were processed using program package PowderCell 2.2.

Results of the investigations and discussion thereof. Chemical analysis of specimens from high speed steel R6M5 (EBCHR) corresponds to the branded one according to GOST 19265–73 (Table 1).

High speed steel relates to the ledeburite class and is characterized in cast state by low parameters of mechanical and technological properties, especially ductility. That's why efficient metal yield in first process stage is low. Peculiarities of the cast steel primary structure are inherited even after complete heat treatment and exert determining influence on formation of high speed steel properties. Significant share of eutectic is present in the structure of high speed steel. In solidification formation of eutectics of four morphological types in tungsten-molybdenum steels, which have wide range of solidification ($1430\text{--}1235$ °C), is possible: skeleton one (on the basis of carbide M_6C), rod and laminar ones (on the basis of metastable carbide M_2C), and carbide MC . For ensuring maximum technological ductility of high speed steel production of the carbide M_2C -base laminar or rod eutectic, fine austenite grain and uniform distribution of structural components all over the ingot volume are desirable [6].

Investigation of lateral macrotemplates of high speed steel R6M5 (EBCHR) ingots showed that their macrostructure has dense homogeneous structure; defects of segregation and shrinkage character are not present, whereby in the surface area structure equiaxial crystals of $0.4\text{--}1.0$ mm diameter (depending upon size of an ingot) and in central part of the ingot columnar crystallites were detected. In macrostructure of longitudinal ingot sections axes of dendrites, oriented at the angle $30\text{--}40^\circ$ to the edge zones (normally to the solidification front zone), are distinguished.

Microstructure of cast high speed steel R6M5 (EBCHR) consists over grain boundaries of martensite (austenite grain score is $9\text{--}10$), residual austenite, torn carbide network (carbide inhomogeneity score, according to GOST 19265–73 scale 2, is $6\text{--}7$) and disperse carbides, uniformly distributed over the whole volume of ingots (Figure 1, a).

Increased ($10\text{--}10^2$ °C/s) cooling rate of overheated in intermediate unit steel melt caused in EBCHR during solidification in copper water-cooled glide mould change of kinetics of its eutectic solidification, which effected quantity, morphology and

**Table 1.** Chemical composition of high speed steel R6M5

Object of investigation	Weight share of elements, %								
	C	W	Mo	Cr	V	Mn	Si	S	P
R6M5 (EBCHR)*	0.89	6.2	5.1	3.8	1.86	0.28	0.3	0.011	0.019
R6M5 (GOST 19265-73)	0.82-0.90	5.50-6.50	4.80-5.30	3.80-4.40	1.70-2.10	0.20-0.50	0.20-0.50	≥ 0.025	≥ 0.03

*Result is averaged for 5 specimens.

character of distribution of eutectic component of the structure. Carbide network around martensite grains is torn (discrete), and the very eutectic of 2-7 μm thickness has a fine delicate structure (Figure 2).

On diffractograms, produced from specimens, made of cast steel R6M5 (EBCHR) (Figure 3, *a*), in addition to interferences of α -solid solution (martensite) peaks of comparative intensity from carbide M_6C , which enters into composition of skeleton eutectic, from metastable M_2C (laminar eutectic), and from refractory carbide MC (VC) are present. General amount of carbide phase in the cast steel structure constitutes 18-22 vol.%.

Interference maximums from austenite are indistinguishable on diffractograms because of the same value of parameter d/n (angular position of interference) for similar maximums of carbide M_6C , coherently connected with it in the eutectic. That's why amount of residual austenite in structure of cast high speed steel R6M5 (EBCHR) was determined by the method of magnetic analysis on magnetic austenometer MAK-2M, using calibration standard from hard-

ened and annealed steel R6M5. It was relatively low (10-12 vol.%).

Results of X-ray microspectral analysis and data of scanning microscopy, obtained in the «phase contrast» mode in backscattered electrons (BEI), confirmed presence in the structure of cast steel R6M5 (EBCHR) of carbides M_6C , M_2C , MC, and disperse secondary carbides, uniformly distributed within grain volume (Figure 4).

Analysis of distribution of basic alloying elements over structural and phase components of cast steel R6M5 (EBCHR) proves high level of solid solution (martensite) alloying. Chromium is uniformly distributed between carbides and solid solution, tungsten and molybdenum are bound mainly in carbides M_6C and M_2C , and vanadium — in MC (VC). Into composition of the carbide phase also enter secondary carbides on basis of chrome M_{23}C_6 and M_3C_2 , which are radiographically indiscernible because of high dispersity.

Produced ingots of steel R6M5 (EBCHR) were subjected to homogenization isothermal annealing according to the scheme: austenization — heating up to 880-

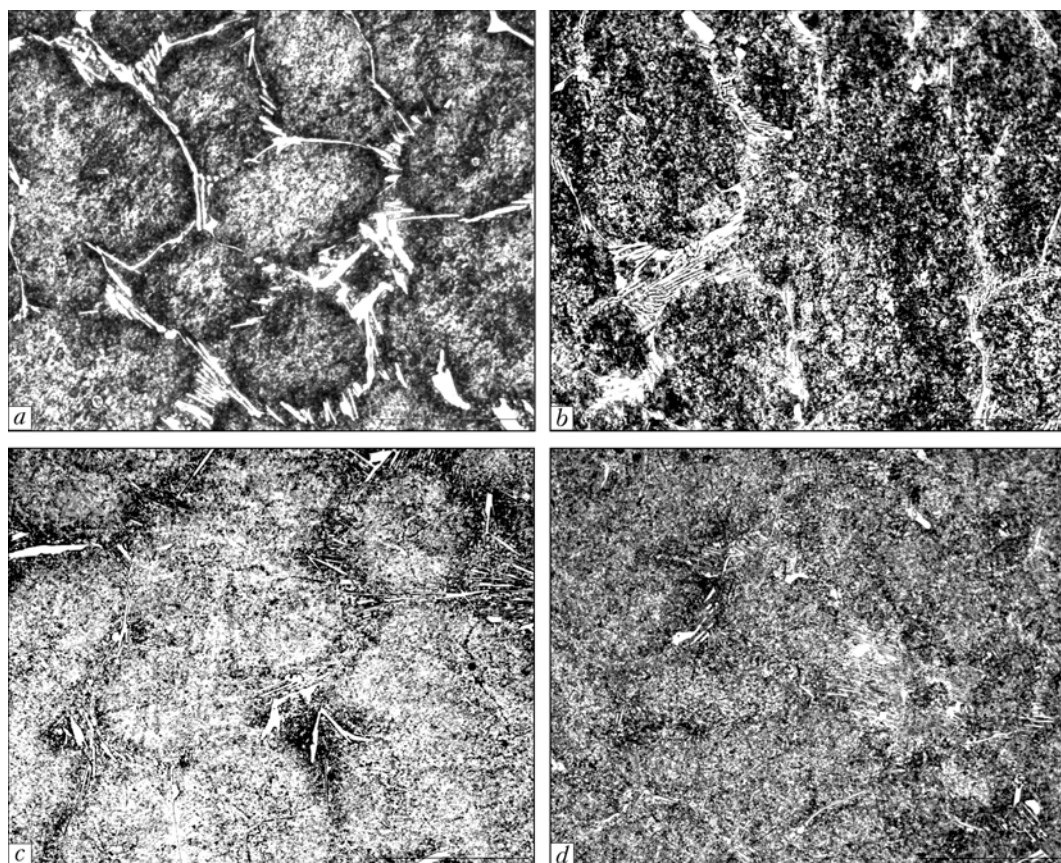


Figure 1. Microstructure of high speed steel R6M5 (EBCHR): *a* — cast one; *b* — after annealing; *c* — hardened one; *d* — after temper hardening ($\times 500$)



Figure 2. Morphology of eutectic in cast steel R6M5 (EBCHR) ($\times 1200$)

900 °C, seasoning for 3 h (eutectoid transformation), cooling down to 760–780 °C, isothermal seasoning for 6 h (diffusion transformation) with subsequent slow cooling with furnace down to 400 °C. For protection of ingot surface against decarbonization and oxidation burden from cast iron chips and protection atmosphere in the furnace (endogas) were used.

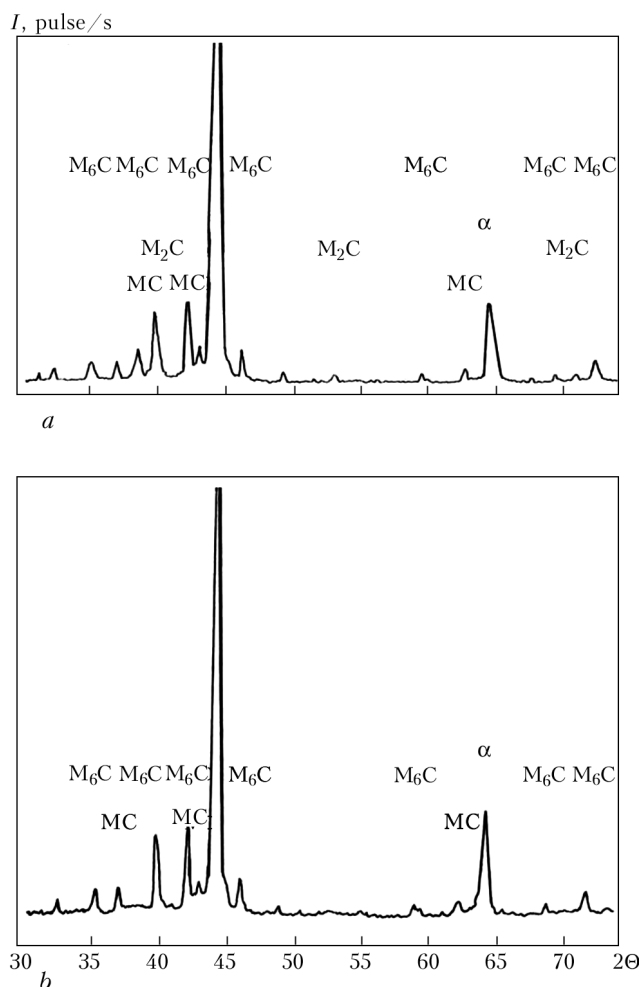


Figure 3. Diffractograms of steel R6M5 (EBCHR): *a* — cast one (M_2C — 4.98; MC (VC) — 5.36; M_6C — 6.33; α -Fe — 83.33 wt.%); *b* — after hardening and tempering (MC (VC) — 4.21; M_6C — 6.36; α -Fe — 89.43 wt.%); α — solid solution of carbon in iron (martensite); *I* — intensity

Table 2. Hardness *HRC* of steel R6M5 (EBCHR) after temper hardening

Heating temperature for hardening, °C	Hardening	Tempering at temperature 560 °C		
		First	Second	Third
1180	61.0–61.5	61–63	62–64	62.5–64.0
1200	59.0–60.5	62–63	63–64	63.0–65.0
1220	58.0–59.5	62–63	63–65	63.0–65.5
1240	58.0–60.0	62–63	62–65	63.0–65.0

Structure of annealed steel according to the presented scheme consists of globular grains of sorbite-like pearlite (the grain score according to GOST 19265–73 is 9–10), residues of torn carbide network over grain boundaries, and uniformly distributed disperse carbides (Figure 1, *b*).

For determining optimum conditions for final heat treatment of high speed steel R6M5 (EBCHR) influence of hardening and tempering parameters on its structure, phase composition, hardness and heat resistance was investigated (Table 2).

Hardness *HRC* values of steel R6M5 (EBCHR) were, depending upon cooling environment for hardening after additional tempering at temperature 580 °C for 180 min, as follows: $KNO_3 + 30\% NaOH$ (400–420 °C) — 61.0–62.0; oil — 61.0–61.5; water — 60.0–61.5; air — 58.5–59.0.

Structure of high speed steel R6M5 (EBCHR) after hardening consists of acicular martensite, residual austenite, residues of carbide network over grain boundaries and structurally isolated carbides of compact form, uniformly distributed over the metallographic specimen section (Figure 1, *c*). High-alloy martensite of high speed steel relatively difficultly yields to etching. Amount of residual austenite constitutes 14–18 vol.%.

In tempering of hardened high speed steel secondary hardening takes place in the metal due to precipitation from solid solution of disperse excessive carbides, and in subsequent cooling transformation of residual austenite into martensite occurs. In the course of the microstructure investigation it was found that in the specimens, heated for hardening below accepted range of temperatures, and after one-time tempering boundaries of polyhedrons (grains) preserve in the structure. Against the background of martensite remain fields, enriched with austenite with low etching capacity. During increase of the heating temperature for hardening size of the grains increases from the score 10–11 at 1180 °C to the score 8–9 at 1240 °C (GOST 5639–65, scale 1). Structure of high speed steel R6M5 (EBCHR) after temper hardening consists of high-alloy tempered martensite, residual austenite (3–5 vol.%), residues of the torn carbide network over boundaries, and carbides, the main of which is M_6C . M_3C_2 and MC , which constitute 8–12 vol.% of the whole carbide phase, are also present (Figure 1, *d*). Martensite structure between carbide lines is of non-acicular nature because of microsegregation, and in the areas of accumulation of carbides acicular martensite with low etching capacity is present.

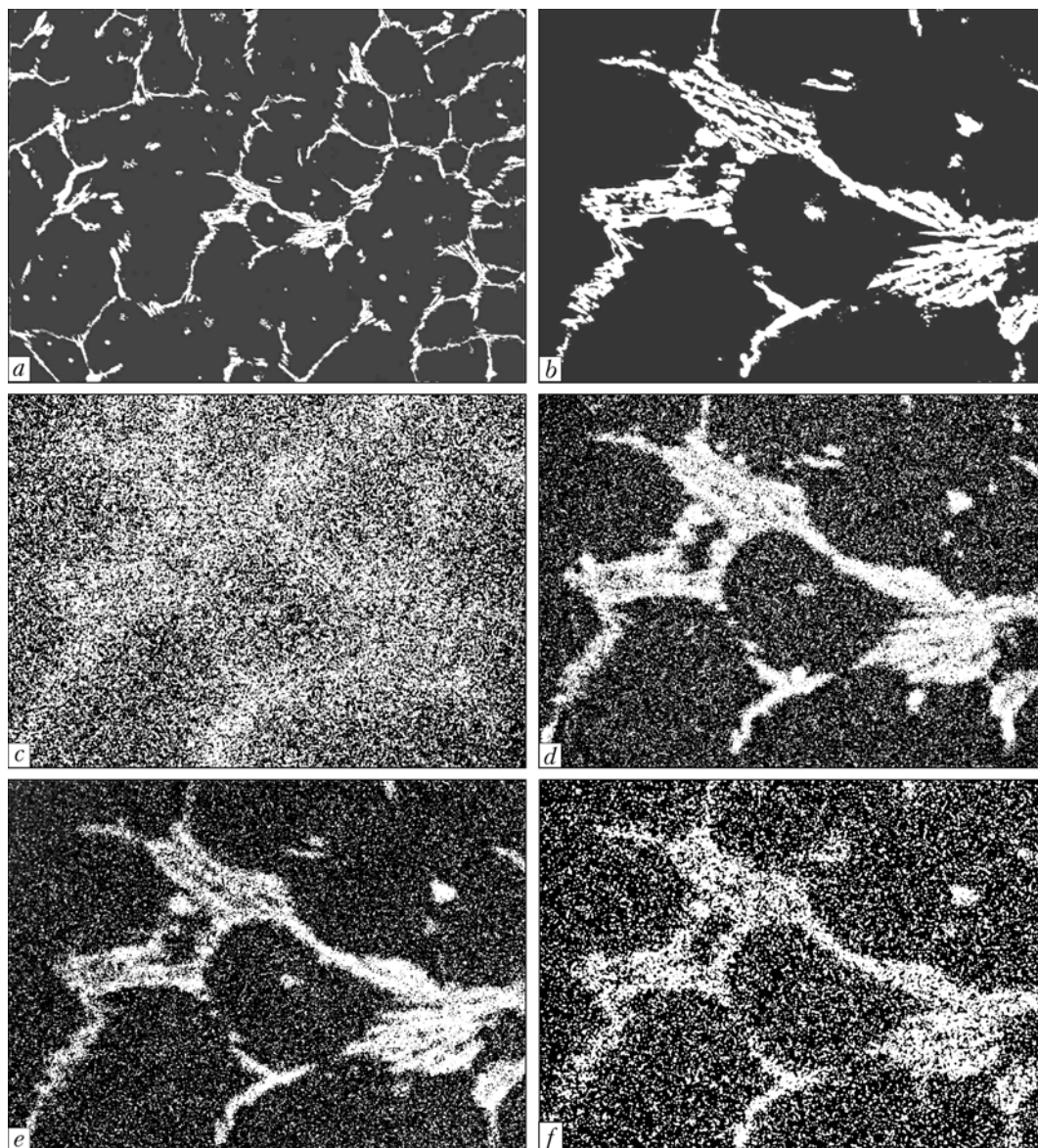


Figure 4. Distribution of alloying elements over structural components in cast high speed steel R6M5 (EBCHR): *a* — $\times 300$, BEI; *b* — $\times 1000$, BEI; *c* — $\times 1000$, CrK_α -radiation; *d* — $\times 1000$, VK_α -radiation; *e* — $\times 1000$, WK_α -radiation; *f* — $\times 1000$, MoK_α -radiation

Analysis of diffractograms from hardened and tempered specimens (Figure 3, *b*) proves that during their heating up to the hardening temperature in initial metastable carbide M_2C takes place its transformation into more stable carbides MC and M_6C with subsequent coagulation. Reduction of specific angular widening of peaks of martensite interferential lines and increase of their intensity was also detected, which proves reduction of internal stresses in solid solution and cubic structure of martensite after two-fold tempering of hardened high speed steel.

CONCLUSIONS

1. It is shown that structural changes, which occur at the stage of solidification of the R6M5 high speed steel melt in EBCHR, exerts favorable influence on phase transformations and formation of homogeneous disperse structure of cast metal.

2. It is determined that in electron beam remelting in the structure of cast high speed steel R6M5 form eutectics of two types: laminar one (55–60 vol.%) on

the basis of metastable carbide M_2C , and skeleton one on the basis of carbide M_6C .

3. It is detected that refractory carbides of MC type precipitate in steel R6M5 (EBCHR) during solidification at the stage of peritectic transformation and don't form eutectic.

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INVESTIGATION OF COMPOSITION OF BURNT GAS IN PLASMA LIQUID-PHASE REDUCTION OF IRON FROM ORE RAW MATERIALS BY GASEOUS REDUCERS

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Change of burnt gas composition in time in the course of plasma liquid-phase reduction of iron from iron ore pellets by gaseous reducers in pyrolysis and air conversion of the pellets is determined with application of chromatographic analysis.

Key words: liquid-phase reduction, plasma, gaseous reducer, chromatograph, gas composition, oxidation rate

E.O. Paton Electric Welding Institute of the NAS of Ukraine has been developing process of iron reduction from ore raw materials with application of plasma heating sources. The process is assumed to be fulfilled in two stages: preliminary reduction in solid phase, and final reduction in liquid phase. Solid-phase reduction of iron is investigated in detail and rather widely used in the industry [1–3]. Liquid-phase reduction, especially with application of plasma sources of heating, is less studied, that's why process of plasma liquid-phase reduction (PLPR) has been investigated in PWI [4, 5], whereby in case of application of gaseous reducers of special interest is determination of the burnt gas composition and possibility of its use for solid-phase reduction.

The investigations were carried out on the improved laboratory installation. Design of the latter and methodology of the experiments are described in [5]. Improvement of the installation consisted in addition to it of a unit for taking gas samples, which represents a water-cooled cooler, through which passes gas channel with a developed surface. This channel is connected to the pipe, designed for withdrawal of waste gases from working space of the installation. When it is necessary to take a sample, underpressure is created at outlet of the gas channel. In this case a portion of waste gases is fed over the channel through the cooler, after which the gases may be taken for chromatographic analysis.

Chromatographic analysis was performed in chromatograph «Gazokhrom 3101», which allows determining content in gas mixture of O_2 , H_2 , CH_4 , CO , and CO_2 .

A series of experiments of iron PLPR from iron ore pellets of the following composition was carried out, wt. %: 9.18 SiO_2 ; 0.32 Al_2O_3 ; 0.87 CaO ; 0.37 MgO ; 0.039 S; 0.007 P; 0.062 C; Fe_2O_3 — the basis. As a reducer and plasma-forming gas propane-butane mixture, containing 6 % of butane, was used. Its flow was 15 l / min. The experiments were carried

out under conditions of pyrolysis and air conversion (air flow was 30 l / min) in plasma directly above the iron ore melt.

Composition of burnt gas under these conditions during different periods of the reduction process is presented (Table). As far as water steam in the process of its passing through the cooler condensates, total concentration of CO , CO_2 and H in gas phase constitutes 100 % in pyrolysis and about 80 % in air conversion due to presence of nitrogen in the gas mixture. In the Table volume shares of hydrogen, carbon mono- and dioxide, measured by chromatograph and obtained due to recalculation, are indicated, assuming that pyrocarbon fully reacts with slag melt with formation of CO , and total concentration of hydrogen and water steam relates to total concentration of carbon mono- and dioxide as 4:3, i.e. as hydrogen to carbon in molecule of propane, total content of CO , CO_2 , H_2 and H_2O equals 100 % in pyrolysis and 81 % in air conversion (19 % should constitute nitrogen proceeding from the ratio of volumes of supplied air and propane-butane mixture).

