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APPLICATION OF MODIFYING FOR IMPROVING PROPERTIES OF ANNULAR BILLETS FROM NITROGEN-CONTAINING STAINLESS STEELS PRODUCED BY METHOD OF CENTRIFUGAL ELECTROSLAG CASTING

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New technology for centrifugal electroslag casting of annular billets from high-strength stainless steels, including modifying of the molten metal by dispersed particles of molybdenum and vanadium, is described. Results of the cast metal tests and advantages of modified cast billets are presented.

Key words: centrifugal electroslag casting, annular billets, nitrogen-containing steels, modifying, structure, mechanical properties

Demand for state-of-the-art production of annular billets is very high. They are especially widely used in ship-building, power engineering, chemical and petrochemical industries, aviation and missile technologies. So, for example, in gas-turbine and turbojet engines annular special-purpose parts constitute 25–30 % of general mass of an engine [1].

Choice of the method for production of hollow billets depends upon their designation. For manufacturing such parts casting and mechanical (processing by pressure, cutting on metal-cutting machines) methods are frequently used.

BILLETS produced by open casting methods have significant shortcomings — not sufficiently high quality of metal and difficulty in producing dense castings. During melting and casting molten metal stays for a long time in contact with refractory brickwork of a furnace, with a ladle, a wiring, a mold, and the atmosphere. As a result it is saturated with gases and non-metal inclusions. Simultaneous casting of big portions of metal and slow solidification enable occurrence in the casting of shrinkage cavities, zonal and dendrite liquation, and structural inhomogeneity. That's why mentioned cast billets are mainly used for manufacturing general-purpose parts.

BILLETS for special-purpose structures are produced from solid-section billets using different methods of hot conversion — forging, piercing, pressing, and expanding [1]. Serious shortcomings of this technology consist in high cost of billets stipulated by use of a great number of intermediate operations (forging of ingots, roughing, cutting into billets, piercing of the billets, distribution, calibration), low metal utilization coefficient, and need to use expensive press-forging and rolling equipment. So, application of hot

deformation in production of annular billets is a compelled measure, to which one resorts because of low quality of casting. That's why production of cast billets, the shape and size of which maximally approach those of the ready item and quality of which is not inferior to the one of the deformed billets, is an actual task.

Everything mentioned above also relates in full degree to annular billets made from nitrogen-containing steels, in particular steels 15Kh12N2AM, 15Kh12N2MVFAB, etc., which are widely used for manufacturing parts and units of power engineering installations that operate under conditions of increased temperatures and are subjected in the course of their operation to significant loads of different character. Requirements, established for items manufactured from these steels, may be mainly met only in case of using deformation processing, because properties of cast steels of these grades even after refining remelting and optimum conditions of heat treatment are inferior to those of forged ones. Manufacturing of parts and units of big overall dimensions and mass is accompanied by excessively high consumption of expensive materials and low productivity.

High potential for solution of this issue has method of centrifugal electroslag casting (CESC), the essence of which consists in remelting of the metal in the melting unit (a crucible), which enables accumulation of the molten metal and slag in necessary amounts and their subsequent casting into a rotating mould, whereby efficient refining and reliable protection of accumulated in the crucible metal against action of the atmosphere is ensured, and melting loss of the alloying elements significantly reduces. An important advantage of the process, in comparison with traditional ones, is simplicity of the equipment and the fitting-out.

At the same time, as showed investigations, level of mechanical properties of cast billets, produced by the method of electroslag casting from high-alloy



steels and alloys, solidification of which is accompanied by significant development of dendrite chemical inhomogeneity because of presence in their composition of strongly sweating elements, is, all the same, lower than that of forged billets [2]. Reduced level of mechanical, and especially ductility properties, have also cast billets, produced from steel 15Kh12N2MVFB.

One of the ways of solving this issue is development of the methods of structure control of the electrosag casting metal and, therefore, of its mechanical properties, because the latter ones are structurally sensitive.

For this purpose complex volumetric modifying of nitrogen-containing chrome-nickel steel 15Kh12N2MVFB in electrosag casting of billets of «flange» type, having mass up to 50 kg and thickness of walls up to 30 mm, was investigated. The modifier was used, composition of which includes molybdenum, vanadium, and nickel. The modifier was selected proceeding from the following ideas. Dispersed particles of molybdenum with high melt point are inoculators — centers of nucleation. Vanadium has crystal lattice, which is similar to that of molybdenum and small difference with the latter in electronegativity and atomic diameter, which stipulates formation of continuous rows of solid solutions between them [3]. Due to the known principle «a similar one is wetted (adsorbed) by a similar one» [4], atoms of vanadium after introduction of the modifier into the melt are selectively adsorbed by surface of molybdenum particles. High affinity of vanadium to nitrogen should increase nucleation activity of molybdenum particles. Nickel ensures isolation of the inoculator (molybdenum) particles from each other, thus preventing their coalescing and coagulation at the stage of the modifier introduction into the melt.

The modifier was produced by mixing of powder components, having dispersity 0.5–1.0 μm , with their subsequent pressing at specific pressure 500–700 MPa into the briquette-pellet of 30 mm diameter and 10 mm thickness (Figure 1). The pellet was pressed in a special gadget (Figure 2). In the course of pressing mutual movement of particles relative each other takes place, due to which oxide film on surface of the pellet is destroyed. Size of the pellets is selected proceeding from their sufficiently quick dissolution in molten metal (30–60 s) and to ensure conditions that one pellet to be per 10 kg of the melt subject to processing. Such pellets have significant density, which stipulates their quick passage through molten slag that ensures high degree of assimilation of the modifiers by the metal pool. The modifier was introduced into the melt at the temperature 1750 °C for 2–3 min before casting the melt into the metal mould. Ratio and number of particles of inoculators and the activating additive were selected experimentally in order to achieve maximum refining of the cast metal structure.

Experiments were carried out on the A-550U installation complete with copper skull water-cooled

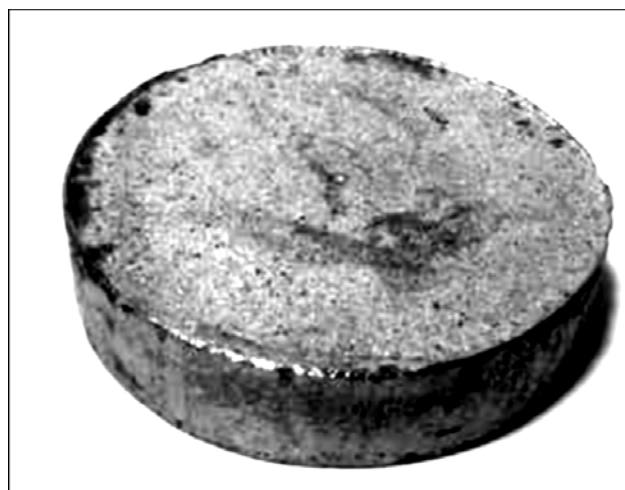


Figure 1. Appearance of modifier pellet

melting unit, a centrifugal device, and a metal mould. The metal to be remelted was represented by the rods of respective steel.

As far as rate of the metal solidification in the zone of an item formation is high in CESC, composition of used flux is of great importance. The latter should have low melting point, wide range of solidification, significant yield at high cooling rate, and ensure stability of skull layer over the whole surface of a billet. That's why flux of the $\text{CaF}_2\text{--CaO--Al}_2\text{O}_3$ system was used with addition up to 10 % SiO_2 , which allowed increasing forming properties of the flux and its ductility in solid state [2].

Data of chemical analysis performed on the ARG-MET-930 SP optical-emission analyzer (Table 1) prove that metal composition of the casting, produced

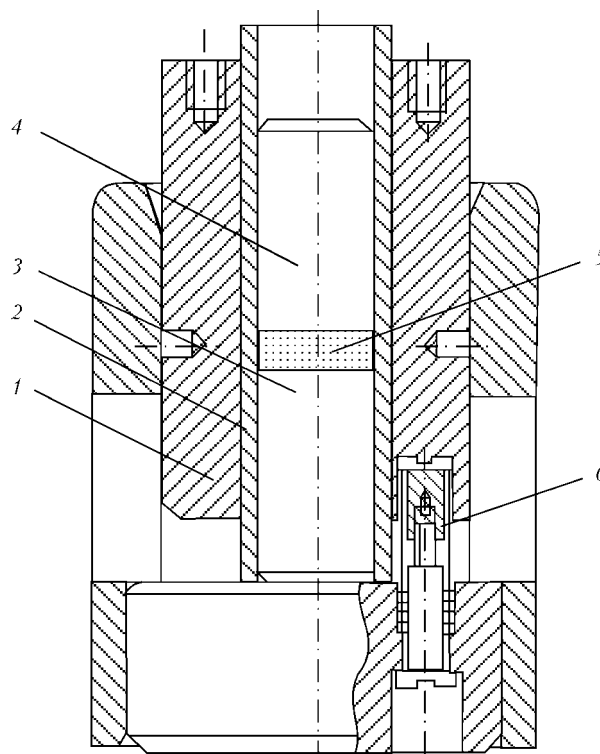


Figure 2. Pressure casting die for manufacturing pellets of modifiers: 1 — holder; 2 — insert; 3, 4 — upper and lower punches, respectively; 5 — modifier pellet; 6 — push-out device