Content of H_2O and CO_2 in the burnt gas in equilibrium state in reduction of higher iron oxides up to wustite exceeds 90 % [6]. However, in reduction of iron from the melt of pure wustite not more than 16 % CO oxidize up to CO_2 and not more than 51 % H_2 oxidize up to H_2O at the beginning of the process. Further these indices reduce. Presence of SiO_2 in the melt also worsens yield of carbon dioxide and water steam [1, 3, 7–9]. Presented in the Table ratios $CO:CO_2$ and $H_2:H_2O$ correspond, as a whole, to the literature data on high reduction capacity of hydrogen in comparison with carbon monoxide at high temperatures and reduction of degree of their utilization in the course of the process, which is connected with reduction of the iron oxide activity. Lower content of H_2O and CO_2 in burnt gas than that indicated in the literature is explained by long duration of the period of equilibrium state achievement.

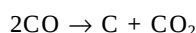
Important index of the reduction process is degree of the burnt gas oxidation, β , which represents ratio



Composition of burnt gas in PLPR of iron from ore raw materials by gaseous reducers

Mode	t, min	CO, vol.%		CO ₂ , vol.%		$\tilde{N}:\tilde{N}:\tilde{H}_2$	H ₂ , vol.%		H ₂ O, vol.%	$\tilde{f}_2:\tilde{f}_2:\tilde{f}$	β_{chr}	β_i
		Measurement	Recalculation	Measurement	Recalculation		Measurement	Recalculation				
Pyrolysis	3	35	22	34	21	1.05	31	19	38	0.50	71	67
	5	45	34	12.5	9	3.78	42	32	25	1.28	54	58
	7	46	35	10	8	4.375	45	35	22	1.59	51	49
	10	48	40	3	3	13.33	49	41	16	2.56	43	38
Air conversion	3	33	24	16	11	2.18	27	19	27	0.70	63	60
	5	40	30	6	5	6.00	30	23	23	1.00	54	51
	7	41	33	2	2	16.50	38	31	15	2.07	45	40

of the number of oxygen moles in the gas mixture to the number of oxygen moles in case of full oxidation of all its components up to H₂O and CO₂ [1]. So, degree of the burnt gas oxidation is index of completeness of the gaseous reducer application. In the Table degree of oxidation is presented, which is determined by two methods: on the basis of chromatographic analysis data β_{chr} and by calculation of the amount of oxygen β_i , which has to be removed from oxides for producing a molten amount of iron. As a rule $\beta_{chr} > \beta_i$. Possible reasons of such discrepancy may be incomplete reaction of pyrocarbon with oxides and passing of the reaction



at a reduced temperature [1]. Confirmation of this is deposition of hydrocarbon black on cold walls of the chamber and in gas channel of the cooler.

Content of CO and H₂ in the burnt gas after drying should correspond to the data, obtained from chromatographic analysis. So, it is advisable to use gas, which emanates from the melting space, for preliminary solid-phase reduction. For the purpose of reducing heat losses burnt gas may be directed directly for preliminary reduction, although in this case its reduction potential will be lower than after drying.

CONCLUSIONS

1. Higher reduction capacity of hydrogen in comparison with carbon monoxide is confirmed at temperature values, characteristic of liquid-phase reduction.

2. It is shown that it is advisable to use burnt after PLPR gas for preliminary solid-phase reduction.

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DISTRIBUTION OF OXYGEN IN SINGLE CRYSTALS OF SILICON AND ITS INFLUENCE ON LIFE TIME OF NON-EQUILIBRIUM CHARGE CARRIERS

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Influence of the background oxygen impurity and total concentration of impurities on life time of non-equilibrium charge carriers (NCC) in single crystals of silicon, grown according to Czochralski method and designed for application in solar power engineering, is studied. Issue of oxygen concentration and NCC life time distribution over a single crystal length is considered.

Keywords: Czochralski method, single crystal silicon, NCC life time, screening, impurity, oxygen, carbon

The issue of creation and development of alternative sources of energy, which will be able to replace liquid- and solid-fuel converters of thermal energy into the electrical one, gets more and more actual because of increased price on traditional kinds of raw materials.

In recent years solar energy intensively develops, which is connected not just with the latest achievements in science and technology, but also with need for environmentally clean generators of electric energy. For example, application of an installation for a solar energy converter of 5 kW power (with conversion factor 15.7 %) allows reducing annual consumption of liquid fuel by 243 l and emission into the atmosphere of carbon dioxide, caused by application of the fossil fuel, by 180 kg [1].

State-of-the-art development of solar energy is performed in two directions: photoelectric power engineering (conversion of solar energy into the electrical one by means of semiconductor elements), and heat power engineering (production of thermal energy by means of solar collectors).

Good prospects for development of solar power engineering are confirmed by huge attention, paid to this problem by such developed countries as Japan, which is the world leader in this field. Japan is followed by Germany. USA is in the third position among world leaders concerning scale of development and introduction of solar energy converters [2].

Significant prospects for application of solar electric power engineering exist in the fields, in which independent power supply systems are needed for operation of the equipment, in the regions, where centralized electric power supply systems are absent, and in space and domestic electronics.

Main material for production of photoelectric converters (PEC) is multi- (58 %) and single crystal (32 %) silicon, produced according to Czochralski method. The former one is characterized by high de-

gree degradation of electro-physical properties that limits its application.

Efficiency of PEC, produced from single crystal silicon, mainly depends upon concentration of defects, which effect main parameter of solar batteries — NCC life time in active layers of the instrument. All defects are divided into two groups: structural and impurity ones [3]. In case of impurity defects special attention deserve so called background impurities (carbon and oxygen), which are electrically non-active.

A state-of-the-art installation for growing single crystals of silicon according to Czochralski method is a complicated complex of technical means. It consists of a melting chamber with mechanisms for rotation and displacement of upper and lower rods, a vacuum system, systems of electric power supply, cleaning, supply, regulation of the inert gas flow, water cooling, and automatic regulation of the crystal growth process [4].

The most important unit of the installation is thermal one (Figure 1), which consists of a resistive heater, a support for the crucible, and a system of screens. Design of the thermal unit determines to a great degree peculiarities of solidification, macro- and microstructure of a single crystal being grown, and distribution of impurities in it.

A resistive heater is manufactured from a high-purity graphite of round shape with a certain number of heating elements, produced in milling of an initial billet. The heater is powered by direct electric current, supplied over water-cooled copper current leads, which pass through the chamber bottom plate. The heater is attached to the current leads by means of graphite bolts.

Screening represents a system of heat baffles and elements, which effect gradient of temperature in the melt and in the growing crystal. It significantly reduces heat losses and ensures creation of necessary temperature gradient in the crystal growth zone for the purpose of obtaining assigned properties.

Goals and tasks of the investigation. The purpose of these investigations consisted in determining influence of the impurities and technological factors on NCC life time in single crystals of silicon.



Performance of the investigation. The investigations were carried out on single crystals of silicon, designed for use in solar power engineering with application of raw materials of uniform composition and crucibles of a single set according to Czochralski method on commercial installation «Redmet-30». As a result single crystals of silicon of *p*-type electric conductivity (alloyed by boron), having diameter 135 mm and length up to 800 mm, were produced at the concentration $1.5 \cdot 10^{16} \text{ cm}^{-3}$. Crystallographic orientation of produced single crystals corresponded to $\langle 100 \rangle$.

Single crystals were grown under the following technological conditions: rate of growing from 1.8 at the beginning and 0.7 mm/min at the end of the process, speed of the crystal rotation was 15 min^{-1} , speed of the crucible rotation — 5 min^{-1} . Voltage on the heater was 45 V, current — 1500 A. Flow rate of inert gas argon corresponded to 30 l/min. Measurement of oxygen concentration in single crystals was performed by the method of IR-absorption [5] with application of infrared spectrophotometer of VECTOR 22 type. NCC life time in single crystals was determined by the method of conductivity modulation in the point contact on installation TAU-102 according to GOST 19658–81 [6].

On the basis of results of measurement of parameters of investigated single crystals curves 1 of oxygen concentration distribution and NCC life time over a single crystal length 3 were built; for analysis of the results obtained total distribution 2 of the impurity concentration over length of a single crystal was theoretically calculated (Figure 2).

Presented in Figure 2 distributions of values of electrophysical parameters are characterized by monotonous diminishing along the single crystal length. Distribution of oxygen is somewhat different. Approximately at half of the single crystal length, angle of inclination of the line, which corresponds to concentration of oxygen, significantly changes. In the same area change occurs, but in opposite direction, of NCC life time distribution and total concentration of impurities (curves 2 and 3), whereby change of NCC life time is more apparent than distribution of impurities. Different character of distribution of electrophysical parameters over length of grown single crystals indicates complexity of the processes, which occur in the melt in the course of growing of single crystals.

Discussion of the results obtained. It is established that concentration of oxygen in single crystals of silicon depends upon conditions of growing — rotation speed of the crucible and a single crystal, rate of growing, ambient atmosphere, and composition of the melt [7]. In this investigation these conditions were maintained at a constant level.

Source of contamination of a single crystal of silicon by oxygen is quartz crucible, the walls of which react with molten silicon in the process of growing with formation of atomically free oxy-

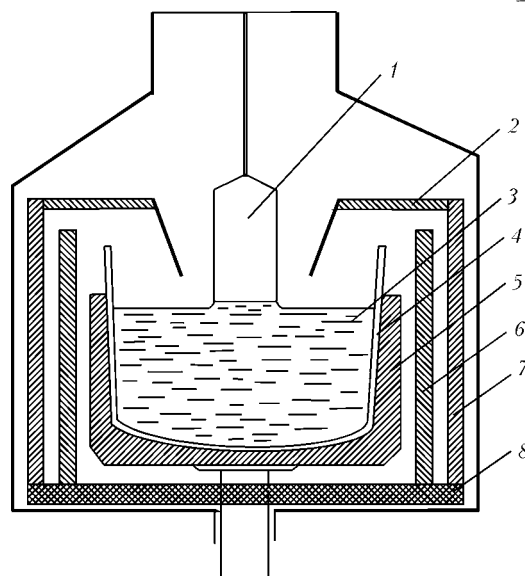
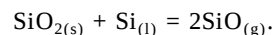


Figure 1. Scheme of thermal unit of installation for growing single crystals of silicon according to Czochralski method: 1 — single crystal; 2 — upper screen; 3 — melt; 4 — quartz crucible; 5 — graphite support for crucible; 6 — heater; 7 — side protection screen; 8 — bottom plate

gen, which transits into the single crystal. Intensity of the crucible dissolution and oxygen transition into the melt depends upon area of contact of the crucible surface and the melt, condition of the crucible internal surface, content of impurities in the quartz, and convection flows in the melt [8].

In crystalline lattice of silicon atoms of oxygen occupy interstitial position and form with the nearest atoms of silicon the chain Si–O–Si. Dissolution of quartz in the silicon melt occurs with formation of SiO according to the reaction



In Figure 3 diagram of oxygen transition from quartz crucible into the melt is shown. In the process of solidification atoms of oxygen are redistributed between liquid, gas and solid phases. Oxygen gets into atmosphere of the work chamber in the form of silicon monoxide, which evaporates from surface of the melt. A certain part of silicon monoxide condensates and precipitates in the form of solid precipitation on less heated parts of the furnace work chamber and the screening, while its other part is carried away by inert gas into vacuum system and caught by the filter.

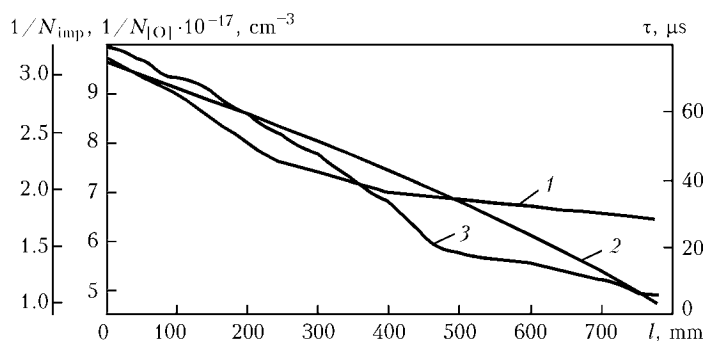


Figure 2. Distribution of oxygen concentration $1/N_{\text{O}_1}$ (1), total concentration of impurities N_{imp} (2) and NCC life time τ over length l of single crystal (3)

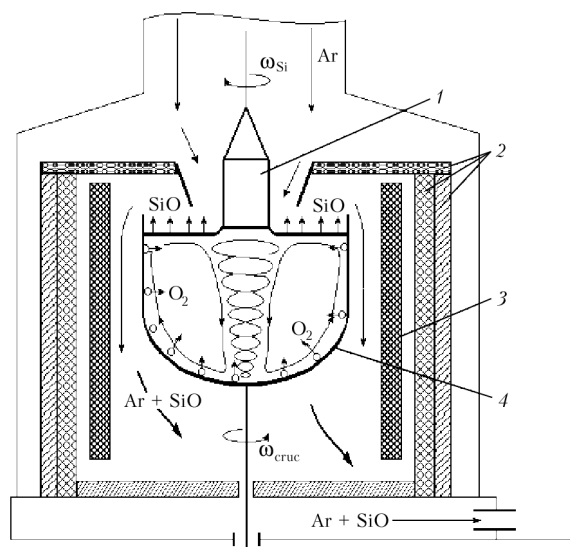


Figure 3. Scheme of oxygen distribution in process of growing of single crystal according to Czochralski method: 1 — single crystal; 2 — system of screens; 3 — heater; 4 — quartz crucible

Proceeding from the character of oxygen distribution over length of a single crystal (see Figure 3), process of growing may be conditionally divided into three stages (areas): the first one — 0–250, the second one — 250–430, the third one — 430–800 mm.

The first stage is characterized by high dissolution of crucible by quartz and saturation of the melt with oxygen, which may be explained by the process of initial charge melting that precedes stage of drawing and is performed at a higher temperature (by 150–200 K above silicon melting point).

After complete melting of the charge seasoning of the melt for its homogenization is performed, during which surface of the crucible continues to intensively dissolve. At the same period starts to form diffusion barrier between quartz and molten silicon in the form of a layer of SiO film [8].

Occurring at this stage in the melt intensive convective flows enable washing out of the originated oxide film, thus accelerating transition of oxygen into the melt.

Concentration of oxygen in a single crystal in this area is the highest, and character of oxygen distribution has a significant inclination. In subsequent areas distribution line gets more flat and inhomogeneity of oxygen concentration reduces, approximately, twofold.

At the second stage significant reduction of oxygen concentration occurs, which is explained by reduction of the area of silicon melt contact with the crucible walls by means of a single crystal growth. In this area a smaller amount of oxygen transits into the melt, because area of free surface of the melt, from which silicon monoxide evaporates within process of growing, remains constant. At the same time intensity of convection flows in the melt reduces, which enables strengthening of oxide layer between silicon melt and walls of the crucible and reduction of oxygen transition into the melt.

The third stage is characterized by stabilization of the process of growing, ordering of convective flows,

and fixation of oxide layer between molten silicon and quartz of the crucible. Gradient of oxygen concentration in this area is low.

Measurement of NCC life time by length of a single crystal is presented in Figure 2, curve 3. Mobile charge carriers, which occur due to energy action on a semiconductor and are not in thermodynamic equilibrium, are called non-equilibrium ones [9].

Change of NCC life time over length of a single crystal in first two areas occurs proportionally to the change of oxygen concentration.

As one can see, curves pass in the first area parallel to each other that allows assuming dependence of NCC life time upon concentration of oxygen in a single crystal.

In the third area NCC life time reduces significantly quicker than concentration of oxygen, which may be explained by significant accumulation of total impurity in the melt due to its pushing off by the solidification front and its influence on NCC life time.

For analysis of the results obtained distribution of total concentration of impurities over length of a single crystal was calculated (see Figure 2, curve 3). Analysis of data on measurement of electrophysical parameters over length of single crystals showed that correlation factor between value of NCC life time and total impurity concentration equaled 0.915, and between NCC life time and concentration of oxygen — 0.950.

CONCLUSIONS

1. On basis of the results obtained one can draw conclusion that value of NCC life time in single crystals of silicon, grown according to Czochralski method, is significantly effected by oxygen impurity. When the concentration increases, NCC life time reduces; similar influence also exerts total content of impurities, concentration of which grows in the process of a single crystal growing due to zone effect, which explains continuation of NCC life time reduction after stabilization of oxygen concentration.

2. It is shown that increase of NCC life time may be ensured by application of «clean» initial raw materials and technological methods, which ensure reduction of the crucible material dissolution in silicon melt, and special crucibles with a coating that reduces their solubility.

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MECHANICAL PROPERTIES AND STRUCTURE OF BRAZED JOINTS OF CASTING NICKEL ALLOY JS26VI

Part 1

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Interconnection between physical-mechanical properties of the seam metal and brazed joints with microstructure of casting nickel alloy JS26VI, produced with application of complex brazing alloys, containing boron and silicon as depressants, is considered. Silicon was added in the form of powder of commercial brazing alloy NS12 (Ni–12 wt.% Si). The best results were achieved when 20 wt.% of NS12 were introduced into the complex brazing alloy. In this case brazed joints are characterized by strength at the level of 670–760 MPa, and their relative elongation achieves 13 % at room temperature.

Key words: *brazing in vacuum, casting alloy JS26VI, boron-containing brazing alloy, silicon-containing brazing alloy NS12, brazed joint, strength, elongation, structure, fracture*

Among national nickel high-temperature alloys (HTA) casting alloy JS26VI is used as one of the main materials in fabrication of heat-stressed components (rotor blades) of turbines. In batch production it is obtained by both equiaxial and directional solidification [1–4]. Service characteristics of the alloy depend to great degree upon technology of melting, in particular temperature of the melt overheating, which determines change of dendrite structure [2] and completeness of the cast metal degassing [3].

Functional properties of components from nickel HTA are improved by application in the process of casting with directional solidification. Oriented solidification of the cast metal prevents occurrence of grain boundaries perpendicular to direction of external load action.

Mechanical properties of alloy JS26 with polycrystalline structure were investigated in work [4]. In [4, 5] dependence of tensile strength and relative elongation of cast alloy upon crystallographic orientation of macrograins in specimens of casts is shown. Maximum ultimate strength value of alloy JS26NK, equal to 1200–1253 MPa at 20 °C, corresponded to direction $\langle 111 \rangle$, whereby relative elongation of the metal constituted about 10 %. Specimens of the alloys, growth axle projections of which corresponded to central part of a stereographic triangle, had minimum strength values (780–840 MPa) at relative elongation 14.5–20.0 %. Disturbance of the specimens relative each other in this case did not exceed 12 degrees. So, mechanical properties of alloy JS26, microstructure of which corresponds to central area of a stereographic triangle, are close to those of a polycrystalline alloy with equiaxial grains. Presented data served as a basis for comparing with mechanical properties of the alloy

JS26VI brazed joints (BJ), which had relative elongation at room temperature 7–13 %.

Main requirement to nickel HTA is thermal stability of their structure at temperature of the item operation, determined by high-temperature strength of solid matrix solution, low rate of coagulation and dissolution of main strengthening γ -phase, and kinetics of carbide reactions. Heat stability is connected with alloying complex of the alloy, i.e. composition and quantity of the components, especially of those having low coefficients of diffusion. Niobium and vanadium like hafnium and tantalum, being distributed among the matrix, γ -phase and carbide phases, limit diffusion processes in the base high-temperature system Ni–Cr–Co–W–Mo–Ti–Al and increase energy of atomic bonds. Vanadium, which enters into composition of JS26, is the weakest γ -forming element. Its role mainly consists in increasing solubility of refractory components in the matrix solution, which enables retarding of diffusion processes in nickel alloys [6–7].

Resistance to coagulation and dissolution of γ -phase in brazing of HTA are determined by alloying complex of the seam metal, in connection with which chemical composition of the low-temperature brazing alloy and the filler are factors, which determine level of the compound heat stability. Reserve for increasing functional reliability of BJ is optimization of chemical composition of the used filler, presence in its composition of elements with high melting point and low coefficients of diffusion, and final heat treatment of the item being renovated.

Level of high-temperature strength, technological ductility and fatigue resistance of cast nickel alloys are determined by amount and shape of carbide phases in the matrix solution. Carbide particles, precipitating along crystallite boundaries, prevent intergrain slippage at high values of temperature and stress and increase creep resistance and long-term strength of



the metal. At the same time, they decrease ductility and durability of metal.

At relatively slow cooling of casts or components, being renovated by brazing, carbides Me_{23}C_6 of complex shape (mainly on the basis of chromium) form in the cast metal, which are the source of origination of cracks and stipulate reduction of ductility and fracture toughness at low temperature. In the process of solidification concentration of internal stresses occurs due to difference of thermal coefficients of linear expansion of the matrix and carbide phases, which also reduces resistance to fatigue. At low content of carbon in cast metal ($< 0.02\%$) carbides acquire orbicular shape instead of that of hieroglyphs, which enables growth of HTA ductility [8].

Isothermal brazing at high ($> 1180^\circ\text{C}$) temperature in vacuum is an effective method for repairing components of hot duct of state-of-the-art turbine engines and installations. Selection of rational systems of brazing alloys, where silicon and boron in combination with powder fillers from multicomponent nickel HTA (of Rene-142, JS6U and JS32 type) are present as depressants, allow in combination with a finishing vacuum heat treatment renovating single and complex components of turbine nozzle guide vanes and nozzle doors, which underwent in the process of their operation heat-fatigue fracture, etc.

Materials and methodology of the experiment.

For producing of the alloy JS26VI BJ by the method of resistance isothermal brazing in vacuum, prefabricated cast plates of 6 mm thickness, having size 45×100 mm, were used. The plates were produced with equiaxial solidification. After the plates were split into thinner billets of 2.6–2.8 mm thickness, they were ground and subjected to vacuum annealing at temperature 1220°C for 1 h. Pressure of residual gases in the chamber constituted not more than $5.6 \cdot 10^{-3}$ Pa. For producing BJ by the method of resistance brazing 12×21 mm plates were used. Filling of gaps, having length about 10 mm and width 550–600 μm , which were made in the 13×60 mm billets by means of spark cutting, was also used. Incised billets were blown by powder SiC and repeatedly annealed.

The plates had arbitrary structure of growth. Prevalent orientation of dendrites in the solidified metal is stipulated by accompanying heat dissipation during pouring into the mould. In formation of BJ factor of dendrite growth orientation in the billet was not taken into account, and butting of the plates, which constituted future joint, was arbitrary. So, BJ was produced from the metal of equiaxial solidification.

Composition from a low-melting component on the basis of system Ni–Co–Cr–Al–2.5 % B (#1) and powders of cast HTA Rene-142 and JS6U was used as a basic brazing alloy. Traditional application of the Rene-142 alloy powder as a filler is stipulated by the fact that tungsten, tantalum and rhenium enabled as the main alloying additives reduction of diffusion mobility of components in the melt and increase of

the interatomic bond energy in the seam metal. Application of the JS6U alloy powder as a filler of the brazing alloy allowed bringing nearer chemical composition of the brazing mixture to that of the basis.

Experience of work with BJ, produced with application of boron-containing brazing alloys, containing powder Ni–12 % Si as a depressant, and with repair of the aviation turbine engine (AGTE) doors from casting alloy VJL12U showed doubtless advantage of the former brazing alloys [9]. Being in solid solution of the seam metal, silicon exerts influence on the shape of carbide phases being precipitated and suppresses formation of primary carbides of «Chinese font» type, reduces dissolution temperature of carbide phases in the matrix, enables precipitation of finer carbide fractions, and disperses carbide phase within the volume of a polycrystal and over boundaries of solidified grains of the seam metal.

For isothermal brazing of alloy JS26 several compositions of brazes, containing additionally commercial brazing alloy NS12 as an additive, and compositions without this alloy were considered. The main filler in brazing mixtures was powder of alloy Rene-142 (Figure 1): 40 % #1 + 60 % Rene-142; 20 % #1 + 20 % NS12 + 60 % Rene-142; 25 % #1 + 15 % HS12 + 60 % Rene-142; 40 % #1 + 30 % Rene-142 + 30 % JS6U.

The brazing alloy was applied on contacting surfaces of the billets, and they were compressed at the force 30 N or the slot was coated, pressing brazing mixture inside. Technological process of the brazing was invariable, and stepwise condition of heating was used [10].

Maximum temperature of brazing in different experiments was $1210\text{--}1230^\circ\text{C}$. Depending upon temperature, duration of isothermal seasoning at T_{max} was 30–10 min; as temperature increased, time of brazing reduced. Brazed specimens were subjected to the final heat treatment. Optimization of vacuum annealing conditions was the most crucial task.

In addition to estimating mechanical properties of BJ, short-term and long-term strength of the base metal — alloy JS26VI — was investigated in the state of supply and after two options of heat treatment of BJ specimens. Both options included homogenization annealing of BJ at 1160°C for 2 h, which allowed redistributing alloying elements in the solution and enabled dissolution of course primary carbide phases and equalization of sizes and shape of the strengthening γ -phase; and ageing at temperature 1050 (2 h) and 900°C (3 h), causing additional precipitation of sub-dispersed γ -phase from solid phase, volume share of which determines strength and ductility of HTA.

Experimental results. Results of mechanical tests of the alloy JS26 showed that heat treatment of the basic alloy according to the conditions, close to those of heat treatment of the BJ metal (annealing at 1220°C , 1 h + 1160°C , 2 h + 900°C , 3 h) increased a little tensile and yield strength of the alloy, ensuring mechanical properties, characteristic of JS26 of equiaxial solidification (Table 1) [4].

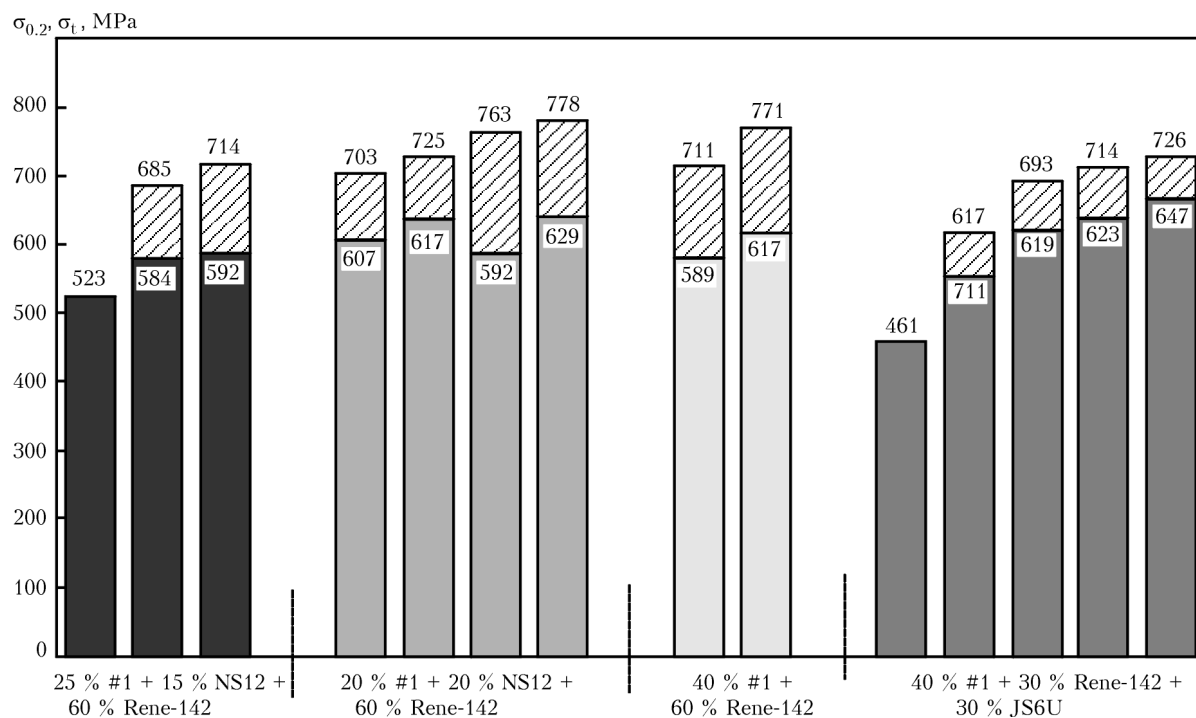


Figure 1. Strength of JS26VI alloy BJ produced by resistance brazing method at 1220 °C for 15 min in vacuum of $8 \cdot 10^{-3}$ Pa with application of composite boron-containing brazing alloys without silicon and with addition of silicon in form of powder of alloy Ni-12 % Si (lower figures designate $\sigma_{0.2}$; upper ones — σ_t)

Influence of different thermophysical conditions of brazing $T_{br} = 1220$ °C, 15 min and 1230 °C, 10 min can be seen in Figure 2, where results of statistical processing of BJ mechanical tensile test data, obtained with application of complex brazing alloy with 20 % NS12, are compared. Increase of brazing temperature by 10 °C caused reduction of ductility and strength values of the seam metal and fusion line of BJ of alloy JS26.

More than 70 % of specimens, produced at $T_{br} = 1230$ °C, had strength 450–550 MPa and zero ductility. At the same time, 85 % of specimens produced at $T_{br} = 1220$ °C, 15 min, combined satisfactory strength (650–800 MPa) with relative elongation (3–13 %). Q -factor of brazed joints equaled $Q = 83$ –110 %.

Increase of the brazing temperature by 10 °C unambiguously caused insignificant increase of yield strength (more alloyed solid solution) and reduction of ductility and ultimate strength of the seam metal. Resistance brazing of plates at 1220 °C within 15 min brought much better result in comparison with seasoning for 10 min at 1230 °C (Figure 2).

Increase of the brazing process temperature did not guarantee improvement of BJ functional characteristics. In case of brazing at 1220 °C metal of the seam preserved density of its structure. At a higher brazing temperature inclination increased to sweating of eutectic component of the solidified brazing alloy from the seam metal in high-temperature homogenization annealing (1160 °C, 2 h), which caused loss of the seam strength.

For BJ formed at 1230 °C, 10 min, two modes of final annealing were used: two- (1160 °C, 2 h + 1050 °C, 2 h) and single-stage (1080 °C, 2 h) ones. Single-stage annealing brought worse results concerning ductility of BJ for both options of brazing alloys. Fracture occurred below yield point. At the same time, a portion of BJ, annealed according to two-stage scheme, demonstrated satisfactory ductility — relative elongation constituted 2.3–8.0 %. So, brazing temperature 1230 °C for the brazing alloy with 20 wt.% NS12 is a threshold one. Selective sweating of low-melting brazing alloy fraction from the seam metal causes occurrence of porosity in it and, accord-

Table 1. Results of mechanical tensile tests of specimens of alloy JS26 after different conditions of heat treatment

Specimen No.	Conditions of heat treatment	Cross-section of specimen, mm	$\sigma_{0.2}$, MPa	σ_t , MPa	δ , %
G1	Initial	5.33	644.0	773.0	16.2
G2		5.21	659.0	738.0	8.5
G3	1210 °Ñ, 1 h + 1160 °Ñ, 2 h + 1050 °Ñ, 2 h	5.17	578.7	719.0	13.2
G4		5.19	567.0	705.0	8.5
G5	1210 °Ñ, 1 h + 1160 °Ñ, 2 h + 900 °Ñ, 3 h	5.27	670.0	774.4	13.2
G6		5.17	683.0	872.8	8.5

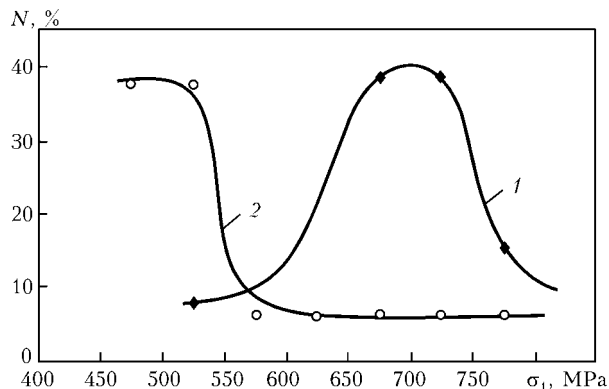


Figure 2. Statistical curves of distribution of strength values of JS26VI alloy BJ produced with application of brazing alloy #1 + 60 % Rene-142 with addition of 20 % NS12 at $T_{br} = 1220$ °C, 15 min (1) and 1230 °C, 10 min (2): N — number of specimens

ingly, reduction of strength and ductility of the BJ metal.

Strength of BJ, produced with application of different brazing alloy systems, was 685–771 MPa ($\bar{\sigma}_t = 721$ MPa). Stability is achieved of high strength values of BJ, produced with application of a complex brazing alloy with 20 % NS12, in comparison with the joints, produced with application of the base brazing alloy 40 % #1 + 60 % Rene-142 (see Figure 2). The base brazing alloy does not ensure reserve of ductility for the joints, subjected to brittle tension fracture. Such effect is connected with migration of boron to the fusion line at brazing temperature. Accumulation of boron near the fusion line is the main reason of this negative phenomenon.

High density of short-term strength values of metal of BJ, produced with application in the brazing composition of powder NS12, attracted our attention.

Main result consists in the same level of strength of the joints, determined by structural state of the metal being brazed, i.e. by conditions of final heat treatment of BJ. In BJ, produced with application of complex brazing alloy with 20 % NS12, fracture occurred, as a rule, over the base metal or over the fusion line, whereby relative elongation of the joint specimens equaled 7–18 %.

According to the adopted technology, final annealing after isothermal brazing and quick cooling consisted of two stages: 1160 °C, 2 h + 1050 °C, 2 h. Mechanical properties of the base metal after mentioned heat treatment are given in Table 1 and correspond to the results of tensile tests of BJ. Coincidence of yield strength values of BJ and base metals is close to the ideal one.

Strengthening of the matrix is ensured due to precipitation in solid solution of intermetallic phases of a complex chemical composition. As far as ultimate strength is concerned, here enters into competition structure of grain boundaries of the metal being brazed and morphology of the phases being precipitated in the thermal diffusion interaction (chemical erosion) zone.

Influence of the final ageing conditions on physical-chemical properties of the BJ metal can be seen in Figure 3. The main result consists in the fact that all BJ, annealed at 900 °C, 3 h, had higher level of strength and somewhat lower ductility in comparison with the specimens, annealed at 1050 °C, 2 h.

Another result consists in the fact that BJ, produced with application of a complex brazing alloy containing 20 % NS12, are characterized by high technological ductility at room temperature and more intensive work needed for fracture of the specimens in tensile tests.

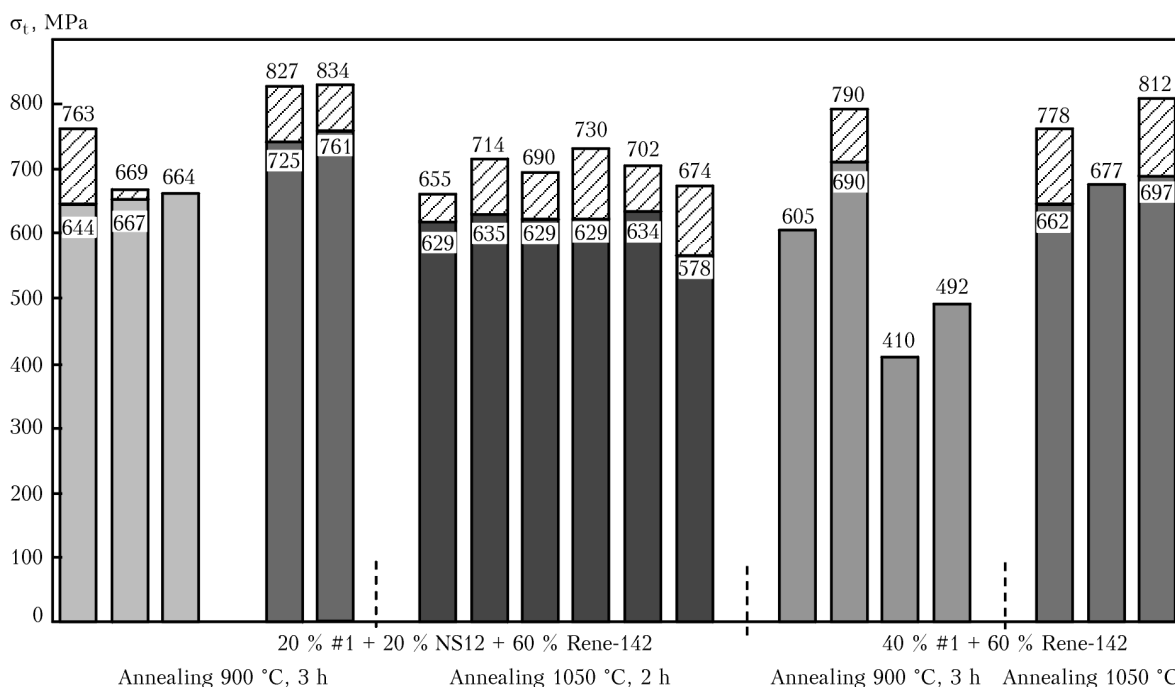


Figure 3. Yield and tensile strengths at 20 °C of JS26VI alloy BJ produced by method of resistance isothermal brazing at 1220 °C for 20 min in vacuum of $5.5 \cdot 10^{-3}$ Pa with application of base brazing alloy 40 % #1 + 60 % Rene-142 and complex brazing alloy with addition of 20 % NS12 (lower figures designate $\sigma_{0.2}$; upper ones — σ_t)



BJ of alloys VJL12U and JS6U, produced by the same brazing alloys under similar thermophysical conditions, had σ_t by 100 MPa higher than that of the joints of alloy JS26VI (Table 1) [9]. Seam metal chemistry of joints of these alloys is approximately the same (due to identity of the brazing mixtures). So, strength of the BJ seam metal of alloy JS26 should be higher than strength of the metal to be brazed, which is registered in a real experiment in tensile tests.

The alloy JS26 BJ fracture sites became defects of base metal structures near the fusion line. Occurring in the base metal cracks near carbide particles or in very carbides propagate in the seam metal over grain boundaries, which have excessive precipitations of carbide phases.

As it follows from Figure 3, final ageing performed at 1050 °C, 2 h and 900 °C, 3 h, guaranteed, approximately, the same level of yield and tensile strength of metal of BJ, for production of which a complex brazing alloy with silicon was used. At the same time, ageing at 900 °C, 3 h embrittled BJ metal on the basis of the base brazing alloy. Annealing at 1050 °C, 2 h allowed producing BJ, fracture of which occurred over the base metal (elongation 6.5–8.5 %) at average strength 756 MPa.

Statistical processing data of test results of the array of JS26VI alloy specimens, produced by composite brazing alloys without silicon and containing as a low-melting component commercial brazing alloy NS12, are given in Figure 4. Presented dependences generalize results of mechanical tensile tests of BJ metal specimens of equiaxial solidification after different options of final heat treatment.

Higher ductility at 20 °C had BJ, for formation of which a complex brazing alloy was used; 50 % of specimens had yield strength 600–650 MPa and ultimate strength 650–700 MPa.

Sharp peak of the yield strength curve (Figure 4) confirms good quality and stability of technological process of the brazing. In this case (more than 50 % of specimens) BJ are able to deform plastically at 20 °C up to final fracture.

The diagram clearly registers ability of BJ to withstand a certain plastic strain, because on presented curves significant difference (up to 100 MPa) between values σ_t and $\sigma_{0.2}$ of tested BJ is presented. Blurred maximum of curve σ_t in comparison with curve $\sigma_{0.2}$ indicates presence of technological deviations in the process of brazing. Probably, there was difference in granulometric composition of the brazing alloy or in the conditions of the brazing mixtures producing in brazing of different specimens. This may cause either reduction of BJ strength, or ensure for them maximum possible value of Q-factor.

Microstructure peculiarities of fracture. Interconnection between mechanical properties of BJ and microstructure of used brazing alloys was investigated by fractograms of tested specimens, which reflected most accurately character of BJ fracture in loading.

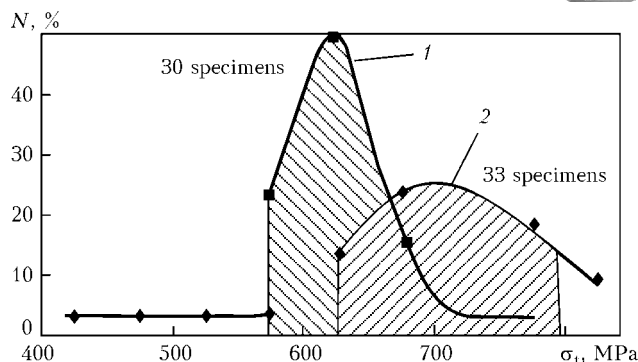


Figure 4. Statistical curves of distribution of yield (1) and tensile (2) strengths of BJ produced by isothermal brazing at 1220–1225 °C of JS26VI alloy after different kinds of heat treatment in course of tests at 20 °C: N — number of specimens

Example of brittle fracture of a BJ specimen of JS26 alloy at $\sigma_t = 460$ MPa and $\epsilon = 0$ %, produced by brazing with boron-containing brazing alloy # 1 with a filler from 30 wt.% Rene-142 + 30 wt.% JS6U at 1220 °C, 15 min, is given in Figure 5, *a, b*. In BJ fracture porosity is discovered, which weakens section of the specimen. This became the reason of low BJ tensile strength. Fracture occurred as a result of confluence of discontinuity flaws in plastic zone before apex of the crack. Fracture mechanism of the joints is a normal tear [11].