**Table 1.** Chemical composition of steel 15Kh12N2MVFB

Metal type	Weight share of elements, %									
	C	Cr	Ni	Mo	W	V	Nb	S	P	N
Electrode	0.16	12.34	1.96	1.48	0.87	0.25	0.32	0.006	0.009	0.05
CESC without modifying	0.15	12.17	1.95	1.41	0.84	0.18	0.25	0.003	0.007	0.06
CESC with modifying	0.15	12.21	1.95	1.46	0.85	0.23	0.28	0.003	0.007	0.07
TU 14-1-1161-75	0.13–0.18	11.0–12.5	1.4–2.1	1.35–1.65	0.65–1.0	0.18–0.3	0.2–0.35	≤ 0.05	≤ 0.030	0.02–0.08

by electroslag casting with application of mentioned flux, changes insignificantly concerning majority of the main alloying elements and remains within the grade composition. Metallographic investigations showed that cast non-modified metal has a directed transcrystalline structure with high length of primary dendrite axes (Figure 3, *a*). Microstructure of such metal represents coarse-needled martensite, plates of which have characteristic orientation and are mainly arranged at the angle 60° (Figure 3, *b*).

Results of mechanical tests of such metal on specimens, cut out in tangential direction, at normal temperature (Table 2) showed that its ductility properties are significantly inferior to those of a deformed metal and do not meet technical requirements.

It was established in investigation of the fracture surface of impact specimens after the tests that micro-fractures are of semi- and brittle character (Figure 3, *c*). Micrographic investigations showed that

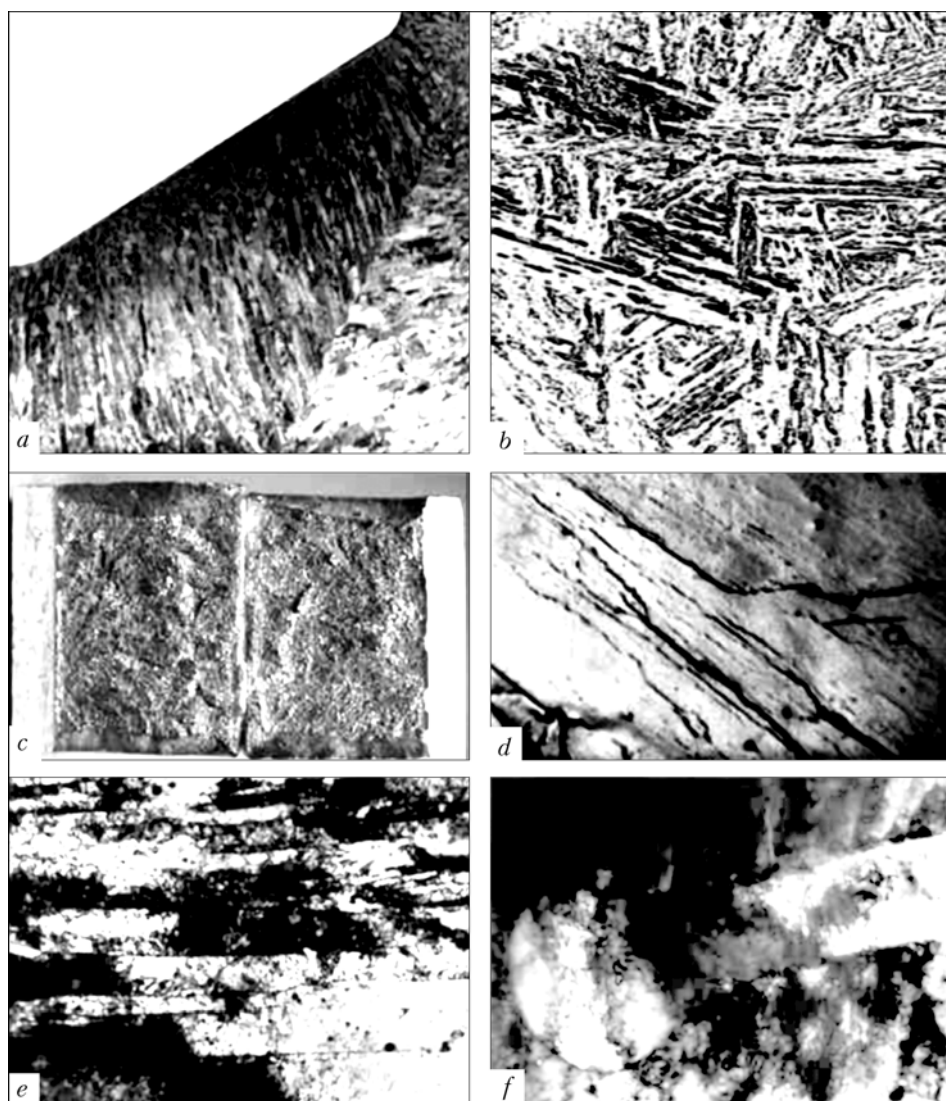


Figure 3. Structure of cast annular billet produced by electroslag melting from non-modified steel 15Kh12N2MVFB: *a* — macrostructure; *b* — microstructure, $\times 500$; *c* — fracture relief; *d* — fracture microfractography, $\times 5000$; *e* — fine structure of α -martensite crystals, $\times 22000$; *f* — β -ferrite in martensite matrix, $\times 27000$

**Table 2.** Mechanical properties of steel 15Kh12N2MVFB

Metal type	σ_t	$\sigma_{0.2}$	δ	Ψ	$KCU, \text{ MJ / m}^2$	Heat treatment
	MPa		%			
CESC without modifying	1067	838	11	27	0.32	Normalizing at 1130 °N, annealing 750 °N, oil quenching from 1120 °N, annealing at 700 °N
CESC with modifying	1056	862	18	59	0.68	
TU 14-1-1161-75	≥ 1030	≥ 830	≥ 14	≥ 55	≥ 0.59	

the fracture represents a trans-crystalline spalling with characteristic «river pattern» (Figure 3, *d*).

Electron-microscopic investigations showed that the main structural component is BCC — α -martensite, crystals of which form packages of plane-parallel plates (Figure 3, *e*). Residual austenite was not discovered. At the same time in martensite matrix there is a certain amount of structurally free δ -ferrite, which was discovered in the form of inclusions, located both inside and over boundaries of former austenite grains (Figure 3, *f*). Evidently, exactly this causes significant worsening of the cast metal ductility. Similar

influence of δ -ferrite on impact toughness and heat resistance of stainless steels was noted in [5, 6].

Introduction of a modifier into the metal causes significant change of produced structure and properties of the cast metal. Structure and mechanical properties achieve the best state at ratio of the particles of inoculators and the activation additive 1:2 and mass of the modifier 0.5–0.8 %. Transcrystallization zones are removed in the annular casts, size of dendrites drastically reduces and they acquire favorable shape all over the volume of the crystallized metal (Figure 4, *a*). Plates of α -martensite do not have