Fracture pattern of the BJ specimen with relative elongation $\epsilon = 7.5$ % is illustrated in Figure 5, *c*. Brazing alloy with 20 % NS12 was used in resistance brazing of this specimen. Failure of the base metal was combined with that of the seam metal in the fracture. Crack in the BJ specimen occurred on the surface (near the defect) of the base alloy, when such brazing alloy was used, and caused final fracture of the joint in the place of the base metal transition into the seam.

Similar picture of BJ fracture was obtained in another experiment (brazing with complex brazing alloy at 1220 °C, 20 min; annealing at 1160 °C, 2 h + ageing at 900 °C, 3 h). Elongation in tensioning of the specimen constituted 10.8 % (Figure 5, *d*). BJ fracture was initiated in the base metal near the fusion line and transferred into the seam metal at final stage of fracturing.

Mixed character of fracture of BJ, produced by a complex brazing alloy, in tension indicates that main crack passed not only over the seam metal, but also touched volumes of the metal being brazed (Figure 5, *g, h*). In the fracture islands of failure, adjacent to the base metal (Figure 5, *e*) or the fusion line (Figure 5, *f*), are present. The same pattern of failure was detected in the BJ specimen with 13 % elongation. In the fracture of this specimen ($\sigma_t = 762.6$ MPa) metal of the brazed seam (20 % NS12 + 20 % #1 + 60 % Rene-142) underwent tough fracture at the microlevel.

Fractures of the BJ specimens demonstrate different amount of carbide phase, detected over grain boundaries in brazed seams without and with addition

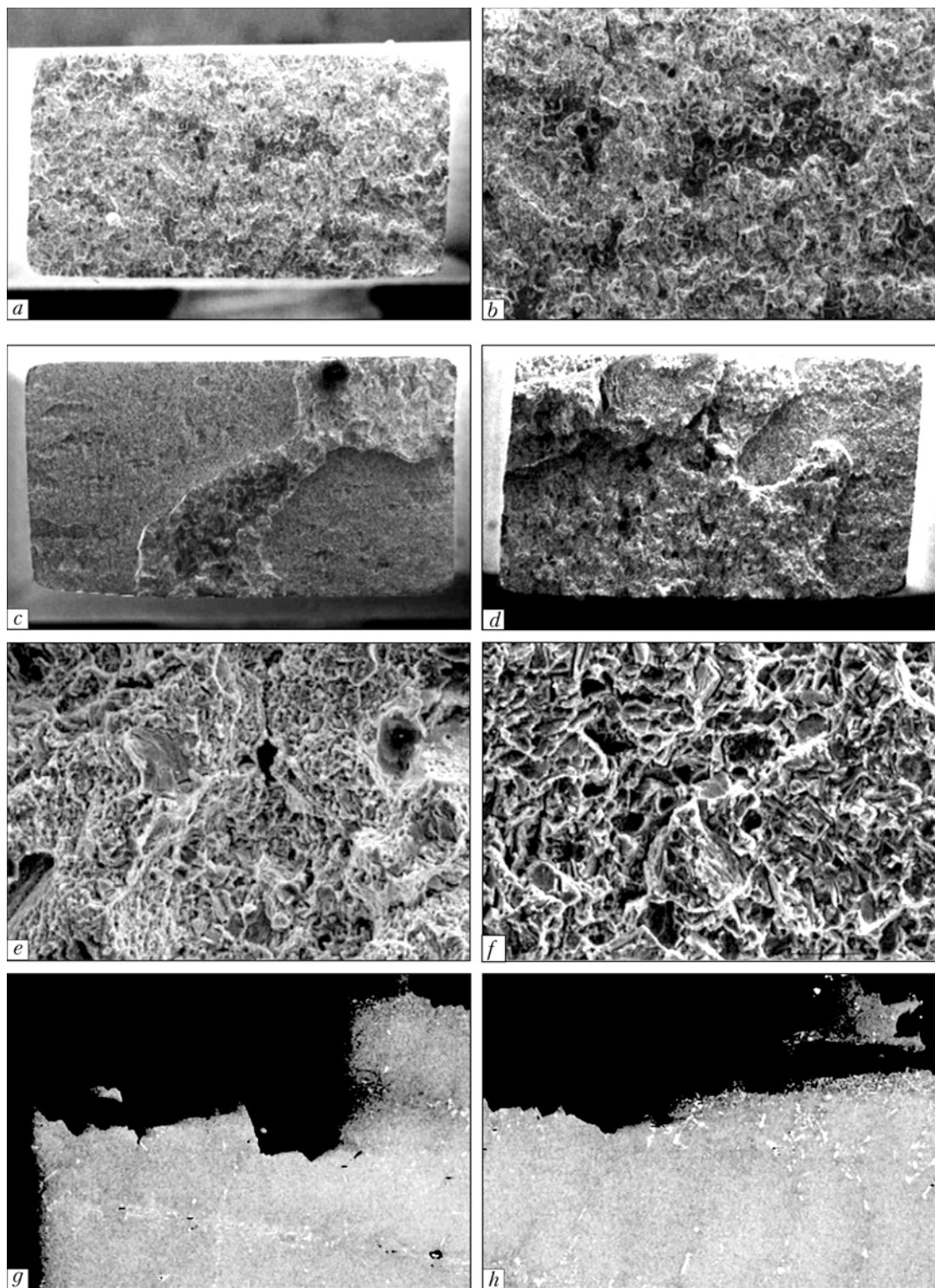


Figure 5. Fracture pattern in short-term strength tests of specimens from JS26VI alloy with BJ formed with application of composite brazing alloy 40 % #1 + 60 % Rene-142 (*a, b*) and 20 % #1 + 20 % NS12 + 60 % Rene-142 (*c–g*): *a, b* — brittle fracture over seam metal of specimen; *c, d* — combined fracture over base metal and further into seam metal (with maximum plasticity $\delta = 7.5\text{--}10.8\%$); *e, f* — fracture of seam metal and diffusion zone in base metal; *g, h* — flat pattern of crack propagation in specimen with BJ; *a, c, d* — $\times 26$; *b* — $\times 50$; *e, f* — $\times 500$; *g* — $\times 120$; *h* — $\times 200$

of 20 % of silicon-containing brazing alloy. Higher amount of carbides in the seam matrix is observed in case of a traditional brazing alloy without silicon. Carbide particles, located over grain boundaries, enable transfer of plastic deformation from a grain to a grain in loading, contributing to uniform plastic flow of the polycrystalline aggregate.

Fractograms of the BJ fracture surface confirm conclusion that the higher is elongation of a BJ, the higher is its strength. Toughness of a joint is determined by ability of the material for plastic deformation.

Long-term strength. According to GOST 10145081 long-term (50 h) strength of JS26VI alloy



Table 2. BJ working life of JS26VI alloy at 900 °C produced by brazing of gaps up to 600 µm width at temperature 1225 °C for 20 min after different conditions of ageing

Specimen No.	Type of brazing alloy	Final heat treatment of BJ before test	$\sigma_{t-9.8^{-1}}$, MPa	τ , min	ϵ , %
OG1	Base metal	1220 °C, 1 h + 1050 °C, 4 h	45	70	0.75
OG0			40	115	1.28
OG2			35	300	3.3
ZG4	20 % #1 + 20 % NS12 + 60 % Rene-142	1160 °C, 2 h + 1050 °C, 2 h	20	105	1.4
ZG1		1160 °C, 2 h + 900 °C, 4 h	20	60	0.7
ZG2			20	90	0.4
ZG3			20	90	2.1
ZG6			20	70	2.6
ZG9	40 % #1 + 60 % Rene-142	1160 °C, 2 h + 1050 °C, 2 h	20	70	0.37
ZG5			20	260	1.5
ZG7			20	75	0

(of equiaxial solidification) should constitute at the test temperature 900 °C not less than 422 MPa (on average 450 MPa), whereby 100-hour long-term strength constitutes not less than 373 MPa (on average 402 MPa).

In testing of specimens of the base metal JS26VI at 900 °C 50-hour long-term strength should be achieved at the level of applied stresses 420–425 MPa [12].

To BJ specimens twice lower stress (196 MPa) was applied than to specimens from the base metal, and main influence on difference in properties exerted chemical composition of the brazing alloy (Table 2).

In the course of long-term strength tests in this work BJ were used with a fixed gap of 600–800 µm width. In this way long-term strength of solidified metal of the BJ developed seam was determined.

Long-term strength tests were performed at temperature 900 and 950 °C. Results of BJ tests, obtained in two experiments, are given in Table 2.

Working life of BJ, produced by a brazing alloy without addition of NS12, is noticeably higher than that of BJ, produced with application of a complex brazing alloy. Long-term strength of BJ, produced with addition of NS12, was characterized by high stability of results.

Two-stage heat treatment of all specimens included homogenization annealing at 1160 °C, 2 h, and at the final stage — ageing.

Conditions of ageing did not exert significant influence on long-term strength of BJ. Satisfactory working life was achieved in the specimens of BJ, which were subjected to final ageing at 900 °C for 3 h. Time till fracture of BJ of JS26VI alloy constituted 1.0–1.5 h at 900 °C and stress 196 MPa (20 kg / mm²) for a complex brazing alloy with 20 %

NS12. Working life of the only specimen constituted 4 h 20 min in case of the gap brazing by the base brazing alloy 40 % #1 + 60 % Rene-142.

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TITANIUM. PROBLEMS OF PRODUCTION. PROSPECTS.

Analytical Review. Part 1

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In first part of the review social-economic aspects of titanium metallurgy, cost of titanium products, problems of spongy titanium production, and potential possibilities of Ukraine and its role in the world titanium industry are considered.

Key words: titanium, distribution and application, ore resources and production capacities, cost of concentrates, cost of titanium sponge, formation of price on metal titanium, problems of spongy titanium production

Earth crust contains about 0.6 % of titanium [1]. As to its prevalence, titanium occupies fourth position after aluminium, iron, and magnesium. Titanium is characteristic of the combination of such valuable properties as low density, high level of specific strength, corrosion resistance, cold resistance, absence of magnetism, and a number of other valuable physical-mechanical properties. Due to its attractive properties titanium is used first of all in aerospace and military industry and in some civil branches, for example, in automotive industry, in production of engines for race cars, in suspension systems, fabrication of crankshafts, coupling rods and exhaust systems, in chemical industry, power engineering, ship building, medicine, etc.

Titanium has been used for more than 25 years in industrial and civil construction of Japan, whereby experience of this country is successfully introduced by architects in USA, Canada, Great Britain, Germany, Belgium and Peru.

According to data of analytical division of «Timet» — the biggest titanium company of USA — designs of construction structures with application of titanium are being developed in Switzerland, Singapore and Egypt. Another area of titanium application is production of sport commodities, for example, bicycles and sticks for golf.

About 10 % of world volume of titanium production consumption constitute wheelchairs, housings for computers and clocks, substrates of hard disks for computers, rims for glasses, and jewelry. In opinion of Edward Rosenberg, president of American jewelry company «Spectore Corp.», despite conservatism of jewelry producers, they lately equate titanium to such noble metals as platinum, gold and silver. Rosenberg considers that under favorable conditions production of mentioned branches may achieve not 10, but 35 and even 45 % [2].

The main obstacle on the way to expansion of the field of titanium application is its price. Production cost of titanium is several times higher than that of

aluminium. That's why owners of the plants look for less expensive methods of production, which may make their products more attractive for the most different markets.

Production of titanium products is a multistage, high-technology, and technologically complex process, which includes plurality of conversions. Ore-mining and dressing works (OMDW) produce the feedstock, dress it, process, and supply the concentrate to the enterprises that fabricate spongy titanium, which is then supplied to metallurgical enterprises that melt metal titanium, used for production of ingots, rolled stock, and press forming.

Let us briefly consider some social-economic aspects of titanium metallurgy, cost of titanium products, and potential possibilities of Ukraine and its part in the world titanium industry.

Period of prompt development of titanium metallurgy, which started late in 1950s, terminated by late 1980s that is stipulated by a number of reasons, the main of which were relaxation of confrontation between big political blocks and military tension, reduction of orders for armament, and deceleration of rates of economic development and subsequent recession in economy of a number of industrially developed countries. The highest economic recession and disintegration of titanium industry occurred in the countries that earlier constituted USSR. All this caused significant reduction of production of military material and civil aircraft in the world (on average by 800–500 pcs per year). As a whole, world demand for titanium reduced in 1990–1994 among main consumers — space and military aircraft construction industries — by 30–35 % [3].

Excess of supply over demand and followed after this fall of prices on the world market compelled to reduce production of titanium. In particular, in 1990–1993 production of concentrates (in recalculation into titanium dioxide) reduced by 555.6 thou t. Subsequent period (1994–2000) is characterized by a certain instability of production volumes and prices (Tables 1 and 2).

In production of another important component — titanium sponge — in technological chain of the titanium metallurgy USSR occupied in 1980–1990 first position in the world (80–95 thou t per year), sig-

**Table 1.** Volume of world production of rutile concentrates, thou t

Main countries-producers	Period, years				
	1995	1996	1997	1998	1999
All together	416.0	366.0	406.0	441.0	390.0
Including:					
Australia	195.0	180.0	214.0	241.0	190.0
SAR	90.0	115.0	123.0	130.0	130.0
Ukraine	112.0	50.0	50.0	50.0	50.0
Brasilia	1.985	2.018	1.742	1.8	1.8
Sri-Lanka	2.697	3.532	2.97	1.93	2.0
India	14.0	15.0	14.0	16.0	16.0

Table 2. Dynamics of average annual prices on titanium concentrates on market of West Europe, USD / t

Concentrate type	Period, years							
	1994	1995	1996	1997	1998	1999	2000	2001
Rutile, 95–97 % TiO ₂ , in bulk	420	<u>508.0</u> 467.5	<u>642</u> 548	<u>562</u> 504	<u>543.0</u> 492.5	<u>476</u> 437	<u>507</u> 454	<u>500</u> 470
Ilmenite, 54 % TiO ₂ , in bulk	77	<u>77.5</u> 71.4	<u>89.4</u> 80.1	<u>87.8</u> 77.3	<u>74.4</u> 69.0	<u>84.7</u> 76.5	<u>99.6</u> 80.6	<u>109.1</u> 89.1

Note. In numerator maximum, and in denominator minimum price is indicated.

nificantly exceeding similar indices in the USA. Disintegration of titanium industry caused reduction of world production of spongy titanium from 134.0 in 1991 to 46.7 thou t in 1994. Its production significantly reduced (by 1998 in comparison with 1990) in the USA — by 55.5, Japan — by 43.7, and USSR / CIS — by 61.7 %. Great Britain in 1993 and Ukraine in 1994 completely stopped production of titanium sponge. In Tables 3 and 4 change of volumes of titanium sponge production is presented both is the world (Table 3) and in CIS countries (Table 4) within the period 1991–1999. Respective changes of prices on titanium sponge are presented in Table 5.

Approximately from the year 2000 conjuncture of the world titanium market started to gradually im-

prove. Despite cyclic recessions characteristics of titanium industry, stable increase of demand for titanium may be noted. After a certain recession in 2003, sharp increase of the demand was registered in 2004–2005 and, therefore, increase of prices first on titanium feedstock and then on products, made from it. So, in 2004 prices on titanium scrap and ferrotitanium even exceeded those on titanium sponge, whereby cost of 70 % of ferrotitanium was 1.5–2.0 times higher than of titanium sponge. Such situation could not continue for a long time, and by early 2005 price on titanium sponge, according to the data of «Platt's Metals Week», constituted 21 USD / kg. According to estimations of different specialists, in 2005 and till September 2006 world prices on titanium sponge consti-

Table 3. World production of titanium sponge, thou t

Main countries-producers	Period, years								
	1991	1992	1993	1994	1995	1996	1997	1998	1999
All together:	134.0	94.1	67.0	46.7	52.5	56.3	70.8	70.5	60.6
Japan	18.9	14.6	14.4	14.8	16.7	21.1	23.1	24.2	19.2
USA	13.4	13.6	14.8	11.0	10.2	12.8	10.5	10.6	10.4
People's Republic of China	1.8	1.7	1.5	0.9	0.8	1.0	0.9	2.5	2.5
CIS countries	95.5	62.4	38.3	20.0	24.5	21.4	36.3	35.9	31.7

Table 4. Production of titanium sponge in CIS countries, thou t

Countries	Period, years							
	1992	1993	1994	1995	1996	1997	1998	1999
All together:	62.4	38.3	20.0	24.5	21.4	36.3	35.9	31.7
Russia	33.4	23.3	10.0	14.7	9.3	23.2	21.9	16.2
Kazakhstan	17.0	15.0	10.0	9.8	12.1	13.1	12.8	13.0
Ukraine	12.0	6.0	5.0	—	—	—	1.2	2.5

**Table 5.** Average annual prices on titanium sponge (titanium of grade TG-100, 12 × 25 mm) on market of West Europe, USD / t

1992–1993	1995	1996	1997	1998	1999	2000	2001
3.2 / 4.5	5.59 / 5.97	6.52 / 6.85	7.55 / 7.83	7.35 / 7.75	6.75 / 6.96	6.02 / 6.56	6.54 / 6.85

Note. In nominator minimum, in denominator maximum values are indicated.

tuted 25–30 USD / kg. By the end of 2006 it somewhat reduced (down to 22–24 USD / kg). The main reason of increased demand for titanium became termination of recession in economy of leading countries of the world. Returned to life plans of construction of big civil aircraft, whereby specific consumption of this metal per unit of the product increased; in metallurgy increased demand for titanium feedstock for microalloying of steels; started construction of plants for water desalination in Near East, petrochemical plants in China, etc.

In connection with increased demand volumes of titanium production increased; the enterprises, which were earlier shut down, renewed their operation. So, in Ukraine as far back, as in 1998 production of titanium sponge was renewed at Zaporozhie Titanium-Magnesium Works (ZTMK Company). While in 1998 production of the sponge constituted only 1.2 thou t, in 2001 it achieved 4.5 and in 2005 — 8.4 thou t. In Japan company «Sumitomo Titanium Corp.» returned in 2004 to full-scale production in amount of 18 thou t per year, having started operation of furnaces, which were earlier shut down. Russian company «VSPMO-Avisma» increased production of sponge from 14.37 in 2000 to 20.1 thou t in 2004.

In September 2005 J. Martin — chairman of board of the biggest titanium US company «Timet» — presented in his annual report [14] data on current state of the world titanium market and forecast of analysts till 2010. Presented statistical macroeconomic indices (Figure 1) convincingly prove growth of activity of market of titanium products not just in aerospace and military branches of industry (163 %), but also in oil-and-gas (803 %) and chemical (2288 %) industries. In Figure 2 real (2004) and expected (till 2010) consumption of titanium rolled stock is presented. It is necessary to note forecasted increase of titanium consumption volumes from 61.8 in 2004 to 86.0 thou t in 2010. It is assumed that it will take place first of

all due to civil aircraft building (where consumption will grow at least till 2009) (1), annual increase, approximately by 3 %, of industry demands of Near East countries and China (3), and oil-and-gas industry of developing countries (4) (Figure 2).

To increase fabrication of titanium products it is necessary, first of all, to use available capacities and explored ore resources.

At present main world capacities for production of titanium sponge (semi-manufactured products for producing ingots and rolled stock) are concentrated in CIS countries — Russia, Kazakhstan, and Ukraine (from 60 [3] to 70 % [5] of the world capacities).

According to estimation of Japanese company «Toho Titanium», loading of world capacities, producing titanium sponge, constituted 69 % in 2001 and continues to grow. In Table 6 available capacities of some producers of sponge and production volumes are presented.

As to titanium reserves, CIS countries occupy first position in the world. Titanium commercial reserves are explored in Russia, Ukraine and Kazakhstan. In Table 7 data on confirmed titanium reserves of these countries are presented.

Extracted from bowels titanium ores are either dressed with production of selective ilmenite, rutile, anatase, and leucoxene concentrates, containing up to 45–70 % TiO₂, or subjected to melting with output of titanium slag (up to 85 % TiO₂) and cast iron, or processed into synthetic rutile. The most high-quality feedstock for production of two main kinds of products (metal titanium and pigment titanium dioxide) is rutile (92–98 % TiO₂), ilmenite (43–70 % TiO₂), and anatase (90–95 % TiO₂). Rutile and anatase, in contrast to ilmenite, do not require for preliminary dressing by means of conversion into intermediate products. Of the whole produced titanium ore only 5 % goes directly for production of metal titanium, the rest 95 % are used in production of dyes, plastics, rubber, paper, etc.

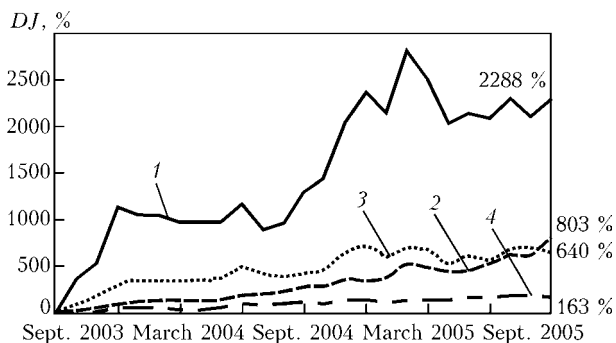


Figure 1 [4]. Activity growth of market of titanium products in chemical (1) and oil-and-gas (2) industries, metallurgy and machine building (3), and aerospace and military (4) branches of industry; GJ — industrial index of Dow Jones

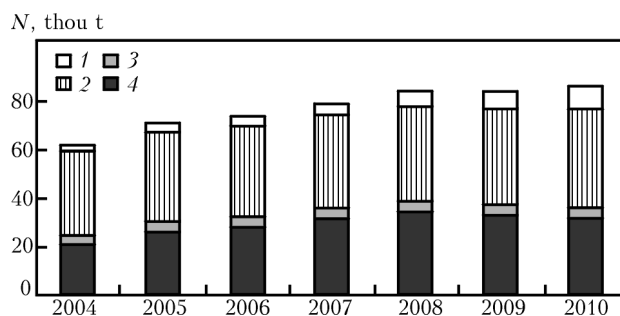


Figure 2 [4]. Consumption *N* of rolled titanium: 1 — oil-and-gas industry of developing countries; 2 — industry of Near East countries and China; 3, 4 — military and civil aircraft construction, respectively

**Table 6** [6]. World production of titanium sponge in 2001

Country	Company	Capacity, thou t / year	Production, thou t
Japan	Sumitomo Titanium Toho Titanium	27	25.6
Russia	Avisma	25	18.0
Kazakhstan	UKTMK	20	12.0
USA	Timet	9	8.0
Ukraine	ZTMK	18	4.5
China	—	3	2.5
All together		102	70.6

In Table 8 data on extraction of titanium ore, used for production of metal titanium, are presented.

Main producers of ilmenite and rutile concentrates are Australia, SAR, Canada and Norway, the share of which constitutes 74–78 %. In CIS countries monopolist in production of the concentrates is Ukraine (about 8 % of the world production).

The biggest producers of titanium sponge Japan and Russia (Table 6) depend upon external factors, because they do not have their own raw materials. For example, small amount of titanium raw materials, produced by Lovozero OMDW «Sevredmet» and Kurnakha mine «Amurtitan» Ltd. (RF), does not meet needs of metallurgical production of the metal. Practically the whole ore feedstock (ilmenite concentrate) is supplied from Ukraine. One of the reasons of this (in addition to disintegration of titanium industry of the former USSR) is low content of titanium dioxide in the extracted ores. So, loparite concentrate, produced in processing of the Lovozero deposit ores, contains 0.6 % TiO_2 , while Irshansky ilmenite from Ukraine — 57.0–59.5 % [3]. Titanium industry of Russia depends upon supplies of not just raw materials (concentrates and sponge) from Ukraine, but also spongy titanium from Kazakhstan. Application of own and imported raw materials allowed Russian company «VSMPO-Avisma» becoming the biggest supplier of leading aircraft construction companies of the world. Its share constitutes 65 % of titanium products of the biggest in Europe concern «Airbus» and 35 % [5] (according to other data 50 % [7]) of American company «Boeing» (by 2008 it should increase up to 70 %).

Ukraine, in opinion of western experts, has high possibilities for increasing its part in the world titanium industry. Feedstock potential of the country is estimated at the level 900 mln t of ilmenite and rutile, which corresponds to 30 % of registered world reserves [3].

However, after 1991 Ukraine lost an essential link in the technological chain of metal titanium production — production of titanium ingots. Mining and processing enterprises (Volnogorsk and Irshansk OMDW, ZTMK) became mainly suppliers of the feedstock abroad. So, on the basis of Irshansk deposit a consortium for production and processing of ilmenite was organized (approximately 200 thou t / year), 50 % of which will be supplied to American company «Kerr-McGee Chemical Corp.» [3]. Zaporozhie Titanium-Manganese Works also exported 95 % of its products in 2003–2004 [5].

Table 7 [3]. Confirmed reserves of titanium in CIS countries

Country	Number of deposits	Share in general reserves of CIS countries, %
All together in CIS:	19	100.0
Russia	13	58.5
Ukraine	4	40.5
Kazakhstan	5	1.0

The enterprises, which produce titanium pipes (Nikopol) and rolled sheet (Alchevsk, Mariupol), got dependent upon external supplies.

In 1994 state program «Titanium of Ukraine» was adopted, in which, in particular, establishment of titanium ingot production was envisaged. Opinions concerning scheme of this production divided. One of the options envisaged selection of a traditional, repeatedly checked technological scheme, based on the titanium sponge pressing into a consumable electrode and its subsequent vacuum-arc remelting (VAR), the method which is sufficiently substantiated, because it is well developed [7], checked, etc. Greater part of titanium ingots is produced according to this scheme in Russia, USA, and other countries. As it is noted in [8], this method «is deemed faulty» under conditions, when for fabrication of a consumable titanium electrode for VAR powerful expensive press-forging equipment is needed, which is not available in Ukraine. First of all, recreating brought to perfection traditional technology, Ukraine will lag behind in development and will be compelled to compete with producers of titanium ingots in cost of the products only due to the cheap labor. During this time other countries, developing new alternative technologies, will go far ahead.

One of such alternative technologies is electron beam remelting. Production of ingots according to this technology was mastered in established in 1966 research-and-production center «Titan» of the E.O. Paton Electric Welding Institute the NASU [9]. In 2003 melting capacities of company «Antares» were constructed and commissioned. General production of titanium ingots in Ukraine in 2002–2004 is presented in Figure 3. Ukrainian titanium industry, which continues to increase its capacities, envisages establishing in ZTMK in

Table 8 [6]. Production of titanium ore in world in 2001, thou t

Region	Ilmenite	Rutile
Australia	1190	220
South Africa	1000	90
Canada	720	—
USA	300	Is included into ilmenite
Norway	270	—
Ukraine	240	55
India	200	15
Other countries	320	4
All together in the world	4200	380



Figure 3 [9]. General production of titanium ingots M in Ukraine by years: 1 — output; 2 — use in Ukraine

2006–2008 one more line for production of titanium ingots by the method of electron beam remelting. It is envisaged to produce at the first stage up to 2000, and by the year 2012–4500 t/year [10].

As it was noted at the first international conference «CIS market of ferrous metals'2006», which was held in Yalta in May 2006, at present vertical integrated titanium production chain is still not available in Ukraine. A unified association, similar to Russian «VSMPO-Avisma», does not exist. Enterprises of titanium industry of Ukraine are involved into internecine war, for example, between RPC «Titan» and company «Fico», due to which production of titanium ingots at the latter is stopped; between ZTMK and company «Antares», which jointly with Zakarpattia Metallurgical Plant (ZMZ) fights for deficient feedstock — titanium sponge. Monopolistic manufacturer of this product in Ukraine — State enterprise ZTMK refused to supply the feedstock to the latter two enterprises in 2005. Kiev plant of company «Antares», which remained without the feedstock, was completely shut down in 2005. Because of the same reason, as it was informed in [10], ZMZ stands idle 27 days a month, and advanced producer of the ingots RPC «Titan», attached to the E.O. Paton Electric Welding Institute, operates on customer-owned raw materials. At the same time Russian company «VSMPO-Avisma» bought Ukrainian plant «SETAB-Nikopol», producing titanium pipes [11].

Lately publications started to appear in mass media [12, 13] about foulness of priorities of state program «Titanium of Ukraine» and program of devel-

opment of ferrous metallurgy of Ukraine for the period up to 2010. Authors of these publications consider that needs of Ukraine consist not in titanium ingots, but in redesign of mining and processing enterprises and replacement of outdated equipment; it is necessary to develop production of not metal titanium, but of pigment titanium dioxide for chemical industry.

Redesign of enterprises and replacement of outdated equipment are, certainly, necessary, as well as attraction of wide investments. However, specificity of titanium production economy is such that extracting assets play in titanium industry insignificant part, almost the whole added value is formed at metallurgical enterprises. Maximum income both in chemical and metallurgical industry get enterprises, producing final products. That's why one has to orient himself at production of not chemical feedstock — pigment titanium dioxide (about 2 USD / kg) — or even metal semi-manufactured product — titanium sponge (about 22 USD / kg), but at production of varnishes, dyes, titanium ingots, rolled stock, and items from them. It is not by chance that Russia, which has a big number of titanium ore deposits, prefers to buy in Ukraine concentrate of higher quality and sponge, having established priority of producing final products from metal titanium.

Let us consider formation of price on titanium. In Table 9 structure of cost of titanium by main process stages is presented [14]. As one can see from the Table, main expenses are connected, firstly, with processing of the sponge into rolled stock (48–62 % of the rolling cost) and, secondly, with the process of direct production of the sponge — magnesium-thermal reduction and separation (26.0–34.9 %). Analysis of the titanium sponge cost structure, presented in [15] (Table 10), differs somewhat from data of Table 9, but there is no doubt that second in cost process stage is magnesium-thermal reduction of titanium.

Expenses, connected with double remelting of titanium (Table 9), can not be considered indicative, because these are data of applicants [16], which propose new method of production, but not expenses in the established technological cycle. Of course, real expenses of remelting are higher, especially if to take into account expenses, incurred in manufacturing of consumable electrodes for vacuum-arc remelting. According to [17, 18], cost of spongy titanium and master alloy, from which a consumable electrode is pressed, constitute from 40 to 75 % of the ingot cost.

High expenses of mentioned process stages are explained by application in the process of production of a number of expensive materials (magnesium, chlorine, argon, etc.) and complexity and high specific material and power consumption of the technological processes. That's why significant reduction of the titanium cost is possible only due to retrofitting of technological processes of various process stages or their replacement for a cheaper method of production.

Search of new methods of titanium reduction is performed by many companies. So, for example, Ital-

Table 9 [14]. Structure of titanium cost by main process stages, %

Technological process	Share of expenses [21]	Calculated data	
Production of concentrate	4	3.5	4.1
Production of slag	8	1.9	2.2
Production of titanium tetrachloride	8	2.1	2.5
Magnesium-thermal process	26	34.9	28.8
Production of titanium sponge as a whole	—	47.0	38.0
Primary melting	12	—	—
Final melting	2	—	—
Production of rolled stock	48	52.9	62.0



ian company «Electrochimica Marco Ginatta» develops technology for production of powdery titanium by electrochemical method [19]. The reduction process is performed in two stages. At the first stage titanium tetrachloride is reduced to titanium dichloride, and at the second stage takes place final electrolytic reduction up to high-purity crystals. Process of electrolysis proceeds in the melt of sodium chloride and titanium dichloride at 800–870 °C. The company intends to produce high-purity titanium at production cost, which will be by 30 % lower than in case of using the traditional method [19, 20].

Another development is so called method «FFC Cambridge process» or «Fray process», proposed by employees University of Cambridge. Essence of the patented process consists in electrolytic reduction of titanium dioxide in calcium chloride melt [21]. In FFC-process cathode plates, manufactured from titanium dioxide and a binding substance, are placed into the pool of molten calcium chloride together with graphite anode. In the process of electrolysis oxygen is removed from titanium oxide in the form of free oxygen, CO and CO₂, leaving on the cathode pure titanium. The process is performed at the temperature 900–950 °C under just 3 V voltage [14, 22].

It is assumed that cost of spongy titanium in such method of production may reduce more than twofold and approach cost of primary aluminium and magnesium. This technology envisages production of not just pure spongy titanium, but also of a sponge, alloyed by different elements, for production of titanium-base alloys, which is one of the most important advantages of the new process. On the way to its application on commercial scale certain success is achieved. In 2003 American Defense Advanced Research Projects Agency allocated 12.5 mln USD to consortium, headed by company «Timet», for introduction of this process into commercial production.

One more new method for electrochemical production of chemically active metals, including titanium, is proposed, in which solid oxide membranes are used [23]. Essence of the liquid-phase process consists in performance of electrochemical decomposition of mixed titanium oxides, such as molten titanium slag, ilmenite, perovskite, leucosene, titanite, natural and synthetic rutile, which are in liquid state.

In the course of the process on the cathode molten titanium or titanium alloy with other components of

Table 10 [15]. Structure of spongy titanium cost

Process stages	Share of general expenses, %
Production of titanium slag	4–6
Charge preparation	4–6
Production of titanium tetrachloride and its cleaning	30–33
Magnesium-thermal reduction, vacuum separation and cropping of spongy titanium blocks	55–60

initial material, and on porous or gas-diffusion anode oxygen are released. The anode is separated from the melt, which has high temperature, by solid ion membrane, which is able to transfer electrolyte anions to the anode. A graphite consumable electrode may be used as the anode. Inert anode of constant size or gas-diffusion anode, to be installed and removed at different stages of the cycle, may be also used. Electrolysis is performed at voltage 3 V, the cathode current density 5 kA / m², and temperature of the melt 1860–1872 °C.

Authors of [14] drew conclusion that it is practically impossible to produce high-purity titanium using the latter method. In the best case this process may be used for production of ferrotitanium. In addition, cost of titanium, produced according to FFC process, will not significantly differ (moreover several times) from that of titanium, produced according to Kroll method (standard method of magnesium-thermal reduction of titanium).

Despite mentioned shortcomings FFC process has such advantage as conditional combination of electrolysis and reduction in one unit. In [14] the need is noted for improving magnesium-thermal process. Works in this field are carried out in direction of selecting optimum ratios of dimensions (diameter and height) of the units [24], development of continuous processes [25–27], and combination of several processes in one unit [28, 29]. In the world practice units of semi-combined and combined types with cyclic output (productivity) up to 10 t are known [29]. Units of semi-combined type are used in Russia and Kazakhstan, combined type — in Japan, China and India. Recently new design solutions of combined type units appeared, which are used as a basis in technical re-equipment of the workshop, designed for production of spongy titanium at ZTMK [30–32].

Table 11 [35]. Grade, chemical composition and hardness of spongy titanium (GOST 17746–96)

Grade	Titanium, at least	Weight share of elements, %, not more than							Hardness HB 10 / 1500 / 30, not more than
		Fe	Si	Ni	C	Cl	N	O	
TG-90	99.74	0.05	0.01	0.04	0.02	0.08	0.02	0.04	90
TG-100	99.72	0.06	0.01	0.04	0.03	0.08	0.02	0.04	100
TG-110	99.67	0.09	0.02	0.04	0.03	0.08	0.02	0.05	110
TG-120	99.64	0.11	0.02	0.04	0.03	0.08	0.02	0.06	120
TG-130	99.56	0.13	0.03	0.04	0.03	0.10	0.03	0.08	130
TG-150	99.45	0.20	0.03	0.04	0.03	0.12	0.03	0.10	150
TG-Tv	99.75	1.90	–	–	0.10	0.15	0.10	–	–



Main difference of the ZTMK combined unit consists in presence of steam pipeline, heated as a result of passing through it of electric current, and in possibility of multiple increase of the titanium reduction rate due to periodically renewed surface of the titanium-containing melt. Productivity of such unit is 3.8 t / cycle. Commissioning of a similar unit, having productivity 10 t / cycle, is envisaged. Investigation of the process of vacuum separation in the unit showed that despite significant increase of the titanium reduction rate at first stage, at subsequent stages the process (like in units of other types, though) significantly decelerates. Residues of magnesium and magnesium chloride are removed very slowly, which is connected with reduction of heat conductivity of the reaction mass by means of magnesium evaporation. This period takes 75 % time of the whole separation process [33].

For reducing duration of production cycle it was suggested to investigate possibility of remelting sponge with increased, in comparison with requirements of the standard (Table 11), content of technogenic impurities. Analysis of possibilities of traditional methods of the titanium sponge remelting, based on concentrated sources of heating (electric and plasma arcs, electron beam), carried out in [34], showed that application of such sources of energy for remelting of a sponge with increased content of chlorine compounds (more than 0.15 wt.%) is economically disadvantageous and sometimes even hazardous. As note the authors, application for this purpose of arc-free heat sources is more promising. Further investigations [36–38] confirmed principal possibility of remelting of spongy titanium with increased content of chlorides (up to 0.52 wt.%) by the method of induction remelting in a section mould.

In second part of the review methods of producing ingots of titanium and its alloys with application of both consumable and non-consumable titanium electrodes, i.e. methods, in which direct remelting of sponge and scrap is envisaged, will be considered.

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EXPERIENCE OF PRODUCING ESPECIALLY LOW-CARBON STEEL FOR PLASTIC WIRE ROD

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Technological peculiarities of production in the complex arc steel furnace–vacuumator–ladle-furnace of especially low-carbon grades of steel with guaranteed content of carbon below 0.01 % are considered. It is established that such content of carbon may be achieved by vacuum decarburization of the non-deoxidized metal. It is shown that for increasing degree of desulphuration before introduction of calcium-containing wire aluminium addition is necessary. Structure of the produced wire rod ensures its drawing without intermediate annealing processes.

Key words: low-carbon steel, vacuum-oxygen decarburization, plastic properties, wire rod, microstructure

Competitiveness of steel on the market may be guaranteed only if items from it are characterized by steadily high operation properties. Characteristic peculiarity of the steel production process in recent years is the need of achieving such stability. Cleanliness of steel is required to be a technological parameter in many cases. This guarantees stable physical and mechanical properties of the final steel product [1].

Requirements to operation characteristics of steel get more rigid as fields of its application get more complex. These characteristics should meet not just present requirements of the consumers to degree of steel cleanliness, but future ones as well. Moreover, it is necessary to foresee technologies, the need in development of which may occur in future. It is very important that absolute understanding of interaction between cleanliness of the metal and its properties exists in the science, so producers of separate structures may embody understanding of this interaction in technical and economic processes. A final consumer can afterwards design structures on the basis of steel, which is characterized not just by the required cleanliness, but also by guaranteed quality, corresponding to its designation. So, cleanliness of steel is the goal at each stage of the chain, along which steel moves from the producer to a consumer [2].

The interstitial free (IF) steel was developed for the first time in Japan in 1970 and became the best internationally recognized material for deep drawing. It is used for wide range of items — beginning from car bodies to electronic components and enameled household appliances. The IF steel is developed as a result of big complex of investigations, directed at improvement of properties of the traditional low-carbon deoxidized by aluminium steel for deep drawing. Combination of very low carbon content (< 80 ppm) and titanium and niobium additives as microalloying elements causes the fact that the IF steels theoretically

do not have interstitial atoms (such as carbon, hydrogen, oxygen, nitrogen or boron) in the crystalline lattice interstices. This combination ensures exclusive capacity for deformation and absence of the ageing effect. That's why excellent properties in the IF steel are preserved for a significantly longer time than in low-carbon steel, deoxidized by aluminium. Super-low content of carbon ensures additional advantages for the IF steel in deformation.

It should be noted that the IF steels are produced according to a special technological scheme. Processes of hot and cold rolled steel production differ significantly from traditional scheme of production of conventional low-carbon steels. Processes of production of these steels are different, as well as chemical compositions of the latter.

So, technological scheme of producing especially low-carbon steels obligatory includes processes of degassing, deoxidizing, and refining of the semi-finished product, molten in the steel-melting unit. This work is devoted to development of parameters of out-of-furnace treatment of especially low-carbon steel for plastic wire rod under conditions of «Moldavian Metallurgical Plant», Ltd. (MMP).

Substantiation of parameters and experimental testing of technology of vacuum-oxygen decarburization of electric furnace semi-finished product. Semi-finished product, molten in electric-arc furnace of MMP, main parameters of which are given in Table 1, was subjected to out-of-furnace treatment. Out-of-furnace treatment of the semi-finished product was performed according to the scheme of arc steel furnace (ASF)–vacuum pan–ladle-furnace–MCCB. Degassing and deoxidizing of the metal is directed at production of especially low content of carbon and impurities in the finished steel.

In the reaction of the metal deoxidizing by carbon (in contrast to all other deoxidizers-elements) form gaseous deoxidizing products, that's why reduction of the pressure increases deoxidizing capacity of carb-

**Table 1.** Parameters of semi-finished product and planned chemical composition of finished steel

Kind of materials	$\bar{O}$, ‰	$\bar{a}_I$, ppm	Weight share of elements, %				
			$\bar{N}$	Mn	Si	P	S
Semi-finished product	1653–1741	1100–2100	0.03–0.09	0.024–0.060	≤ 0.01	0.005–0.006	0.038–0.080
Finished steel (recommended composition)	–	10–20	≤ 0.03	≤ 0.15	≤ 0.03	< 0.015	< 0.008
Finished steel (targeted composition)	–	10–20	≤ 0.02	≤ 0.12	≤ 0.01	< 0.012	< 0.005

on, whereby significant influence exerts temperature. Temperature increase shifts equilibrium of the vacuum-carbon deoxidizing reaction, due to which at the same concentrations deoxidizing capacity of carbon exceeds that of manganese and silicon at temperatures above 1600 °C and pressure below $1 \cdot 10^4$ Pa. That's why for the steel of targeted chemical composition equilibrium concentrations of oxygen are calculated within the temperature range of the MMP technological process at assigned concentration of the deoxidizing agents, while for carbon — at normal and reduced pressure (Figure 1).

Calculations showed that pressure reduction in the vacuum chamber down to $1 \cdot 10^4$ Pa is sufficient for prevailing oxidizing of carbon, in comparison with manganese and silicon, over the whole considered temperature range of the technological process.