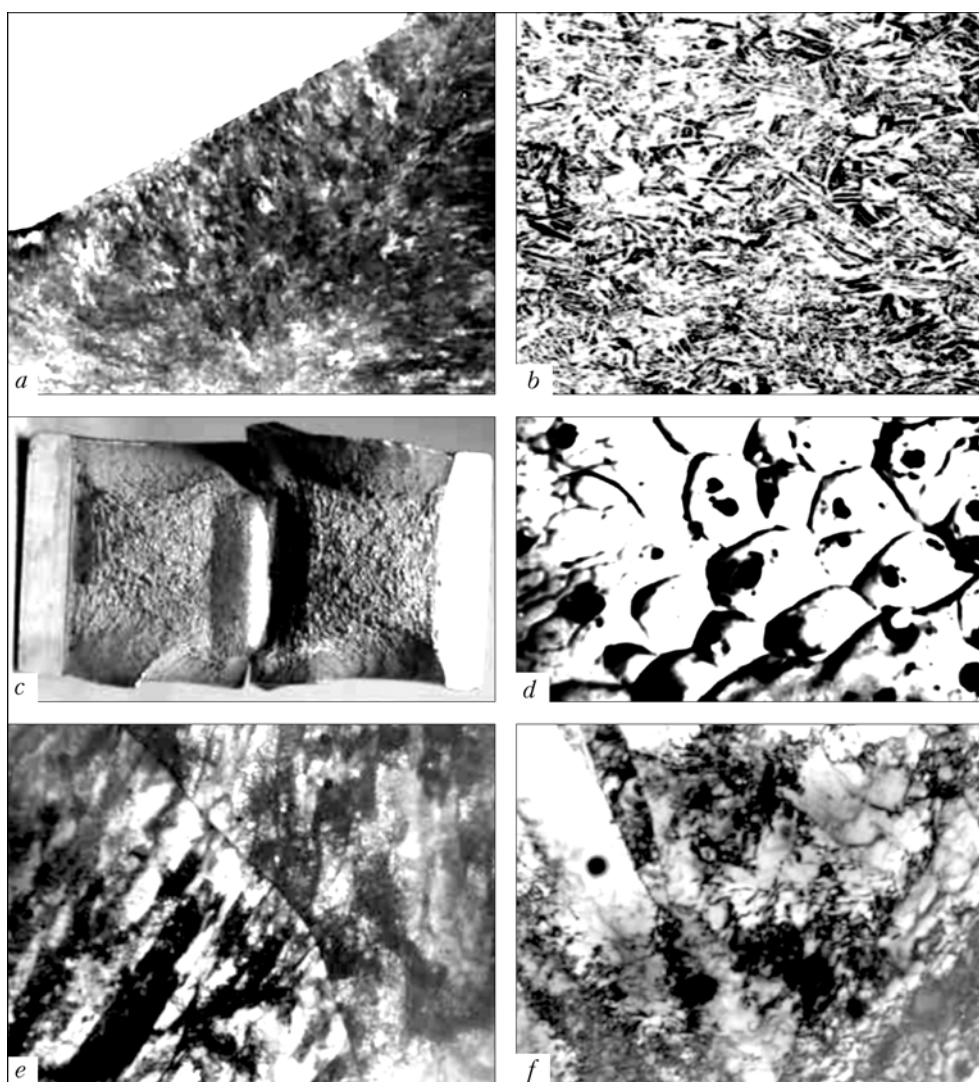


Figure 4. Structure of cast annular billet produced by electroslag melting from modified steel 15Kh12N2MVFB: *a* — macrostructure; *b* — microstructure, $\times 500$; *c* — fracture relief; *d* — fracture microfractography, $\times 5000$; *e* — fine structure of α -martensite with interlayers of residual austenite, $\times 22000$; *f* — oxycarbonitrides, $\times 50000$

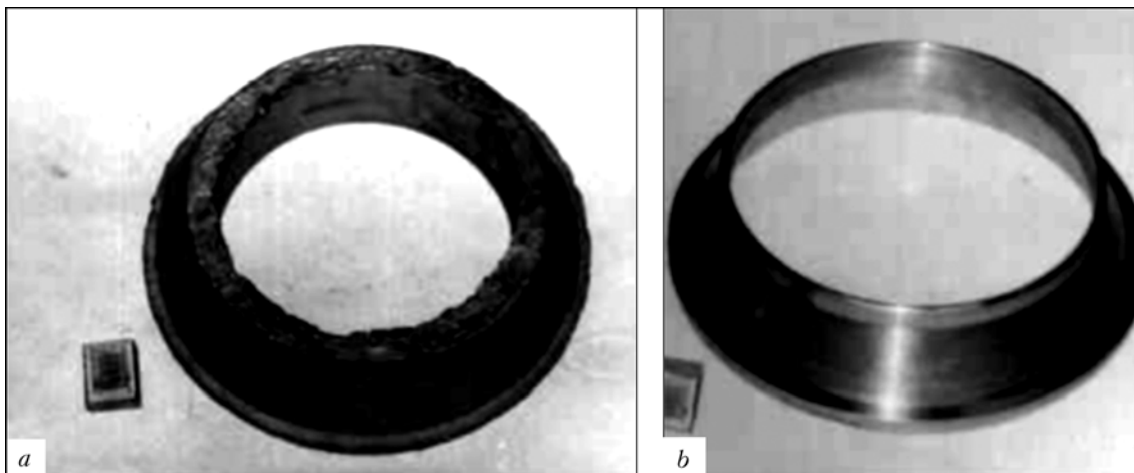


Figure 5. General view of cast annular billet (a) and ready part produced from it after machining (b)

preferential orientation (Figure 4, b). Mechanical tests showed that all characteristics of the modified metal are higher than those of non-modified metal and are at the level of the deformed metal properties.

It was established in investigation of the impact specimens that all failure zones (central, side, and additionally broken zones) have practically the same, characteristic of tough fracture, relief (Figure 4, c). The main micrographic characteristic of failure is a hole-like fracture (Figure 4, d). Significant precipitations of δ -ferrite were not detected in microstructure of such metal. At the same time in addition to martensite residual austenite occurs, located mainly between martensite crystals in the package in the form of thin interlayers (Figure 4, e). Boundaries between adjacent α -crystals are, as a rule, located at a small angle. In addition, in all places of the structure dispersed particles, evidently of oxycarbonitrides, were detected, which looked like orbicular black inclusions of different size (Figure 4, f).

Presented data allow drawing conclusion that used modifier is optimal for formation of the metal structure of electroslag castings, which determines ductility characteristics of nitrogen-containing martensite and martensite-ageing steels. Occurrence of residual austenite and absence of δ -ferrite, evidently, deter-

mine higher ductility properties of the modified cast steel 15Kh12N2MVFB.

As a result of the investigations technology for casting annular billets of gas-turbine engines from high-strength nitrogen-containing steels was developed. One of such cast billets and a manufactured from it component are shown in Figure 5.

So, properties of annular billets, produced by CESC method with application of the metal modifying by dispersed inoculators, are not inferior to those of hot-deformed billets. At the same time they are less labor-consuming and cheaper.

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ON TRANSPORTATION OF NITROGEN THROUGH MOLTEN SLAG

V.V. LAKOMSKY, Yu.M. POMARIN, G.M. GRIGORENKO and V.Yu. ORLOVSKY

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Feasibility of nitrogen transportation through the molten oxide and fluoride-oxide slags is considered on the basis of analysis of literature sources. Assumption is made that nitrogen permeability can be defined not by solubility of nitrogen in slag, but, probably, by the value of chemical potential of gas in the slag and the metal.

Key words: nitrogen, slag, permeability, chemical potential

Nitrogen in steels is considered not just as a harmful impurity, but also as an independent alloying element. So, in melting or secondary remelting it is necessary in some cases to remove nitrogen from the metal, while in other cases retain it in the metal or alloy metal by it. It is considered that it is impossible in presence of a molten slag, which participates in many metallurgical processes, to alloy metal by nitrogen directly from gaseous phase. That's why alloying of a metal by nitrogen should be performed by introduction into molten metal of nitrated ferroalloys [1, 2] or nitrides of alloying elements [3]. Removal of nitrogen from the metal occurs only as a result of assimilation by slag of nitride inclusions, but not due to transportation of nitrogen to the metal through slag into the gaseous phase [4].

Investigation of nitrogen behavior in melting of steel in electric furnaces and electroslag remelting showed that denitration and nitration are possible, depending upon created conditions of melting [5, 6]. So, in order to answer the question about feasibility of nitration of the metal, covered by a layer of molten slag, directly from the gaseous phase, it is necessary to consider metal melting process for the purpose of determining conditions of nitrogen transportation through slag.

Transportation of nitrogen through slag is called gas permeability, which is determined as product of ultimate nitrogen solubility in slag C_N and nitrogen diffusion coefficient in slag D_N [7–9]:

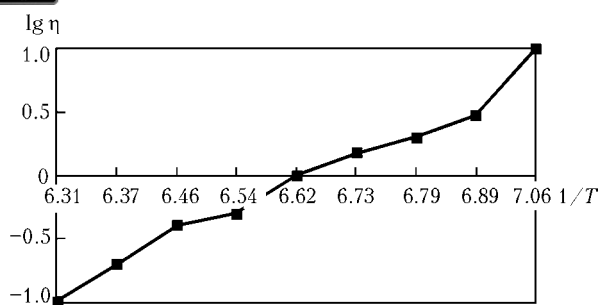
$$P_N = C_N D_N.$$

Two kinds of diffusion (molecular and convective ones) are present in the slag thickness, but it is not found out yet, which of them limits nitrogen transportation process. Taking into account methodology of estimation using Peclet number [10, 11], one may state that in the process of nitrogen mass transfer in slag the share of molecular diffusion, in comparison with the convective one, is negligently small.

Solubility of nitrogen in slag was determined in investigation of the double system gas–slag, while nitrogen permeability assumes transfer of the gas phase nitrogen through slag to the metal in the triple system gas–slag–metal. It was established in investigation of the latter that transportation properties of slag are determined by thermodynamic conditions, created not just on the interface gas–slag, but also on the interface slag–metal [12–14]. That's why it's not so much solubility of nitrogen in slag, as driving force of the whole process of nitrogen transfer from gas to the metal, which consists in difference of the nitrogen chemical potential value in different areas of the gas–slag–metal system, has to be taken into account. So, nitrogen permeability, as well as diffusion, is an energy-dependent process and occurs more intensively under action of additional energy pulses supplied from outside, for example, in case of arc action on the gas–slag–metal system [6].

For the purpose of checking mentioned assumptions we carried out comparative experiments — two series of melting in the Tamman furnace in nitrogen with application of graphite crucibles. In the first series slag, and in the second series metal (steel Kh18N10) under layer of slag was melted. Slag of oxide and fluoride-oxide systems was used. Content of nitrogen in the slag and the metal was determined using Kjeldahl method.

Results of the investigations showed that weight share of nitrogen in slag is higher in case of interaction of the gas phase nitrogen with slag without participation of metal than in case of interaction of nitrogen with slag in presence of metal. So, for example, in case of the gas phase contact with slag without metal solubility of nitrogen in slag CaO–Al₂O₃–15 % TiO₂ constitutes 0.136 %, in flux AN-295 (16 % CaF₂–51 % Al₂O₃–31 % CaO) — 0.119 %, while in presence of metal solubility in them equals 0.026 and 0.052 %, respectively. Content of nitrogen in the metal equals 0.035 % (slag CaO–Al₂O₃–15 % TiO₂) and 0.026 % (slag AN-295), which is lower than equilibrium concentration 0.17 %, calculated for conditions of interaction of molten metal with the nitrogen atmosphere.



Dependence of viscosity of slag 50 % CaF₂, 25 % CaO, 25 % Al₂O₃ upon temperature in coordinates lg η-1 / T

So, slag under described conditions transfers nitrogen from gas phase to the metal and does not keep it in its volume.

For explanation of noted ambiguities of gas permeability processes of slag melts it is necessary to present on the basis of literature data mechanism of nitrogen transport through molten slag, and consider for this purpose structure of the latter.

There are several models of slag structure, which originated not simultaneously, but by means of the liquid structure theory development. According to state-of-the-art assumptions, a slag represents solution of ions [15] with available in the solution free electrons [16]. Ions may be in the form of inactive multi-atom complexes and in the form of freely moving multi-atom and free complexes. Presence of free ions in oxide systems is improbable, but it is probable in fluoride and fluoride-oxide systems, in which exchange reactions may proceed with formation of volatile fluoride compounds and free ions [17–19]. Constructively the slag melt is a set of closely packed spheres (single- or several atom ions [20, 21]), between which, according to the Frenkel's liquid «hole» model, cavities («holes») are present. In them (depending upon their size) may be located dissolving in slag single or complex ion. These cavities, in contrast to vacancies in crystal bodies, may have different sizes and changeable parameters [22].

Number of «holes» determines value of such structurally-sensitive properties of a molten slag as density and surface tension. According to the «hole» model, probable volume of a «hole» V and surface tension σ are connected by the following dependence:

$$V = 0.68 \left(\frac{kT}{\sigma} \right)^{3/2}, \quad (1)$$

where k is the Boltzmann's constant; T is the absolute temperature.

Having determined radius of the «hole», one can estimate size of the particles, which are able to be placed in them.

Viscosity of a liquid depends upon both value of the viscous flow activation energy and free volume level. This dependence is expressed by formula of A.I. Bachinsky [9]:

$$\eta = \frac{A}{V_s}, \quad (2)$$

where A is the constant; V_s is the free volume of the liquid equal to the difference of its own and specific volumes.

So, free volume of the liquid equals total of the volumes of all «holes» $V_s = nV$, and its viscosity is connected with surface tension by the expression, obtained as a result of integration of the dependences (1) and (2):

$$\eta = \frac{A}{0.68n} \left(\frac{\sigma}{kT} \right)^{3/2}.$$

The higher is number of «holes», the lower is viscosity, and the higher is surface tension, the higher is viscosity. It is stated in descriptions of some investigations [23, 24] that when the slag melts are saturated by nitrogen, their viscosity and surface tension increase. So, during dissolution nitrogen and its compounds fill the «holes» and reduce free volume, thus causing growth of the value of structurally sensitive properties.

Mentioned changes of the structure are proved by the following. If, for example, to construct dependence of viscosity of the slag melts upon temperature in coordinates lg η-1 / T (in the Figure the dependence is shown for slag 50 % CaF₂, 25 % CaO, 25 % Al₂O₃), registered breaks on the diagrams will correspond to the temperature of structural change of the melts that causes variation of the number (or size) of the «holes» [24, 25]. Similar regularities were detected in processing of the results of electric conductivity investigations of various kinds of slag [26].

Solubility of nitrogen in slag, in opinion of many researchers, follows Sieverts law and depends upon degree of oxidation of the gas phase above molten slag [16, 27]. Driving force of nitrogen movement is difference of its concentrations according to the degree of oxidation of different molten slag layers. And at the same time it should be noted that nitrogen is present in molten slag not as an independent ion, but in the form of compounds with a cation, characterized by high affinity to nitrogen. From the whole set of frequently occurring slag components, one may single out such cations with high affinity to nitrogen as titanium, aluminum, calcium and silicon, and carbon.

Silicon is present in slag in the form of thermodynamically strong dioxide formed strong oxide complexes. That's why silicon, evidently, can not be bound with nitrogen. Titanium, as well as silicon, is present in slag in the form of thermodynamically strong oxides and, probably, can not form nitride compounds. Calcium (under certain conditions and, possibly, aluminum) can precipitate, as a result of exchange reactions, in free state and form nitride compounds in the slag melt [28, 29].

Metal calcium, added into slag in remelting, not just deoxidizes molten slag, but, when evaporating (due to high pressure of its vapor) reduces oxidation potential of the gas phase and enables improved transportation of nitrogen from gas into the metal [30, 31].



In opinion of many researchers, carbon can form in slag melts radicals of the type of cyanides CN^- or cyanamides CN_2^{2-} [32, 33]. But these radicals can not, in all evidence, exist by themselves and should have connection with cations of metals.

That's why our further investigations will be directed at study of transport properties of fluoride-oxide slag systems.

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INVESTIGATION OF PROCESS OF MANUFACTURING HOT-ROLLED AND COLD-FORMED PIPES FROM CAST NON-DEFORMED PIPE BILLET OF TITANIUM ALLOY VT1-0 PRODUCED BY METHOD OF ELECTRON BEAM MELTING

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Technology of manufacturing hot-rolled and cold-formed pipes directly from ingots of electron beam cold hearth melting has been developed. Quality of pipes of intermediate and finished sizes was investigated. It is shown that mechanical properties of pipes are in compliance with requirements of State standards.

Key words: vacuum electron beam melting, pipe billet, ingots, incoming inspection

At present ingots of 400 and 600 mm diameter, molten by electron beam or vacuum-arc method, are used for manufacturing pipe billets of 110–150 mm diameter [1, 2]. A pipe billet is manufactured by forging of ingots on hydraulic presses and forging machines within temperature range 1000–1050 °C. Then produced billets are subjected to turning for removal of defects and gas saturated (alphirated) layer.

For significant reduction of power inputs, manpower, and metal consumption coefficient under industrial conditions, a cast non-deformed ingot was used as a pipe billet on the TPA 140 assembly unit.

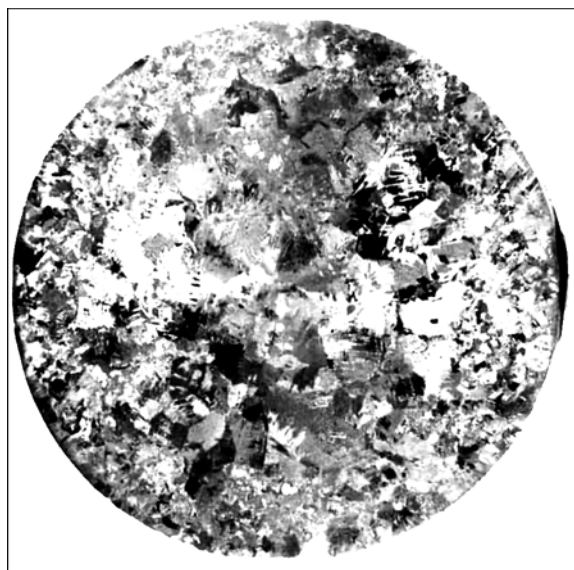


Figure 1. Macrostructure of cross section of ingot

The most efficient and economical method of manufacturing titanium-base ingots is vacuum electron beam melting. The main national supplier of such ingots for their subsequent conversion into pipes is SPC «Titan» of the E.O. Paton EWI, in which ingots of 110 mm diameter and length 1500–1600 mm were cast from titanium alloy VT1-0 according to the technologies of electron beam cold hearth melting (EBCHM) and semi-continuous casting in vacuum into the open-bottom water-cooled mould. Surface of the ingots was subjected to electron beam melting for removal of surface defects without machining and increase of suitable product output by 8–10 % [3].

Incoming inspection of the ingots showed that quality of their surface and geometric dimensions corresponded to requirements of TU U 27.5-23712944-005–2001 «Cast pipe billet from titanium alloys of grades VT1-00, VT1-0, VT6, PT-3V».

It was registered in the course of investigations that macrostructure of the ingots is dense and homogeneous, and is characterized by grains, structure of which is close to the equiaxial one (Figure 1). Size of the grain in the main area of the template (cross-section) corresponds to the index 10 according to ten-point scale of macrostructures (guidelines No. 1054–76 VIAM), and over circumference of the template at the depth 15 mm the structure is more fine-grain and corresponds to the index 6. Macrostructure of a forged billet, used according to the existing technology, corresponds to the indices 4–5. Defects in the form of pores, pits, cracks, and foreign inclusions were not detected.