To prevent popping in the ladle during tapping because of high level of the metal oxidation, preliminary deoxidizing of the latter by aluminium was performed. Consumption of aluminium should be sufficient for ensuring removal of excessive oxidation (difference between really measured oxidation and minimal amount of oxygen, necessary for decarburization) in the semi-finished product, and at the same time it should not prevent reaction process of vacuum-oxygen decarburization of the metal in degassing (Figure 2).

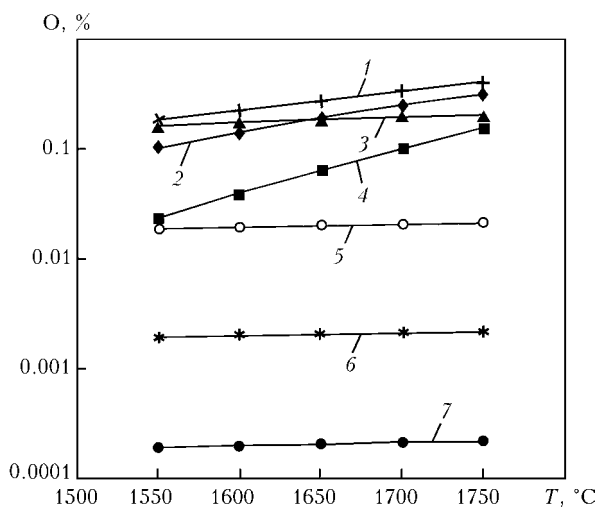


Figure 1. Equilibrium content of oxygen in steel with assigned content of elements (separately) at different values of temperature: 1 — solubility of oxygen in iron; 2 — 0.12 Mn; 3 — 0.01 C at P ($CO + CO_2$) of $1 \cdot 10^5$ Pa; 4 — 0.01 Si; 5 — 0.01 C at P ($CO + CO_2$) of $1 \cdot 10^4$ Pa; 6 — 0.01 C at P ($CO + CO_2$) of $1 \cdot 10^3$ Pa; 7 — C at P ($CO + CO_2$) of $1 \cdot 10^2$ Pa

Calculation of the CO amount, being released in vacuum decarburization of steel up to 0.005 %, was made allowing for determined necessary initial oxidation level (Figure 3).

Calculation of the gas release in the metal degassing showed that steels with relatively high content of carbon (0.05–0.08 %) can foam rather essentially in case of the pressure reduction, because volume of CO being released is rather significant. As at mentioned concentrations of carbon reaction of its oxidation proceeds practically without kinetic limitations, intensity of the gas release will be also high, which has to be taken into account when developing vacuum.

At registered values of the metal oxidation level amount of CO being formed depends upon volume of carbon being removed (difference between initial and assigned content of carbon) and according to calculations, made in experimental melts, it constituted 53–124 m³, which is significantly higher than volume of argon, blown into the metal in the process of degassing.

It was experimentally established that using method of vacuum degassing of the metal it is possible to achieve required low content of carbon (less than 0.01 %) both in degassing of the metal with preliminary deoxidizing by aluminium and without introduction of the latter. The practice shows that in degassing of not deoxidized by aluminium metal 0.01 % final content of carbon in the metal is achieved even when

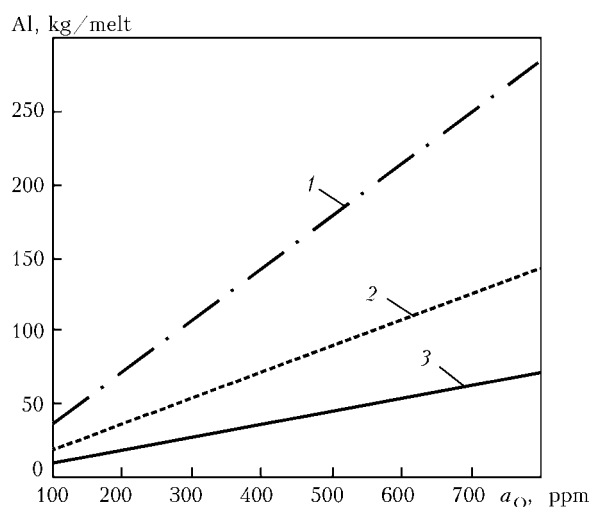


Figure 2. Consumption of aluminium at tapping for removal of metal overoxidation for different values of aluminium melting loss: 1 — 75 %; 2 — 50 %; 3 — without taking into account melting loss



its initial content (according to chemical analysis data) equals 0.0742 %.

Introduction of aluminium into the metal before degassing reduces initial oxidation level of the metal, due to which intensity of CO formation in degassing decreases and foaming of the metal reduces.

Averaged indices of the degassing process of the pilot-commercial testing melts were as follows: content of carbon before degassing was 0.0293–0.0564 %; after degassing — 0.01 %; all together 0.0193–0.0464 % C was removed in degassing; reduction of oxidation level in degassing due to carbon was 257–619 ppm; calculated amount of CO, released in degassing, was 36.03–86.61 m³; oxidation level before degassing was 644–884 ppm; actual oxidation level after degassing was 573 ppm.

In the course of degassing of the melts additives were not introduced into the ladle. During development of vacuum and within the whole cycle of degassing the melt «boiled» intensively. Free edge constituted not less than 800 mm. Splashing and outbursts of the metal in the vacuum chamber were not registered, baring of the metal surface (according to visual estimation) constituted 40–60 %, depending upon intensity of the melt «boiling». General consumption of argon for blowing in all melts constituted 2 m³. In the process of degassing content of carbon reduced by 0.019–0.046 %, which caused reduction of oxidation level by 257–619 ppm. Calculated oxidation level after degassing is due to self-deoxidizing by carbon rather close to the actual one, which confirms calculations, made above.

After degassing the ladle was placed on the ladle-furnace installation for correcting composition and temperature of the metal.

Substantiation of conditions of finishing steel with especially low content of oxygen on ladle-furnace installation. It should be noted that content of sulfur in the metal before the ladle-furnace is unstable (0.0306–0.0748 %) and in majority of cases significantly higher of the required branded one. Hence, one of the tasks of out-of-furnace treatment in the ladle-furnace is desulphuration of the metal, which under MMP conditions is performed by both induction of high-basic slag (by additives of lime and fluoride) and due to desulphuration capacity of calcium-containing materials (silicocalcium and ferrocalcium). According to the literature data [3], average degree of desulphuration due to such slag constitutes 20.5 %. So, greater part of sulfur is removed in the ladle-furnace due to interaction with the calcium-containing materials. At the same time one has to take into account that calcium from calcium-containing ferroalloys interacts not just with sulfur, but with oxygen too.

When silicocalcium is used for modification of steel, silicon, which enters into composition of the said silicocalcium, may exert deoxidizing influence, provided oxide phase (of calcium silicates) is formed, in which activity of SiO₂ will be less than one, and

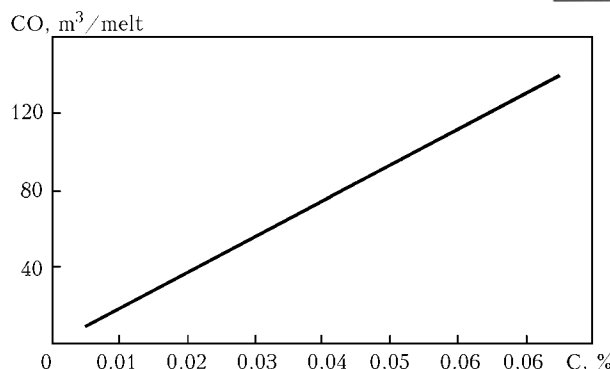


Figure 3. Amount of CO released in degassing of metal depending upon necessary reduction of carbon content: $y = 1866.7x - 1E-13$; $R^2 = 1$

the lower is α_{SiO_2} , to the greater degree mentioned activity will be less than one.

Minimum activity of SiO₂ is characteristic of two-calcium silicates and equals 0.024. Calculation of equilibrium content of oxygen, characteristic of especially low-carbon steel being melted, showed that silicocalcium silicon is able to exert deoxidizing action with formation of silicate non-metallic inclusions.

Equilibrium content of oxygen in steel in case of deoxidizing of silicocalcium by silicon (the temperature equals 1600 °C) is as follows:

Activity of oxygen $a_{[\text{O}]}$, ppm	0.01	0.02	0.03	0.04
Weight share of silicon, %	61.50	43.50	35.60	30.80

To avoid formation of calcium silicates it is necessary to ensure content of active oxygen below mentioned values.

For performing maximally full desulphuration by calcium-containing ferroalloys it is necessary to estimate conditions of competitive interaction of calcium with oxygen and sulfur according to the following reactions:



Solution of the system of thermodynamic equations allows obtaining temperature dependence of the ratio of activities of oxygen and sulfur in the metal, expressed by the following equation:

$$\lg \frac{a_s}{a_o} = \frac{5141}{T} - 1.191.$$

In Figure 4 equilibrium values of oxygen and sulfur activities are presented in case of their interaction with calcium at different temperatures.

For temperature values 1550 and 1600 °C we obtain that when ratio of sulfur activity to activity of oxygen equals 42.5 and 35.8 respectively, simultaneous interaction of calcium both with sulfur and oxygen takes place.

If mentioned ratio is not observed, interaction with one of mentioned elements will mainly occur till this ratio is achieved.

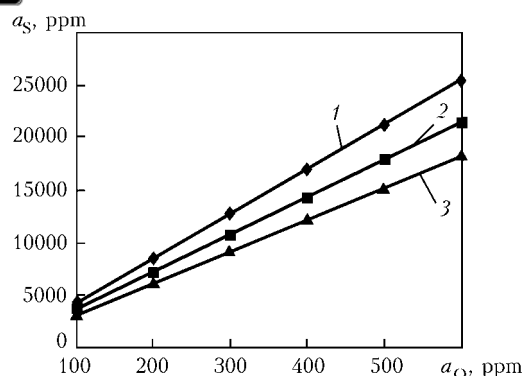


Figure 4. Equilibrium values of oxygen and sulfur activity in case of their interaction with calcium under conditions of different temperatures, °C: 1 — 1550; 2 — 1600; 3 — 1650

Calculation of conditions of sulfur and oxygen interaction with calcium, based on real data of experimental-commercial test melts, is presented in Table 2.

So, the calculation has shown that for efficient desulphuration of steel by means of introduction of calcium it is necessary first to perform deoxidizing of the metal up to the oxygen activity level below the value, stipulated by the ratio of sulfur and oxygen activity at the additive introduction temperature. Results of calculation confirm experimental data on need of introducing aluminium before introduction of calcium-containing ferroalloys.

Degree of the calculated values correspondence to the real ones depends upon temperature of the metal and kind of the material being used, because efficiency of calcium use increases as pressure of its vapors reduces, i.e. when ferroalloys, containing less calcium, are used and when temperature of the steel being treated is lower.

In experimental melts insignificant increase of carbon content in the metal was registered due to

Table 3. Change of carbon and silicon content in out-of-furnace treatment in ladle-furnace

Element	Weight share of element, %	
	Before ladle-furnace	After ladle-furnace
Carbon	Less than 0.01	0.0100–0.0122
Silicon	0.01	0.0100–0.0248

contacts of the latter with graphite electrodes, which may be excluded by performance of heating in slag mode. One has to take into account that refractory lining of the ladle contains 5–12 % C and in the course of casting increase of content of the latter (up to 0.01 %) may occur. Detected reasons of the metal carburizing in the ladle-furnace after degassing were taken into account in experimental-commercial testing — heating was performed in slag mode and duration of melting under current in the ladle-furnace was reduced to minimum. Main results of out-of-furnace treatment of the metal in the ladle-furnace are given in Table 3.

Analysis of structure and properties of produced especially low-carbon steels. Cross-section microstructure of all investigated specimens of the wire rod of 5.5 mm diameter from especially low-carbon steel consists from practically pure ferrite with inclusions of tertiary cementite in the form of relatively uniformly distributed fragments of the net over grain boundaries (not more than 1/6 of ferrite grain perimeter, dotted and fine-globular rash). Characteristic view of the microstructure is shown in Figure 5. Such structure enables achieving high values of plastic properties of the wire rod.

Size of the actual grain and degree of contamination by non-metallic inclusions meet, according to

Table 2. Calculation of necessary oxygen activity reduction before introduction of calcium-containing materials

Conditional number of melt	Real a_i , ppm	$\dot{O}$, °N	a_S / a_i	$\dot{a}_S$, ppm	Real a_S , ppm	Calculated a_i , ppm	Reduction of a_O , ppm
1	573	1648	30.56	17513	477	15.60	557.40
2	472	1576	38.85	18338	418	10.76	461.24
3	186	1592	36.78	6840	410	11.15	174.85

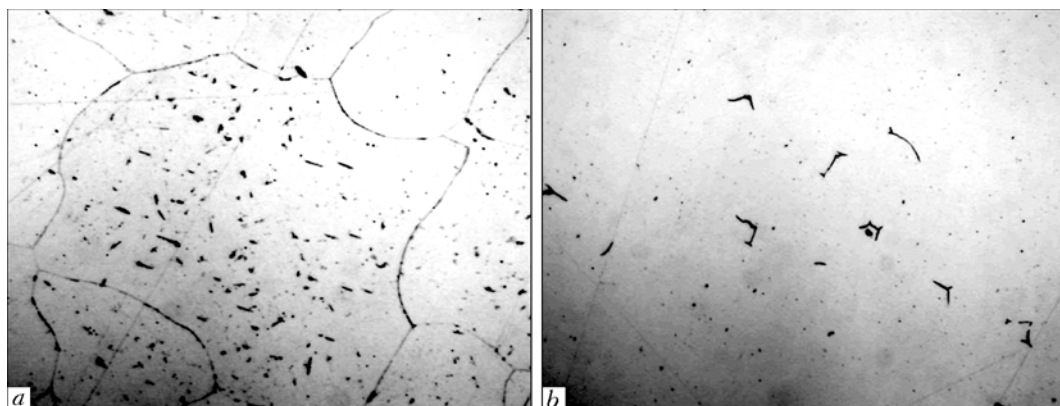


Figure 5. Characteristic microstructure of investigated specimens in cross-section of wire rod: a — etching in 2 % solution of nitric acid in ethyl alcohol; b — etching in solution for detection of cementite (×1000)



GOST 1778–70 (method Sh) and ASTM E45 (method A), requirements, established for low-alloy steels of C4D type.

Results of mechanical tests showed that ultimate strength of the wire rod metal of one of the melts was 321 MPa, and in two other melts this value was close to the assigned one (345–362 MPa). Reduction in area ψ constituted 84–85 %, and relative elongation was $\delta_5 = 42$ –44 % and $\delta_{10} = 33$ –36 %.

Mechanical properties of produced metal with the tensile strength–general elongation diagram for sheet steels [4], in production of which especially low-carbon compositions are most frequently used, prove that the latter correspond to the level of high plasticity IF steels both by their chemical composition and their properties.

Structure and properties of the produced metal ensure process of the wire rod drawing at the metalware enterprises without using intermediate annealing, which significantly reduces cost of its conversion. In addition, billet from the metal of this composition

may be needed in production of low-carbon stainless, high-temperature and special alloys.

So, possibility is confirmed of producing especially low-carbon grades of steel under MMP Ltd. conditions with application of the installation for degassing (due to using reaction of vacuum-oxygen decarburization without additional introduction of oxygen in gaseous form or in the form of oxides) with guaranteed content of carbon below 0.01 % and low content of impurities and alloying elements, which ensures high plastic properties of the wire rod being produced.

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STATE AND VECTORS OF DEVELOPMENT OF ELECTRIC STEEL PRODUCTION IN UKRAINE

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Review of electric steel production in Ukraine is presented. Dependencies of economic development of the country upon structure of metallurgical production are shown. Reasons of lagging of electric steel production of Ukraine behind the world level are analyzed. Ways of development of electric steel production of Ukraine are scientifically substantiated.

Key words: electric steel production, iron ore feedstock, continuous casting, quality steels, alloying elements

During period of recession in production of world metallurgy (2001–2005) Ukrainian metallurgy demonstrated positive dynamics. In 2004 production of cast iron increased in comparison with the year 2003 by 5.4 %, of steel — by 4.9 %. In the world metallurgy these indices achieved 7.1 and 9.1 %, respectively. Ukraine, which was in the seventh position in the world rating of the refined steel production, produced 38.6 mln t of steel in 2005 [1]. This brought Ukraine 40 % of hard currency proceeds and constituted 27 % of industrial production of Ukraine, profitability of the product being 26.3 %. Volume of internal market of the country's metal consumption makes up about 21 % of the whole production of Ukrainian metal-

lurgy. That's why metallurgical production of Ukraine has a clearly pronounced export-oriented character. For comparison, in China, which occupies leading positions among producers of metal and had 20 % increment of steel production rate in 2002–2004, share of internal consumption makes up 90 %, and in industrially developed countries volume of the internal metal consumption market achieves 80 %.

For ferrous metallurgy of Ukraine a very high share of open-hearth production (45 %) and casting of steel into moulds remains to be a characteristic feature, while at state-of-the-art plants these technologies are not used since long (Figures 1, 2).

Because of these and a number of other reasons (low quality of the iron ore feedstock, reducers, refractory materials and fuels; insignificant — approximately 3.6 % — share of electric melting, excessive terms of operation, etc.) specific consumption of energy and materials is by 30–50 % inferior to the world indices, which in combination with rather low quality of metal products reduces their competitiveness.

At the same time, needs of Ukrainian economy are satisfied to a greater degree by low-refinement products, while metal products with high added value are mainly imported from other countries. Steel consumption constituted in 2001 in Ukraine 187.3 kg per capita (Figure 3).

The main share of profit in metallurgical branch of developed countries is created at the stage of production of high-refinement products with high added value on the basis of relatively expensive energy and manpower [2]. Due to high labor productivity center of the profit is transferred to production of high-refinement products. Till cheap feedstock, electric energy, and manpower are considered a competitive advantage, and exactly such situation exists in Ukrainian metallurgy, till it will be impossible to solve the issue of increasing share of products with a higher added value.

It is possible to single out a number of the following problems, which are peculiar for present metallurgical branch of Ukraine:

- high degree of wear of fixed assets;
- prevalence of products with low added value in structure of the production;

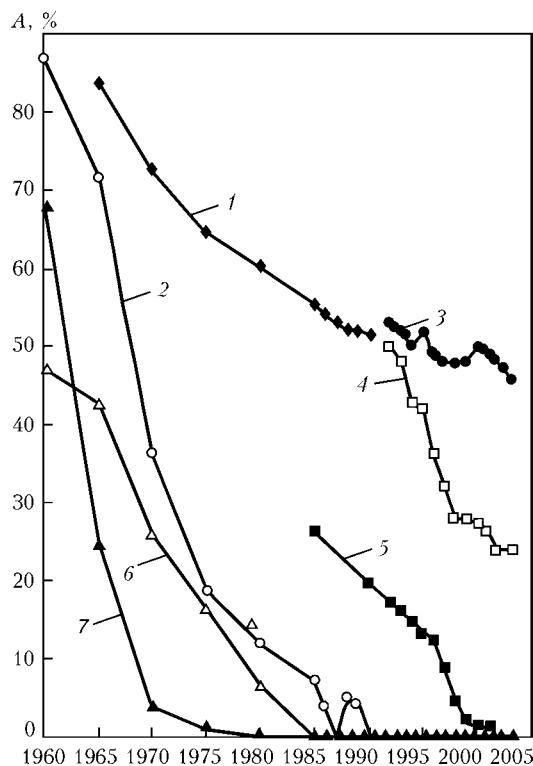


Figure 1. Change of share of open hearth steel production, A, from 1960 through 2005: 1 — USSR; 2 — USA; 3 — Ukraine; 4 — Russia; 5 — China; 6 — Germany; 7 — Japan

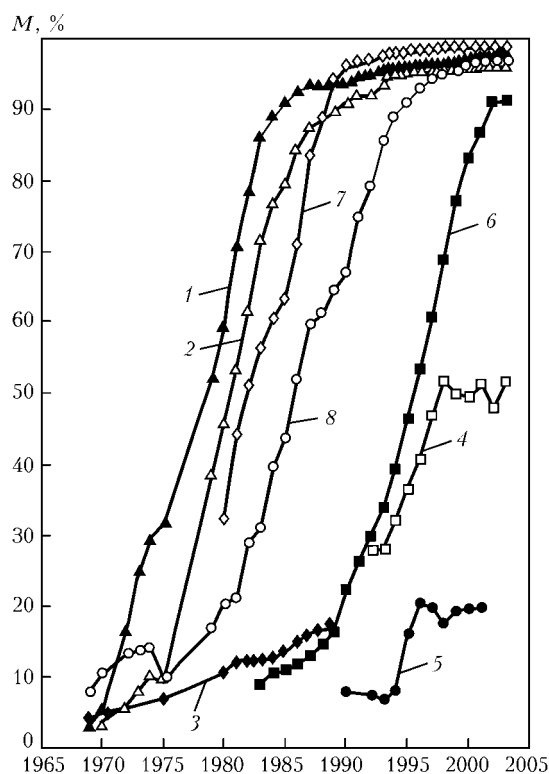


Figure 2. Change of share of continuously cast steel, M , from 1968 through 2005: 1 — Japan; 2 — Germany; 3 — USSR; 4 — Russia; 5 — Ukraine; 6 — China; 7 — South Korea; 8 — USA

- low technical level of the equipment and technology;
- low productivity;
- low level of metal consumption per capita.