Microstructure of the billets is course-grain, has course-acicular martensite structure, and corresponds to the indices 8–9. Content of hydrogen in the billet is 0.003 %.



Mechanical properties of a cast billet are characterized by non-uniformity because of the coarse-grain structure (Table 1).

As far as till now piercing of a cast pipe billet on the cone mill was not performed under commercial conditions, it was interesting to determine its optimum temperature-deformation parameters. For this purpose cast metal was tested for «pierce-ability» and its allowable critical reduction was determined. For this purpose cone specimens, having dimensions $30 \times 35 \times 100$ mm, were manufactured. Rolling of the specimens was performed on the laboratory disk mill of TsKB-78 type. Prior to rolling the specimens were heated in electric furnace G-30. Rolling was performed at four temperature values (950, 1000, 1050 and 1100 °C).

For determining critical reduction after rolling the specimens were cut over diameter along the generatrix. Value of critical reduction was calculated by formula [1]:

$$\delta_{cr} = \left(1 - \frac{1}{1 - \sqrt[3]{1 + \frac{6 \tan \beta \cdot l_{cr}}{d_c}}} \right) \cdot 100 \%,$$

where β is the angle of the cone specimen generatrix inclination; d_c is the diameter of the cone specimen in section, where the cavity formation begins; l_{cr} is the distance from the front end of the specimen to the place, in which the cavity formation begins.

Analysis of carried out investigations showed that all specimens were rolled without fractures, and exposure of the cavity in central part was not detected.

On the basis of data obtained degree of reduction of the billets for manufacturing hot-rolled pipes was selected at the level 16–17 % within temperature range of 950–1050 °C.

Hot rolling of conversion pipes into size 108×15 mm was performed on the TPA 140 pipe-rolling automatic installation according to existing technology. The metal was heated in the continuous furnace in center up to the temperature 980–1010 °C.

Table 1. Mechanical properties of cast billet at 20 °C

Specimen No.	σ_t , MPa	σ_y , MPa	δ_5 , %	ψ , %	KCU_2 , J / cm ²
1	415	330	24	42	17.5
2	345	310	13	36	21.7

Deformation process at all stages of conversion (a disk mill for helical rolling, expansion cone and sizing mills, a leveler) [4] proceeded under stable conditions and did not differ from the rolling process of pipes manufactured from a forged billet, whereby rolling-out coefficient constituted 2.168, deformation degree — more than 50 %.

Hot-rolled conversion pipes of $108 \times 15 \times (3180-3500)$ mm size were subjected to check on correspondence to requirements of GOST 21945–76 «Seamless hot-rolled pipes from titanium-base alloys» in the group of quality B, i.e. with conventional quality of surface without machining. Visual inspection of external and internal surfaces showed that surface quality corresponded to GOST 21945–76. Geometric dimensions and curvature of the pipes were also within requirements of mentioned standard.

Metal of the pipes has coarse-grain martensite structure (Figures 2 and 3).

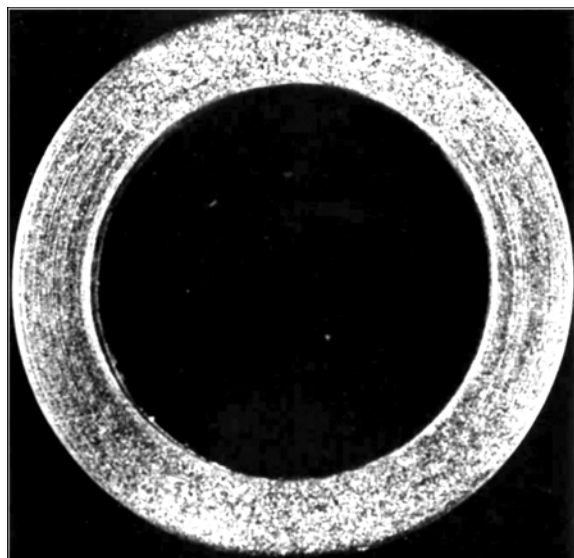
Depth of the gas-saturated layer does not exceed that of the layer formed in the process of rolling of pipes according to existing technology.

Mechanical properties of pipes in hot-rolled state correspond to properties of heat-treated pipes according to GOST 21945–76, non-uniformity of distribution of values of relative elongation in pipes within one melting being detected.

Cold conversion of pipes was performed in «Zavod SETAB Nikopol» Ltd. The pipes were delivered for production after machining (boring and turning at the depth 1 mm from internal and external surfaces). All pipe processing operations from delivery for production to acceptance control were performed according to the valid technology.

Table 2. Mechanical properties of hot-rolled conversion pipes

Specimen No.	Tensile strength σ_t		Yield strength σ_y		Relative elongation δ_5 , %	Reduction in area ψ , %
	kgf / mm ²	MPa	kgf / mm ²	MPa		
1-1	51.0	499.8	43.0	421.4	21.0	45
1-2	52.0	509.6	50.0	490.0	21.0	44
1-1	42.5	416.5	36.5	357.7	32.0	64
1-2	47.0	460.6	41.5	406.7	24.0	55
1-1	44.0	431.2	39.0	382.2	25.0	61
1-2	45.5	445.9	41.0	401.8	27.0	60
1-1	51.0	499.8	45.0	441.0	24.5	48
1-2	49.5	485.1	46.0	450.8	23.0	52
Standard	35–58	343–568	Not less than			
			25	245	20	42

**Figure 2.** Macrostructure of hot-rolled pipes

A conversion billet after machining and pipes of intermediate sizes were subjected to annealing in the continuous furnace according to existing conditions for alloy VT1-0 at the temperature $(770 \pm 10)^\circ\text{C}$.

From pipes specimens were taken at each process stage for investigation of mechanical properties, microstructure, and content of hydrogen (Table 3).

Microstructure of pipes of intermediate sizes represents a mixture of recrystallized grains of the worked α -phase and remnants of non-worked hot-rolled structure, which is characteristic of such pipes.

As number of runs in the process of cold deformation increases, refining of the grain and equalization

**Figure 3.** Microstructure of hot-rolled pipes ($\times 100$)

of the structure takes place, which enables gradual increase of ductility of pipes of intermediate sizes in comparison with hot-rolled state and improvement of their surface quality.

Microstructure of pipes of finished sizes differs from that of the pipes manufactured from a forged billet (Figure 4). It is fine-grain, but consists of a mixture of equiaxial recrystallized grains of α -phase and remnants of non-worked grains of fine-acicular structure (Figure 5).

Estimation of quality of finished pipes was performed according to requirements of GOST 22897-86.

Mechanical properties, content of hydrogen, quality of flattening and expansion of pipes of finished

Table 3. Mechanical properties and content of hydrogen in pipes of intermediate sizes under conditions of room temperature

Run No.	σ_t , MPa	σ_y , MPa	δ_5 , %	ψ , %	KCU, J / cm ²	Weight share of hydrogen, %
Billet	510	445	24.0	54.0	11.0	0.0060
I	485	345	23.0	61.0	10.6	0.0060
II	490	350	23.5	60.5	11.0	0.0061
III	530	390	26.0	N / D	Same	0.0061
IV	550	415	32.0			0.0060
I	490	355	25.0	62.0	14.8	N / D
II	485	340	25.0	61.5	15.0	0.0060
III	455	325	27.0	N / D		
IV	465	335	37.0			

Table 4. Mechanical properties of pipes of finished sizes

Size of pipes, mm	20 °C						150 °C			
	σ_t , MPa		σ_y , MPa		δ_5 , %		σ_t , MPa		σ_y , MPa	
	Ends of pipes									
	I	II	I	II	I	II	I	II	I	II
32.0 × 1.5	470	460	335	345	39	40	370	370	275	275
25.0 × 3.0	560	570	450	470	29	35	440	460	360	370
Standard	343–568		245		24		216		147	

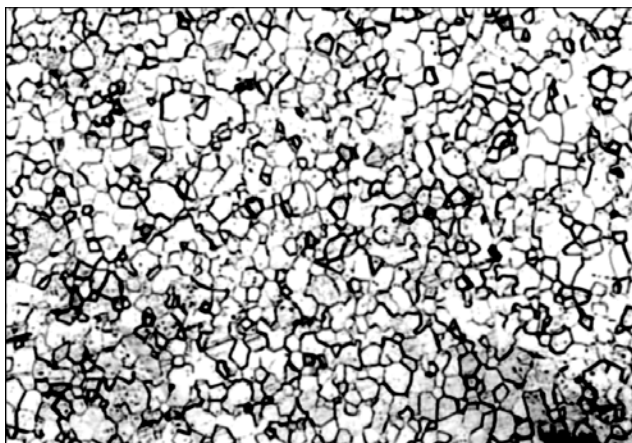


Figure 4. Microstructure of cold-rolled pipe produced according to traditional technology from forged billet ($\times 200$)

sizes were determined according to requirements of GOST 22897–86 on specimens taken from two ends of pipes.