It should be emphasized that mentioned problems are characteristic of majority of the participant-countries of the world metal market.

It should be especially noted that globalization of the world economy revealed a trend of transferring environmentally dirty production into developing countries. Developed countries concentrate their resources on production of highly processed and finished commodities, while environmentally hazardous primary production is transferred to less developed countries, where production resources are relatively cheap and environmental control is not developed [3].

Exactly because of mentioned reasons metallurgical industry of Ukraine preserves its positions on the world market.

At the same time, growth of the cost of fuel and energy resources, which started in Ukraine in 2006, in addition to increase of production cost of Ukrainian metal products and (in a number of cases) reduction of the production volumes (especially of open hearth steel) causes need in reorientation of metallurgical technologies at production of the following kinds of products with high added value:

- high quality alloyed steels;
- sheet and structural rolled corrosion-resistant steels;
- pipe and sheet products with galvanic and polymer coatings;

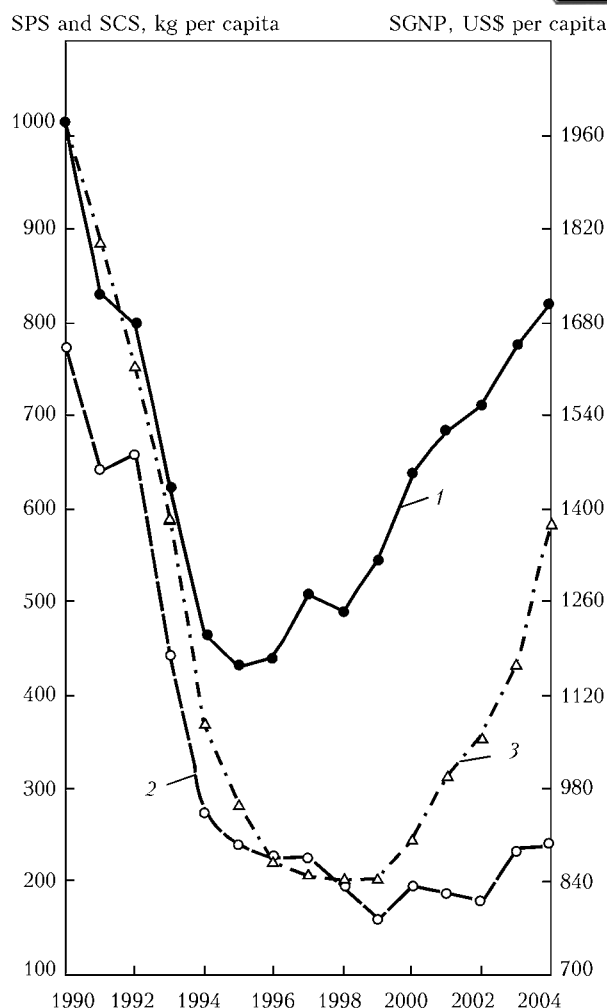


Figure 3. Change of specific production (SPS) and specific (home) consumption of steel (SCS), as well as specific gross national product (SGNP) within period from 1990 through 2004: 1 — SPS; 2 — SCS; 3 — SGNP

- products of remelting processes of special electrometallurgy.

Cabinet of Ministers of Ukraine approved by its decree No. 967 of July 28, 2004, state program of development and reformation of mining-metallurgical complex of Ukraine for the period till 2011. Goal of the program is ensuring of efficient use of production and scientific-technical potential of the mining-metallurgical complex and determining of the priorities in restructuring of the branch and its production capacities. The program envisages implementation of the following measures in development of steel-melting production:

- maximum use of capacities of oxygen-converter workshops;
- increase of the steel production volume in electric furnaces due to commissioning of new and restructuring of available capacities;
- application of special electrometallurgy methods;
- technical reequipment of steel-melting workshops with construction of the furnace-ladle installations for out-of-furnace treatment of steel and machines for continuous casting of billets;

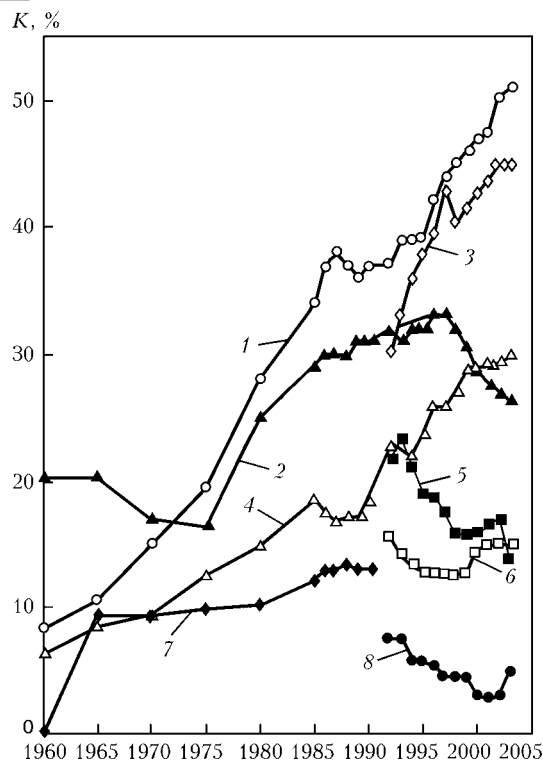


Figure 4. Change of share of electric steel production, K, from 1960 through 2005: 1 — USA; 2 — Japan; 3 — South Korea; 4 — Germany; 5 — China; 6 — Russia; 7 — USSR; 8 — Ukraine

- development and introduction into production of economically alloyed grades of steel with application of national raw-material base of non-deficient alloying components.

Production of electric steel in Ukraine is concentrated in significant volumes at two plants: «Istil», Donetsk, and «Dneprospetsstal», Zaporozhzie. In 2005 at mentioned enterprises 1320 thou t of steel were produced, including at «Istil» — 812 thou t and at «Dneprospetsstal» — 508 thou t. In addition, about 60–70 thou t of electric steel are produced by foundries and repair shops of metallurgical enterprises.

In steel-melting workshops of machine-building complex of the country steel is melted both in open-hearth and arc furnaces. At majority of enterprises electric steel for casting is produced in low-capacity (3–6 t) electric furnaces. All together about 100 arc and induction electric furnaces are installed in steel-melting workshops of machine-building plants. General production of electric steel in Ukraine constitutes about 1400 thou t per year — 3.6 % of the total volume of molten steel (Figure 4).

Within the framework of implementation of the national program diversification of steel-making production was initiated, directed at withdrawal from operation of open-hearth furnaces of «Nizhnedneprovsky Pipe-Rolling Plant», Ltd. and creation in its structure of electric steel complex «Dneprovsky Metallurgical Plant», Ltd., construction of a state-of-the-art electric steel complex for processing of oxidized pellets of Poltava Ore-Mining and Dressing Works on the basis of the plant «Vorsklastal» being designed with volume of production 3 mln t of continuously

cast billets per year with subsequent construction of the rolling complex.

It is planned to equip mentioned enterprises with complexes for continuous casting of steel and out-of-furnace treatment on the electric furnace-ladle and vacuumizer installations, which will ensure reduction of power consumption, higher quality of ready rolled stock, and production of competitive products (due to increase of added value by efficient use of the existing infrastructure, including preservation of the employed high-skill personnel), whereby share of steel, melted by the electric furnace method, will increase from 3.6 in 2005 to 17.4 % (without taking into account commissioning of electric steel capacities, being designed at «Petrovsky DMZ», Ltd.), which will change structure of not just metallurgical production of Ukraine in direction of the world trends of the ferrous metallurgy development, but also of metal consumption at the internal market due to increase of import-substituting technologies.

It is, evidently, planned to increase volumes of electric steel production within the tasks, assigned by the national program, by development of high-capacity production of steel of ordinary designation by using melting units with increased up to 130–200 t capacity of the furnaces and subsequent production of long rolled stock [4].

Out of the national program range remain problem issues of metallurgy of special designation steels and alloys, improvement of technologies, and upgrading of low-capacity furnaces, which prevail in the stock of melting equipment of foundries and metallurgical enterprises of machine-building complex and constitute the basis of melting capacities of the only in Ukraine plant of quality steels — «Dneprospetsstal», Ltd.

In melting of steel in mentioned units specific consumption of electric power constitutes 850–1000 kW·h / t, which is 2.0–2.5 times higher than in high-capacity furnaces of ferrous metallurgy. In operation of these units environmental safety of metallurgical production practically is not observed, and technologies of quality improvement of metal products by out-of-furnace treatment of the metal are excluded. The latter is the reason of increased metal consumption and, as a result, reduction of competitiveness of the machine-building products.

Alternative to low-efficiency melting equipment of low-capacity production units is introduction of arc furnaces and two direct current electrode furnace-ladle installations for out-of-furnace treatment.

Mentioned design and technical solutions create premises not just for improving technical-economic indices of the production, but also for expansion of the range of grades in production of high-alloy steels. High significance of the alloyed steel metallurgy in state-of-the-art machine-building industry strengthens role of its internal problems and brings their solution outside of the limits of a separate enterprise and a region. This is enabled by the processes of glo-



balization of production, export, import, and consumption of metallurgical products.

In such situation, in addition to increase of the added value as a positive factor of competitiveness on the external market, increases share of the metal consumption on the internal market due to increase of the import-substituting metal products for needs of the national machine-building industry.

Volumes of production of special high-quality metals, alloys with special qualities, and composite materials are, as a rule, low (1.0–1.5 % of total volume of the ferrous metallurgy production), but high added value makes their production economically profitable.

The highest quality of steel with certain functional properties may be achieved only provided it is alloyed by a number of high-efficient alloying elements, which enter into composition of ferroalloys of different kinds and grades. High-quality steels and alloys contain 6–8 alloying elements in different combinations.

Total electric power of ferroalloy furnaces of three ferroalloy plants of Ukraine constitute 1780 MV·A (in Russia 1030 MV·A), namely Nikopol «NZF», Ltd. — 1000; Zaporozhie «ZFZ», Ltd. — 467; Stakhanov «SFZ», Ltd. — 220; «Pobuzhsky Ferronickel Works» («PFK», Ltd.) — 100 MV·A, etc. At Ukrainian plants manganese ferroalloys and ferrosilicon are mainly melted, and at «PFK» — ferronickel. At the same time, for melting low-, medium- and high-alloy steel of different grades, functional designation and operation characteristics, it is required that the steel be alloyed by one or several ferroalloys in various combinations, the list of which includes more than 10–12 metals (manganese, silicon, chromium, nickel, tungsten, molybdenum, vanadium, titanium, niobium, cerium, boron, calcium, rare-earth metals, etc.).

That's why majority of electric ferroalloys, except manganese ones and ferrosilicon, are imported from Russia, Kazakhstan and other countries. The reason of present situation with production of a number of ferroalloys consists in absence of mineral kinds of raw materials and use at full capacity of all ferroalloy furnaces.

Taking into account requirements of market economy relative improvement of steel quality, the investments are necessary at present into establishment of ferroalloy production for melting of the alloys, containing vanadium, tungsten, molybdenum and, first of all, ferrochromium of wide grade range. Production of ferroalloys of mentioned kinds may be organized in Ukraine with significant economic effect by use of imported ores and concentrates. The best example is

production of electric furnace ferronickel at «PFK», Ltd. (18–23 % Ni) with application of New Caledonian nickel ore (2.0–2.5 % Ni), although the plant was designed for melting ferronickel (5–8 % Ni) of Pobuzhsky lean ore (0.9–1.1 % Ni). Despite high cost, consumption of electric power, and high transportation expenses, production of ferronickel with application of imported nickel ore is characterized by high economic efficiency.

When implementing increased electric power consumption in electric steel and ferroalloy production, it is expedient to use surplus of electric power, exported at present by Ukraine, and planned increase of electric power production at nuclear power plants for production of high-quality alloyed steels and «elite» ferroalloys, which, certainly, will increase potential and efficiency of metallurgical branch of Ukraine as a whole.

CONCLUSIONS

1. It is shown that trends and prospects of the world metallurgy development confirm need of restructuring metallurgical production of Ukraine, which has export-oriented character.

2. It is established that the structure and the state of metallurgical branch of Ukraine requires for more dynamic development of electric steel production both in respect of increasing volume of electric steel production and expansion of the range of quality high-alloy steels.

3. The following priorities of electric steel production are considered: reorganization; increase of share of the products with high added value; maximally possible reorientation of the production at satisfaction of the internal market and increase of the import-substituting technologies.

4. It is determined that one of cardinal directions of structure modernization of Ukrainian ferrous metallurgy is establishment at the state level of the mechanisms of financial-credit relations, which would stimulate steel producers to perform technical and technological reequipment of electric steel and electric ferroalloy capacities of the enterprises.

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INCREASE OF UTILIZATION FACTOR OF REFRACTORY ALLOY WASTE BY ELECTROMETALLURGY METHODS

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Simultaneously with the system of intraplant accountability, classification, and certification of the wastes improvement the authors proposed, using example of the enterprise «Zorya–Mashproekt», new technology for filtration and refining of the melt in vacuum remelting of off-grade wastes of multicomponent nickel alloys in the serial melting unit PMP-4M for the purpose of producing a secondary charge billet. The process envisages seasoning of the liquid metal in a specially designed multilevel mould with ceramic filter. This ensures efficient zone cleaning of the metal due to pushing off of the impurities from solidification front with subsequent removal of the cast ingot problematic zone by machining. Carried out organizational-technical measures in experimental-commercial testing of the proposed technology showed possibility of increasing utilization factor of cast waste in casting of items from 30–40 to 70–80 wt.% depending a type of the items.

Key words: refractory alloys, cast waste, GTE vanes and blades, vacuum-induction remelting, electron beam remelting, modified ceramics

In technological process of manufacturing cast and deformed components of turbine engines (GTE) nickel-, cobalt- and iron-base cost intensive refractory alloys are used, which are not produced in Ukraine.

At the same time, national industry has big centers for manufacturing stationary (power engineering) and transportation (aviation, shipbuilding) gas turbines (SE «Zorya–Mashproekt», Nikolaev, OJSC «Motor–Sich», Company «Progress», Zaporozhie, «Turboatom», Kharkov) that explains actuality of solving technological tasks for efficient use of primary materials and recovery of the formed wastes. Choice of technology for conversion of cast and mechanical waste depends completely upon their clear preliminary ranking not only by grades of alloys and quantity thereof, but also by the degree of their contamination with foreign impurities (residues of forming and rod ceramic masses, harmful impurity elements, gases, etc.).

In this work authors carried out analysis of intraplant accountability documentation concerning formation and dynamics of accumulation of cast waste of various kinds of products (nozzle guide vanes and rotor blades, struts, fairings, etc.), using example of SE «Zorya–Mashproekt», for the purpose of increasing efficiency of using cost intensive waste of nickel- and iron-base refractory alloys and proposed improved system for classification and certification of the cast waste formed in production of components of power engineering and transportation GTE.

State of the issue, materials and technological processes. It should be noted that in recent years the main supplier of corrosion-resistant refractory alloys, used for manufacturing GTE blades and vanes with service life 5,000–10,000 h for power engineering and gas pumping power stations is Chelyabinsk Metallur-

gical Works; for ship and energy turbines with long service life (up to 100,000 h) — such known companies as INCO, First Rixson (both Great Britain), and Teledyne (USA). So, beginning from the year 2000, First Rixson has been supplying to the enterprise alloys CM88UVI (Russian analogue is alloy ChS88UVI), CM104VI (ChS104VI), and CM648VI (of VKh4L type) (Table 1).

An example of efficient implementation of low-waste production at foreign enterprises is a technological chain, established between the plant-manufacturer of alloys (First Rixson) and the enterprise-manufacturer of GTE (Howmet, Great Britain). So, for melting of a secondary charge billet First Rixson uses from 10 to 50 % of production wastes of the Howmet company (cast and mechanical ones), preliminary sorted by melts and cleaned of ceramics. Such sorting of the waste ensures for the secondary charge billet correspondence of chemical composition, including impurities, to the standard [1], established for refractory alloys of the type IN 738.

In the national practice it became possible to employ carefully controlled system of return of the cast production waste for manufacturing charge billets only for some especially expensive rhenium-containing alloys (of JS32 type) on «Progress» company (Zaporozhie).

For the rest Ukrainian enterprises of the branch it is economically inexpedient to return wastes to foreign metallurgical enterprises-manufacturers of alloys, while intraplant technology of using own cast production waste envisages till now addition to the primary billet of only 30–50 wt.% of conditioned waste in melting of items by the method of vacuum-induction remelting.

Such method of remelting can not ensure efficient refining of the melt from impurities, including refractory ceramics, alkaline metals, gases, etc. Develop-

**Table 1.** Full chemical composition of refractory alloys ChS88U and IN 738 LC of different producers according to valid standards [1–3]

Element	Ñ Ì 88UVI «First Rixson»	ChS88UVI Russia, Stupino	IN 738 LC	Element	Ñ Ì 88UVI «First Rixson»	ChS88UVI Russia, Stupino	IN 738 LC
Weight share of element, %							
Ni	Base	59.88	Base	Ta	0	0.030	1.600
C	0.09	0.084	0.10	P	0.006	0.005	0.005
Cr	15.43	15.56	16.00	S	0.001	0.002	0.001
Co	10.97	8.59	8.30	Ga	< 0.002	0.001	--
Mo	2.13	0.76	1.70	In	0	1·10 ⁻⁵	--
Fe	0.08	0.49	0.13	Mg	< 0.005	0.002	< 0.005
Al	3.16	3.90	3.50	Ag	< 1·10 ⁻⁴	1·10 ⁻⁵	< 1·10 ⁻⁵
Ti	4.76	3.99	3.40	N	8·10 ⁻⁴	0.006	0.002
B	0.093	0.011	0.10	O	0.0015	0.0014	6·10 ⁻⁴
W	5.35	6.38	2.70	As	< 0.0015	3.8·10 ⁻⁴	--
Nb	0.26	0.29	0.90	Bi	< 5·10 ⁻⁴	6.27·10 ⁻⁴	< 1·10 ⁻⁵
Zr	0.04	0	0.40	Pb	< 5·10 ⁻⁵	7.5·10 ⁻⁴	< 3·10 ⁻⁵
Hf	0.50	0.029	--	Sb	< 2·10 ⁻⁴	1.4·10 ⁻⁴	--
Y	0.03	--	--	Se	< 1·10 ⁻⁴	3.7·10 ⁻⁵	--
Ce	0.015	--	--	Sn	< 0.002	0.0024	--
Cu	0.01	--	< 0.20	Te	< 5·10 ⁻⁵	0.0016	< 5·10 ⁻⁵
Si	0.03	0.07	< 0.10	Tl	< 2·10 ⁻⁵	2·10 ⁻⁶	N / D
Mn	0.01	0.06	< 0.20	Zn	< 4·10 ⁻⁴	6·10 ⁻⁵	Same

Note. Weight share of Hg, Ge, Au, K, Na, U, Th constitutes ≤ 50 ppm.

ment of both efficient refining technology for intraplant waste regeneration process, and rational system of waste classification and certification for each enterprise, according to the types of products, are necessary for increasing waste utilization factor in the mentioned system.

Analysis of terms of reference of foreign companies, established for refractory alloys [1, 2] concerning allowable quantity of impurity elements, including non-ferrous metals (lead, bismuth, tellurium, gallium, selenium, silicon, etc., totally up to 0.05 wt.%) proves the need of their strict control in the cast item. National standards, unfortunately, do not establish such strict requirements for primary billets of alloys.

According to existing standards, total amount of impurities, brought with initial charge materials, may constitute more than 1 % of the alloy mass. In addition, in the process of direct melting of items a significant source of contamination may be non-metallic inclusions, which get from the lining of a melting crucible, which represents molten magnesite (melting of the charge billet), and mullite-corundum crucibles (melting of items) [4]. In this connection of utmost importance is development and application in production cycle of new thermostable and heat-resistant ceramic materials [4].

As shows analysis, carried out at enterprises of the branch, amount of conditioned wastes, formed in melting of items of the considered assortment, constitutes on average 23 % of total mass of the consumed charge (Table 2). Off-grade wastes, to which relate pouring basins with residues of ceramic nets for filtration of the metal, and blades and vanes, rejected in LUMMA-control because of defects of internal cavities, constitute on average 28 % of the consumed charge mass, irrespective of the alloy grade. So, results

of statistical analysis showed that total amount of wastes, formed in melting of GTE blades and vanes, constituted on average 60–70 % of the loaded charge mass, of which it was allowed till now to use repeatedly not more than 30–40 % because of absence of systemic record-keeping of the wastes and efficient regeneration process.

For economically substantiated solution of the problem of as full as possible recovery of conditioned and off-grade wastes of refractory alloys, rejected, as one of the reasons, because of their chemical composition, the authors propose technology of two-stage remelting of refractory alloys with inclusion into the technological chain of developed at SE «Zorya–Mashproekt» jointly with PTIMA of so called method of directed zone remelting [5].

Horizontal vacuum resistance furnace PMP-4M was used as a casting unit. Standard ceramic filter K657-2783ChI, installed into upper part of a specially designed multilevel corundum mould, which allowed performing filtration directly in it, was used for ensuring primary mechanical filtration of the melt from course non-metallic inclusions.

Refining of the melt from non-metallic inclusions takes place due to presence in the horizontal furnace of three thermal zones (heating, melting, and solidification). Rate of solidification under stationary conditions is regulated by speed of movement of the moulds with molten metal along the furnace from one zone into the other. According to thermodynamic characteristics of the alloys temperature of the melt is maintained at the level, not exceeding 1460 °C. Thermal gradient at the grain growth front constitutes 15–20 °C / cm that enables casting-off of impurity elements to the boundary of solidification front and their subsequent removal by machining.

Table 2. Structure of consumption of alloys in manufacturing of GTE blades and vanes, %

Grade of alloy	Yield of efficient alloy, %	Off-grade wastes		Conditioned wastes		Machining waste	Melting and irretrievable losses	Total amount of waste
		Blades and vanes	Pouring basins	Blades and vanes	Runners, feeders			
ChS70	34	8.2	20.3	9.3	17.1	8	3.1	66
ChS88U	32	9.6	19.4	12.6	13.2	10	3.2	68
ChS91	43	6.6	20.8	7.3	10.0	9	3.3	57
ChS104	32	8.1	20.8	9.2	16.7	10	3.2	68
EK9	37	7.2	20.0	8.5	16.3	8	3.0	63
EP648	42	5.3	20.5	6.1	12.9	10	3.2	58
Mean value	37	7.4	20.3	8.7	14.3	9.1	3.2	63

*Amount of loaded charge is assumed as 100 %.

In the process of the melt solidification within assigned thermal and time parameters precipitation in intergrain space of lump-like carbide phases, which are concentrators of stresses and stimulate origination of cracks, was not registered.

An important factor is correct choice of refractory materials and technology of producing crucibles, filters and casting moulds, provided effect of the melt refining from gases and non-metallic inclusions in the process of solidification and after hardening of the billet is preserved. Criterion of serviceability of refractory materials is, first of all, degree of contact interaction between the refractory and the melt.

A series of experiments was carried out for investigation of interphase interaction of such materials as quartz, distensilimanit, corundum, zircon and alumomagnesian spinel with melts of refractory alloys of the grades ChS70, ChS88U and ChS104. Experimental meltings were carried out in the commercial vacuum-induction furnace UPPF-2 according to the technological conditions, established at the enterprises-manufacturers of GTE blades and vanes for each grade of the alloys (pressure in the furnace was 1.2–2.5 Pa, temperature of pouring into the moulds — 1560–1580 °C, and temperature of the mould — 800 °C). Depth of change of the cast layer (so called contact zone), measured by means of the metallographic microscope, was selected as the main parameter, which characterized degree of the interaction. Structural-chemical peculiarities of the contact zone were investigated by methods of X-ray microspectral analysis, auger-spectroscopy, and optical metallography; microhardness of the cast along cross section of the specimens was also studied. The investigations showed that depth of the zone constituted from 0.5–5.0 in interaction with alumomagnesian spinel to 150–200 µm for quartz, and diminished along the row quartz–distensilimanit–zircon–corundum–alumomagnesian spinel.

Analysis of structural changes of the contact zone showed absence in it of carbide precipitations, which proved carbon impoverishment of the interaction zone. In the course of X-ray microspectral analysis reduction of content of such elements as aluminium, titanium and chromium in the near-surface zone was registered. Probably mechanism of interaction of the alloy with the mould is stipulated by oxidation of the alloy components (carbon, aluminium and titanium by oxygen) released in dissociation of SiO₂ from the

mould and redistribution of these elements in the near surface zone of the casts.

On the basis of the results obtained, taking into account application as binding agents in manufacturing of GTE blades and vanes of mainly hydrolyzed ethylsilicate or silica gels (sources of faintly structured amorphous SiO₂), we developed method for binding SiO₂ into more thermostable compounds [6].

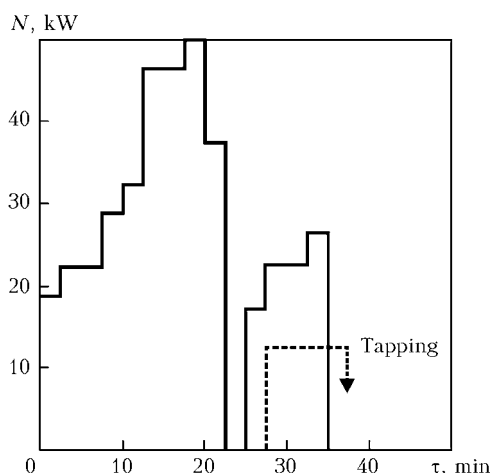
The authors have experimentally shown that finely dispersed powder of metal aluminium may serve as efficient modifier for binding SiO₂. This allows transforming SiO₂ in heat treatment of the moulds into alumosilicate-mullite. So, depth of changed layer of the cast, poured into corundum mould with binding ethylsilicate, containing 14–16 % SiO₂, constituted 30–40 µm in contrast to the cast, poured into the modified mould (20–25 µm).

Long- and short-term strength tests of the specimens showed that temperature below 800 °C and depth of the contact zone within 40 µm do not exert significant influence on values of mechanical characteristics, but fatigue strength of the specimens, poured into moulds from different materials, clearly depends upon depth of the contact zone. So, utmost endurance on the basis of 2·10⁷ cycles at temperature 800 °C of alloy ChS70 constituted for the specimens, poured into moulds without a modifier, 400–420 MPa, while with application of a modifier — 430–440 MPa. Similar trend was registered in tests of specimens from alloy ChS88U [7].

On the basis of the results of investigations, carried out for the purpose of choosing refractory materials for manufacturing filters and crucibles, it was recommended to use corundum and alumomagnesian spinel. Technological process for manufacturing shell forms from modified ceramics was developed under manufacturing conditions.

For increasing degree of cleaning of a secondary charge billet in manufacturing of the GTE special purpose parts (blades of the first and second stages) it was recommended to carry out after zone cleaning second stage of refining remelting of produced billet by developed in PTIMA, method of combined melting [8], which envisages remelting of wastes in vacuum-induction installation, erected on the basis of a serial commercial furnace UPPF-3M.

Melting of the charge and overheating of the melt is performed in a ceramic crucible by means of induction heating, and refining and thermal and time treat-



Melting conditions of alloy ChS88U: solid line shows vacuum-induction heating; dash line indicates electron beam heating; N — power; τ — time of melting

ment — due to additional electron beam heating of the melt by the electron beam gun [9]. Technological remelting modes vary depending upon the ratio of conditioned and off-grade wastes, used in manufacturing of a secondary billet. Power of the vacuum-induction inductor was increased in melting (Figure) up to the maximum (50 kW) for the purpose of the melting time reduction. After induction of the liquid-metal pool electron beam gun was switched on and the pool was heated by the beam in addition to the vacuum-induction heating for removal of slag from the surface and intensification of the melt refining process for fuller evaporation of slag from the surface. Integral temperature of the pool after these manipulations constituted 1600–1700 °C.

Efficiency of the new method was tested in refining of conditioned wastes of refractory corrosion-resistant alloys, used for manufacturing blades of aviation, ship and stationary engines [10, 11]. It was established that combined melting ensured efficient reduction in the alloys of gases, impurity elements, and non-metallic inclusions in all investigated types of alloys and enabled refining of the structure and cleaning of the grain boundaries in comparison with the castings, produced according to the standard technology.

So, sulfur and phosphorus relate to the most harmful impurities, which form low-melting eutectics from sulfides and phosphates of certain metals, that's why their content in the alloys is strictly limited by valid standards by the concentration 0.010–0.001 %. It is important to stress that after two-stage remelting according to the presented conditions in the alloy ChS88U the trend was registered to reduction of phosphorus content (from 0.0050 in the primary charge billet to 0.0037 % in the secondary one) and content of sulfur did not exceed assigned by the standard level when ratio of conditioned and off-grade wastes in the charge was 1:1.

As far as yield of efficient metal is concerned, which was estimated by the ratio of the metal mass in the billets to the mass of the charged wastes, in refining of conditioned wastes by the VIR + EBR method it constituted 98 %, while in refining of conditioned wastes in the mixture with the off-grade ones — 89.5 %. Although remelting of off-grade wastes is accompanied by significantly higher irre-

trievable losses of metal in comparison with the conditioned ones, application of the developed technology is efficient, because it allows to return into the production about 90 % of the wastes.

CONCLUSIONS

1. Analysis of intraplant accountability documentation concerning formation and dynamics of accumulation of cast waste in production of cast GTE parts (rotor blades and nozzle guide vanes, struts, fairings, etc.) on the basis of SE «Zorya–Mashproekt» was carried out. According to the obtained data on formation of conditioned and off-grade wastes (quantity, degree of contamination) norms of their ratio in remelting into secondary charge billet were drawn and recommendations of allowable content of the types of wastes according to each grade of alloys, taking into account responsibility of each part, were given.

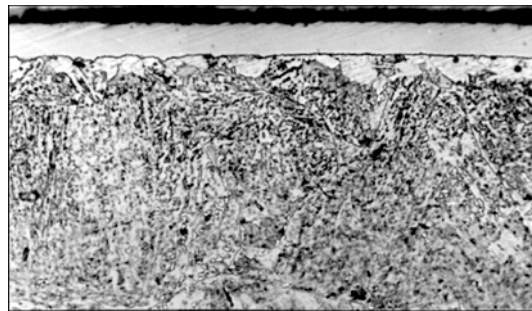
2. It was shown that significant increase (up to 90 % of the charge mass) of the off-grade waste utilization factor was achieved by development and testing of the technology of zone remelting of the refractory alloy waste in horizontal melting unit PMP-4 with application of original design of a multilevel ceramic mould, which allowed performing primary mechanical refining of the melt due to the inserted ceramic filter. Thermal gradient at the grain growth front, which equals 15–20 °C / cm, enables casting-off of impurity elements to the boundary of solidification front and their further removal by machining of the billet.

3. The investigations showed that main reason of the melt interaction with material of the mould was SiO₂ of the binder — hydrolyzed ethylsilicate. For elimination of this phenomenon technology for binding SiO₂ (mullite) was developed, which is a thermo-chemically stable element and does not interact with the melt.

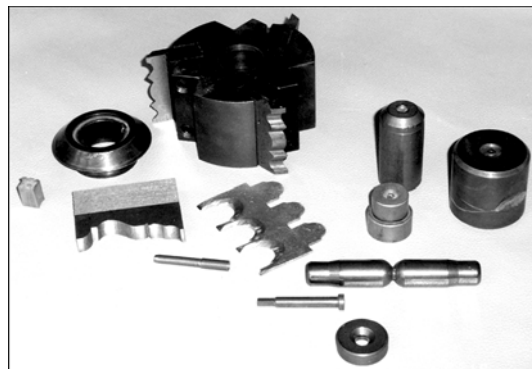
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DEPOSITION OF CARBIDE COATINGS FROM SALT MELTS

- The process of deposition of carbide coatings on parts of carbon steels and cast iron is performed by immersing the parts into a salt melt at a temperature of 800–1200 °N for 0.5–3 h.
- Thickness of carbide coatings ranges from 5 to 30 µm. Surface roughness as a result of the treatment does not deteriorate, providing that its initial value is $R_a \geq 0.5$ µm.
- Microhardness of coatings of vanadium carbide is at a level of 26–28 GPa, and that of chromium carbide is 14–16 GPa.
- The carbon content on the surface of a part hardened should be not less than 0.45 % and 0.30 % for formation of vanadium carbide and chromium carbide, respectively.
- The technology is environmentally clean, harmful gas emissions and sewages are absent. The technology allows coating deposition to be combined with oxidation-free heating in a salt melt for hardening.
- The process is intended for hardening of parts operating under friction and wear conditions, including under impact loading, as well as for hardening of cutting, bending, drawing, pressing, forming and blade tools.
- Performance of parts and tools grows by a factor of 2–25 as a result of the treatment.



Microstructure of vanadium carbide coating on steel



Parts with vanadium carbide coatings

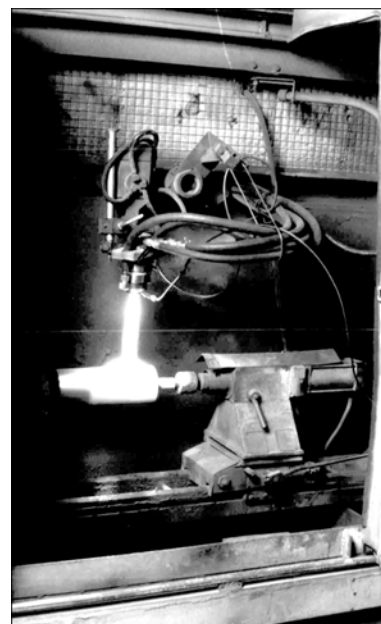
MACHINE «KYIV-S» FOR SUPERSONIC AIR-GAS PLASMA SPRAYING

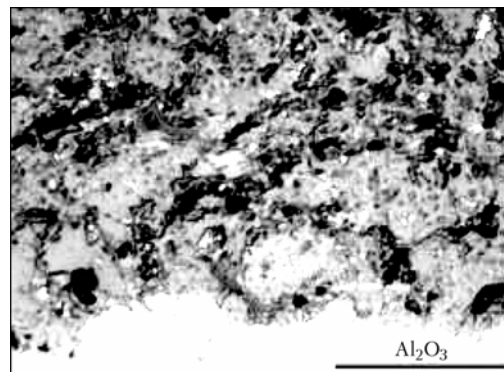
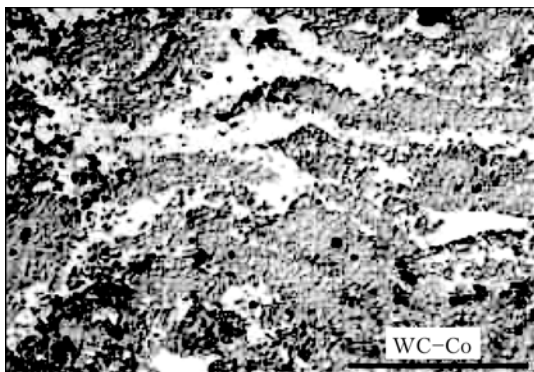
The machine is designed for deposition of wear-, heat-, corrosion-resistant, thermal barrier and other types of coatings of metals, alloys, oxides, carbides and other refractory compounds.

Specifications of machine «Kyiv-S»

Working gas	air + 5–15 vol.% hydrocarbon
Working gas flow rate, m ³ / h	10–40
Power, kW	70–160
Current, A	200–400
Voltage, V	350–450
Productivity, kg / h:	
metals, alloys	up to 50
oxides	up to 20
Material utilisation factor	0.65–0.80
Properties of coatings:	
adhesion strength, MPa	60–150
porosity, %	0.5–5.0

Supersonic air-gas plasma spraying provides quality of the coatings at a level of that of the HVOF process. At the same time, it is characterised by higher (3–8 times) productivity.



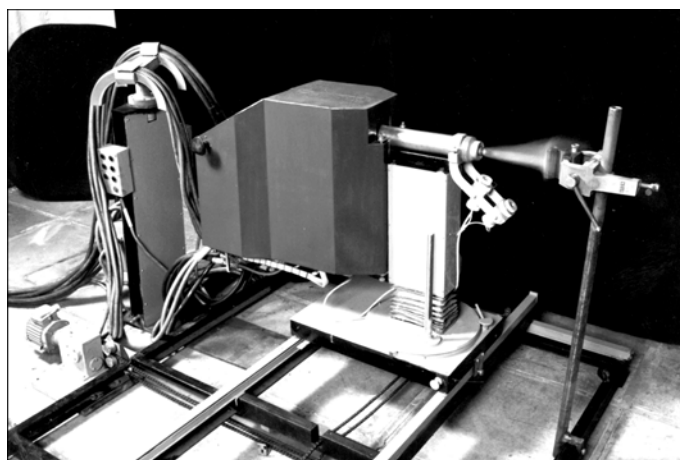


Application. Plungers of hydraulic systems, rods, turbine rotor shafts, pump pistons, components of power generation, metallurgy and pulp and paper industry equipment, screws of conveyer systems, etc.

MACHINE «PERUN-S» FOR DETONATION COATING

Purpose. «Perun-S» is a highly productive stationary unit, whose industrial application is particularly efficient for mass and large-series production of coated parts, as well as for manufacture of wide ranges of products.

«Perun-S» provides versatility and simplicity of the process, substantial extension of service life of parts, durability of sprayed coatings, saving of materials, low power consumption (1 kW / h), wide diversity of parts treated, and safe operation.



Specifications of machine «Perun-S»

Frequency, cycle / s	3.33; 6.66
Surface area covered per cycle, mm ²	320
Average thickness of one coating layer, μm	2–25
Powder consumption, kg / h	1–4
Powder utilisation factor	0.4–0.6

Detonation coatings allow a 2–50 times extension of service life of parts, replacement of scarce materials, as well as reduction of cost and weight of parts.

The coatings are sprayed by detonation on pistons and cylinders of engines, shafts or their journals, bearings, cams, guides, holders, sealing or bearing surfaces, elements of electric switching devices, cutting and measuring tools, dies, moulds, etc.

Application. Aircraft and motor industries, power engineering, chemical engineering, instrument making, mining equipment, hydraulic machines, agricultural machinery, etc.

MACHINE MPN-004 FOR MICROPLASMA SPRAYING OF COATINGS

Microplasma spraying provides deposition of coatings on small-size parts and components, including those with fine sections, this being unachievable with any other methods. This makes it possible to expand the application of plasma spraying and produce various-purpose coatings (wear- and corrosion-resistant, antifriction, electrically conducting, etc.) to repair microdefects and recondition after wear the small-size and thin-walled parts of ferrous, non-ferrous and refractory metals and alloys, as well as ceramics.

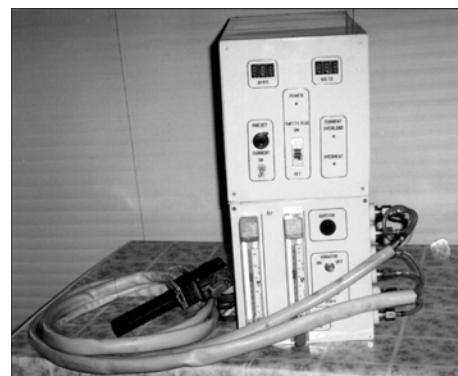
Specifications of machine MNP-004

Power, kW	0.5–2.0
Current, A	20–50
Plasma and shielding gas	Argon
Flow rate of plasma gas, l / h	12–200
Flow rate of shielding gas, l / h	120–240
Productivity, kg / h	0.25–2.50
Weight of plasmatron, kg	0.3
Dimensions of the machine, mm	390 × 220 × 200
Weight, kg	14

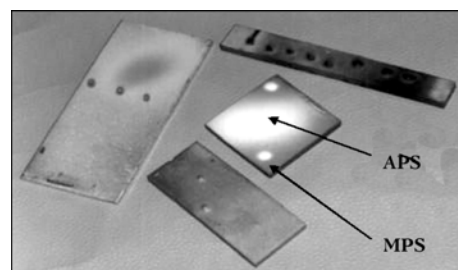
Distinctive features of microplasma spraying

Spraying spot size, mm	1–5
Noise level, dB	30–50
Specific power consumption, (kW · h) / kg	0.8–2.0

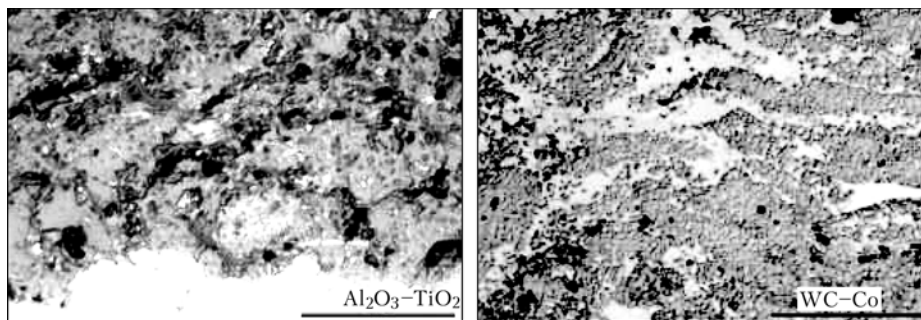
Spraying materials. Metals (Al, Ni, Mo, etc.), alloys (Al-, Fe-, Ni-, Co-, etc.), oxides (Al_2O_3 , ZrO_2 , etc.), carbides (WC, Cr_3C_2 , etc.).



Machine MPN-004



Spraying operation



Structure of coatings

Application. The process and equipment for microplasma spraying are of interest for enterprises of instrument design; motor industry; domestic appliances industry; electrical industry; electronic engineering; medical engineering; various repair companies, including small and medium businesses.

Proposals for co-operation. Services in deposition of coatings, training, technology transfer, manufacture and supply of equipment.

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