Results of tests are given in Table 4.

Mechanical properties of pipes, despite presence of fine-acicular structure, meet requirements of GOST 22897–86, their ductility properties being at sufficiently high level (Table 4).

Technological tests of flattening and expansion quality of all pipes showed satisfactory results. Content of hydrogen in all pipes constituted 0.006 %. The pipes were subjected to UST (100 %), whereby defects were not detected.

So, carried out investigations showed that for the purpose of obtaining equiaxial recrystallized grain in

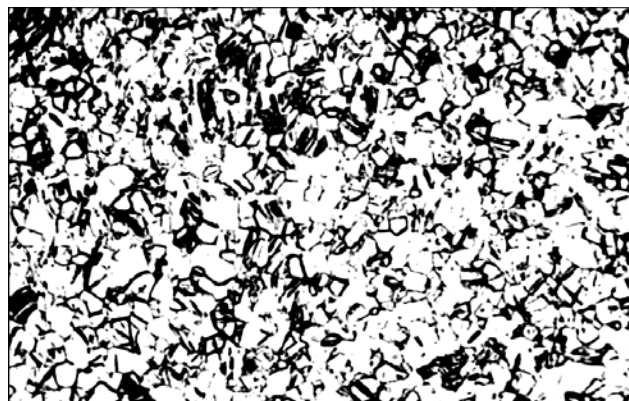


Figure 5. Microstructure of cold-rolled pipe produced from cast billet ($\times 200$)

finished pipes and uniform distribution of mechanical properties it is advisable to use in piercing on helical rolling mill ingots of big diameter, which will allow increasing degree of deformation and thus cause more complete working of structure of hot-rolled conversion pipes.

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STRUCTURE AND PROPERTIES OF THICK MgO CONDENSATES PRODUCED BY ELECTRON BEAM EVAPORATION

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Effect of substrate temperature on structure, morphology of surface, microhardness, and fracture toughness K_{Ic} of MgO condensates of up to 100 μm thickness, produced by electron beam evaporation and deposition in vacuum on substrates of steel St3 within temperature range 300–1000 $^{\circ}\text{C}$, is investigated. Temperature relationship of width of MgO columnar crystallites is presented. It is shown that microhardness of MgO is constant within preset range of temperatures and does not change at high-temperature annealing. It is established that temperature of condensation predetermines nature of the relief formation and texture of condensates.

Keywords: electron beam evaporation and deposition, MgO, thick condensates, substrate with temperature gradient, microhardness, fracture toughness, morphology of surface, microstructure, structural zones

Interest to application of MgO-base materials as structural, wear-resistant and other tribotechnical coatings is predetermined by such properties of ceramics as thermal and corrosion stability, satisfactory heat con-

ductivity, low coefficient of electrical conductivity, and high level of strength properties. At present thin MgO coatings are used as a connecting (matching) sub-layer in production of oxide coatings, such as high-temperature superconductors or ferroelectrics on semiconductor substrates [1, 2]. MgO coatings are used as protection for dielectrics on the plasma display panel that improves their discharge characteristics and service life of the panel [3]. Increase of the coating

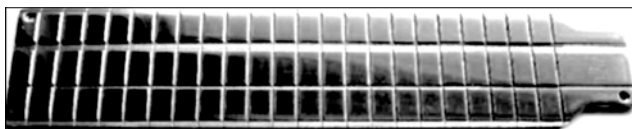


Figure 1. Appearance of substrate

thickness can ensure its multipurpose application as a damping sub-layer and, for example, for structural purposes. Absence of polymorphous transformations in MgO allows using it within wide range of temperatures.

In this work influence of the substrate temperature on structure and some properties (microhardness and fracture toughness K_{Ic}) of MgO condensates of up to 100 μm thickness, produced by electron beam evaporation on substrates from steel St3 within temperature range 300–1000 $^{\circ}\text{C}$, is investigated.

One of the main factors, which determine nature of formation of the structure and properties of the condensates, is substrate temperature. In many cases optimum physical properties of condensates are achieved within a certain narrow range of temperatures. Investigation of condensates under fixed temperature conditions of deposition is rather laborious. Presented in the work methodology of deposition of condensates on a substrate with present along its axis gradient of temperatures allows obtaining within one experiment information on structure and properties of condensed materials within a preset continuous range of deposition temperatures.

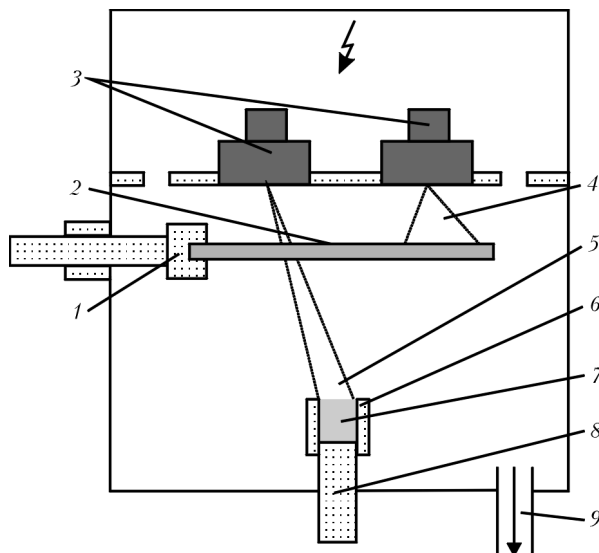


Figure 2. Scheme of MgO deposition process in vacuum chamber: 1 — water-cooled copper rod; 2 — substrate; 3 — electron beam guns; 4, 5 — electron beam for heating and evaporation, respectively; 6 — crucible; 7 — MgO pellet; 8 — rod for feeding MgO; 9 — to vacuum pump

The substrate (Figure 1) represents a plate from steel St3 of 237 mm length, 48 mm width, and 2.4 mm thickness. For easy separation of the condensate into separate specimens on both sides of the substrate cross grooves of 0.9 mm depth were milled; width of a specimen was 9 mm. Working surface of the substrate was processed up to the 6th surface finish class and

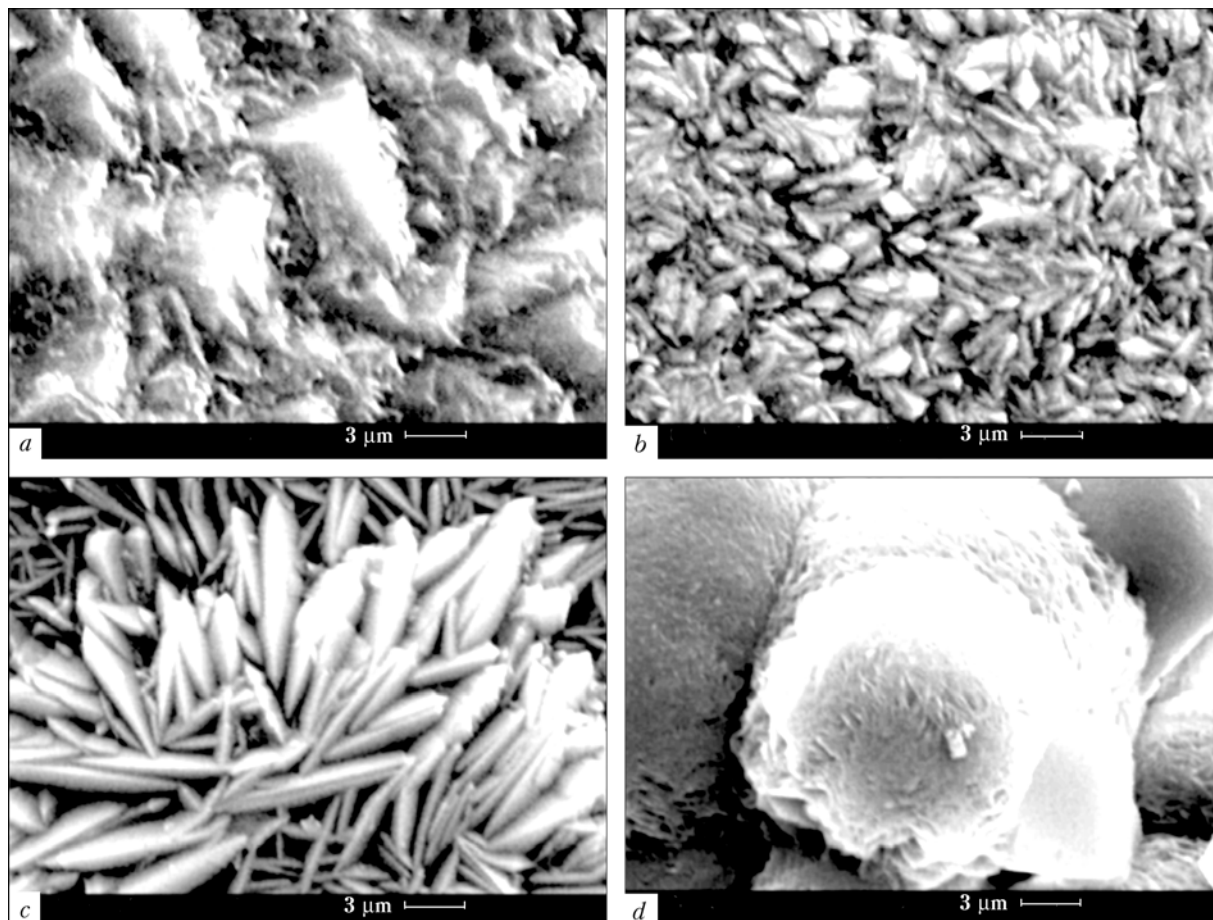


Figure 3. Microstructure of MgO condensate surface at T_s , $^{\circ}\text{C}$: a — 500; b — 600; c — 750; d — 950

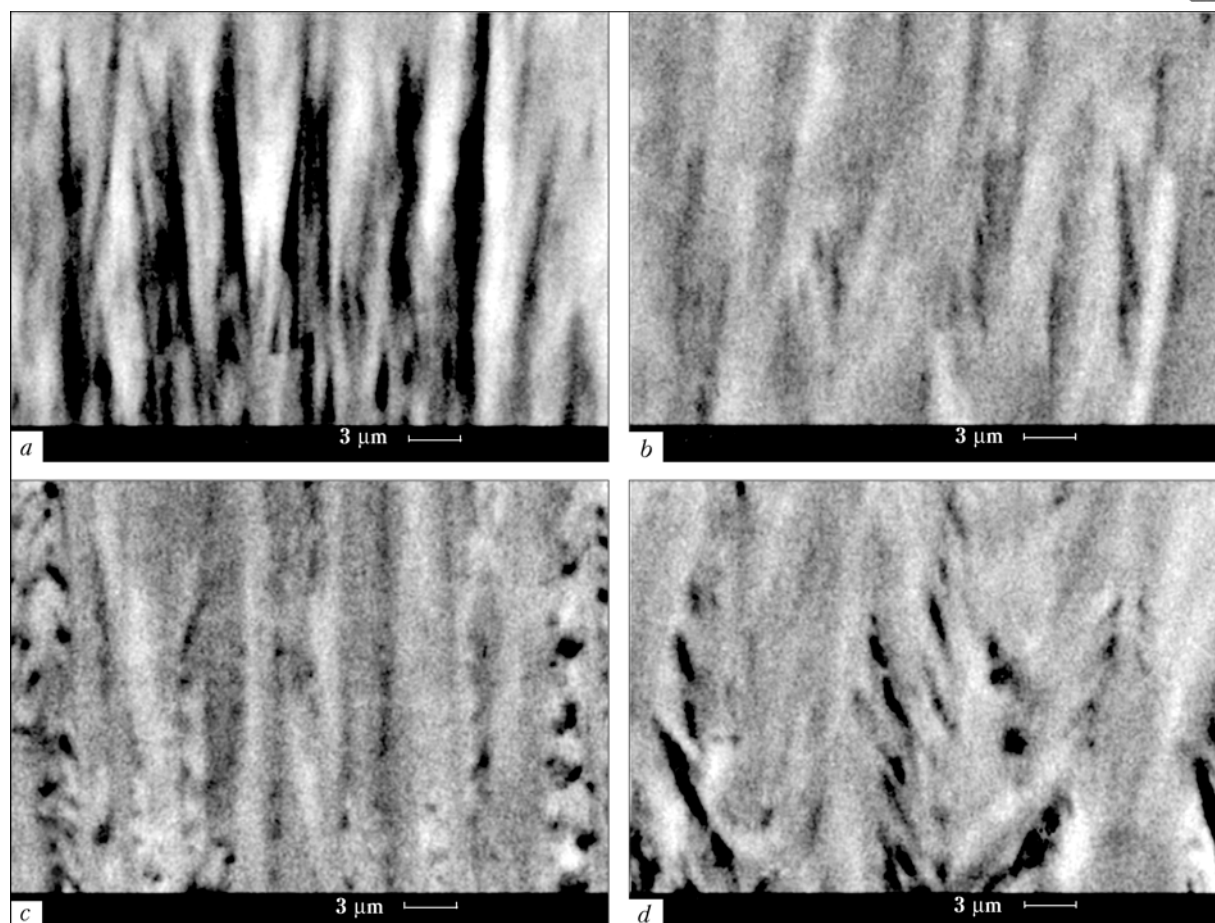


Figure 4. Microstructure of MgO condensate at T_s , °C: *a* — 320; *b* — 500; *c* — 600; *d* — 750

defatted by acetone. Mentioned model of the substrate allows its quick separating into specimens without using traditional methods of cutting, which cause damaging of the coating.

Powder of magnesium oxide of purity Ch (99.4 % of pure MgO), pellets of which were produced by the method of cold compaction with subsequent annealing at temperature 1100 °C, was used as an initial material.

Deposition of MgO condensates was performed according to the scheme shown in Figure 2. The substrate was fixed in a horizontal water-cooled rod. Opposite end of the substrate was heated by electron beam, due to which temperature gradient 300–1000 °C was established. Surface of the specimen was cleaned within 30 min by flow of argon ions. Then at vacuum in the working chamber $(2-3) \cdot 10^{-2}$ Pa evaporation by electron beam and deposition on the substrate were performed. Rate of condensation was 4–9 $\mu\text{m} / \text{min}$. Temperature was controlled by means of 5 chromel-alumel thermocouples, which were connected to the computer and allowed precise (with accuracy up to 15 °C) measuring temperature distribution along the substrate.

Structure and composition of the condensates were analyzed using a scanning microscope CamScan, equipped with energy-dispersion system of local analysis Energy 200. Measurement of microhardness of the condensates was performed according to the

Vickers method at the load 0.098–0.5 N using optical microscope Polyvar-Met. Fracture toughness K_{Ic} was determined by indentation of condensates according to the Vickers method at the load 1 N. X-ray diffraction analysis of the condensates was performed on the «Dron-4» installation in the $\text{CuK}\alpha$ radiation (length of wave is $\lambda = 15.4178$ nm).

Surface microstructure of the condensates is presented in Figure 3. Condensation temperature defines character of formation of surface relief of MgO condensates. Increase of the substrate temperature causes surface roughness increase of the condensates. Microstructure of cross sections of the condensates, produced at various temperatures, is shown in Figure 4. The condensates have columnar structure, size of crys-

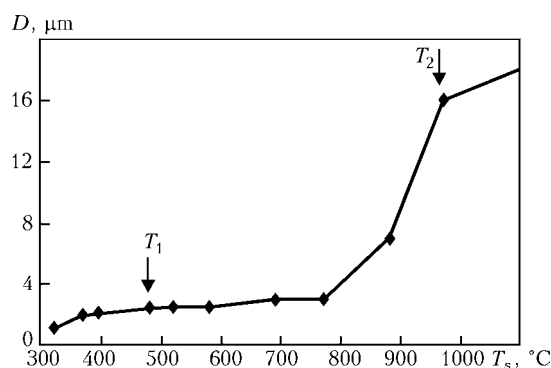


Figure 5. Dependence of width D of MgO columnar crystallites upon substrate temperature T_s

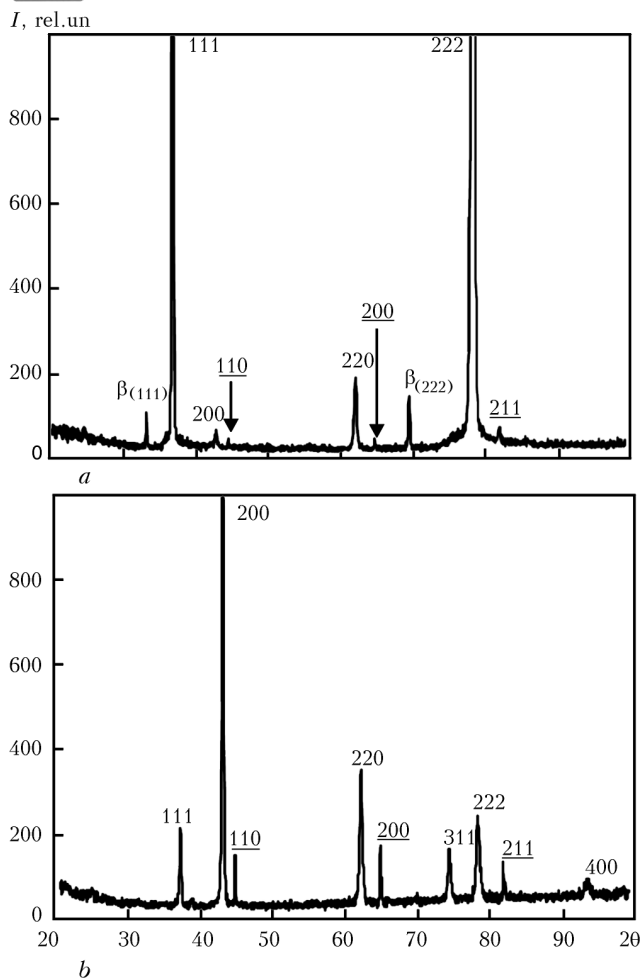


Figure 6. Diffraction patterns of MgO condensate specimens at T_s , °C: *a* — 500; *b* — 950; *I* — intensity of radiation; (*hkl*) — MgO ($d = 4.212$); ($\underline{hkl}$) — substrate

tallites of which depends upon a condensation temperature. As the latter increases, width of columnar crystallites increases from 1 μm at 320 °C to 18 μm at 1100 °C (Figure 5).

Analysis of microstructure of the condensates and temperature dependence of width of columnar crystallites allowed determining critical values of the condensate structure formation temperature $T_1 = 0.24T_m$ and $T_2 = 0.4T_m$ (T_m is the melting point of MgO, K),

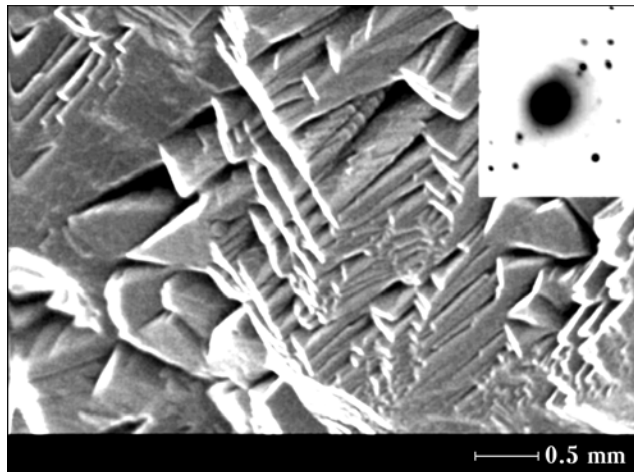


Figure 7. Fracture surface structure of MgO condensate produced at substrate temperature $T_s = 500$ °C

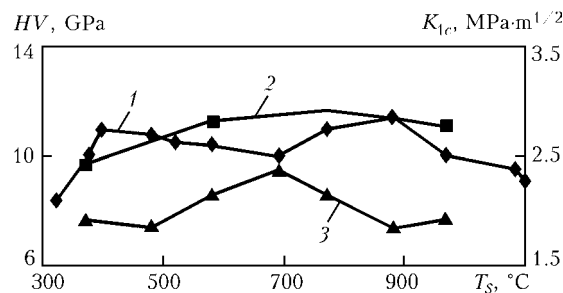


Figure 8. Dependence of microhardness and fracture toughness of MgO condensates upon temperature: 1 — initial condensate; 2 — after annealing at 1000 °C for 1 h, $P = 1.33 \cdot 10^{-4}$ Pa; 3 — K_{1c}

which, according to the structural model proposed in [4], limit temperature zone of columnar structure formation.

In the area of temperature $T_1 < T < T_2$ dominant significance have processes of surface diffusion, which causes formation of columnar crystallites, whereby difference in surface energy of separate facets of crystallites ensures development of the texture. This fact is confirmed by results of X-ray diffraction analysis, according to which on diffractogram of the condensate, produced at temperature 500 °C, intensity of peaks (111) and (222) of MgO is several dozen times higher than of peaks (220) and (311) (Figure 6).

Analysis of condensates with application of transmission electron microscopy showed that separate crystallites consist of microcrystals with advantageous orientation (Figure 7), size of which does not exceed 0.1 μm . At condensation temperature $< T_1$ under conditions of a limited surface diffusion and influence of the shadow effect formation of cone-like crystallites with high density of defects over their boundaries takes place (see Figure 4, *a*). Increase of condensation temperature above T_2 is accompanied by development of volume diffusion that causes growth of size of crystallites and disturbance of their oriented growth (see Figures 4, *c* and 6, *b*).

It should be noted that formation of MgO condensate in the area of high temperatures has its peculiarities. Nature of structure formation of condensates on the basis of oxides is determined by composition of the vapor phase [5]. In the process of MgO electron beam evaporation a vapor phase forms, consisting of MgO, magnesium, atomic and molecular oxygen vapors [6]. Increase of the substrate temperature causes interaction of two competing processes — increase of energy of adsorbed atoms of magnesium and oxygen on the substrate surface and reduction of adsorption capacity of magnesium atoms at the substrate temperature above melting point of magnesium, which enables re-evaporation of magnesium in the process of condensation.

Re-evaporation of magnesium is proved by reduction of concentration ratio Mg / O down to 1.35 (for stoichiometric magnesium oxide Mg / O = 1.52). Increase of the substrate temperature up to 1000 °C enhances action of mentioned processes that causes formation of the condensate with coarse crystallites,



high porosity over boundaries of crystallites, and loose surface (see Figure 3, d).

Temperature dependence of microhardness of MgO condensates is shown in Figure 8. As it follows from presented dependence, condensation temperature does not exert significant influence on MgO microhardness. Its insignificant reduction in the area of low (< 400 °C) and high (> 900 °C) temperatures is connected with increased porosity over boundaries of crystallites, stipulated by directedness of vapor flow in relation to the substrate and shadow effect.

Specimens of the condensate from different temperature zones were subjected to annealing according to the following conditions: 1000 °C, 1 h, $P = 1.33 \cdot 10^{-4}$ Pa. Analysis of the annealed condensates showed that MgO microhardness does not change at high-temperature annealing. This is an additional confirmation of thermal stability of MgO condensates. This fact is noted in [7], in which it is shown that oriented growth of the condensate is determined to a greater degree by the deposition temperature than by subsequent annealing, whereby formation of orientation occurs at the stage of nucleation due to the surface diffusion.

For estimating crack resistance of produced condensates fracture toughness K_{1c} was used as a criterion, which was determined according to the known Evans method, improved in [8]. The method is based on determination of a crack length, occurring in the material around an imprint in indentation of the diamond pyramid according to Vickers method at a low load. Fracture toughness K_{1c} is calculated by formula

$$K_{1c} = 1.018Ha^{1/2}(E/H)^{0.4}(c/a - 1)^{-1/2} [\text{MPa}\cdot\text{m}^{1/2}],$$

where H is the microhardness, GPa; E is the Young's modulus equal to 245 GPa; a is the half of the imprint diagonal, m; c is the length of a crack from center of the imprint, m.

Results of fracture toughness determination are presented in Figure 8. Temperature dependence of K_{1c} correlates with temperature dependence of microhardness with reverse sign. Formation of texture in the process of condensation may influence crack resistance of the condensate. So, it was noted in [9] that formation of cracks around an imprint in indentation of diamond pyramid depends to a great degree upon orientation of single crystal MgO.

So, electron beam evaporation allows producing MgO condensates of up to 100 µm thickness characterized by rather high microhardness (up to 14 GPa) and satisfactory crack resistance. Formation of structure and relief of the condensate surface depends upon condensation temperature.

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WELDING AND REPAIR OF COPPER MOULDS



At the E.O. Paton Electric Welding Institute of the NAS of Ukraine the highly-effective technological processes of automatic, mechanized and manual welding of copper of large (above 25 mm) and medium (10–25 mm) thicknesses have been developed for manufacture and repair of moulds of electroslog and vacuum-arc remelting furnaces.

Depending on the metal thickness being welded and design characteristics of the moulds the following methods of welding are used:

- automatic: submerged-arc, plasma-arc and consumable electrode shielded-gas welding;
- mechanized: consumable electrode shielded-gas welding;
- manual: non-consumable shielded-gas and covered-electrode welding.

To guarantee the required weld quality, vacuum tightness, high heat- and electric conductivity, special welding consumables (fluxes, electrode and filler wires, covered electrodes, etc.) have been developed. Application of optimum conditions and special methods of the processes realization allows a single-pass welding of copper of the above-mentioned thicknesses to be performed without preheating and auxiliary heating (plasma-arc welding and submerged-arc welding) or using a low preheating (multi-pass shielded-gas welding and welding with covered electrodes).

The offered technologies are used successfully both in a serial manufacture of welded copper moulds and also in case of a single manufacture and repair.

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KINETICS OF NITROGEN ABSORPTION BY MOLTEN HIGHLY REACTIVE METALS IN ARC AND PLASMA MELTING

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Kinetics of nitrogen absorption by molten vanadium, zirconium and niobium, using methods of arc and plasma melting of metal within temperature interval 2273–2873 K and nitrogen partial pressure range 0.09–25 kPa has been investigated. Methodology of direct measuring metal temperature in melting using color pyrometers has been developed. It is shown that as temperature grows, rate of nitrogen absorption increases, while threshold concentration does not change in comparison with nitrogen absorption in conventional oscillation state (levitation melting). Rate of nitrogen absorption in plasma melting is higher than in arc melting that is connected with higher energy activation of nitrogen molecules in gas phase.

Key words: nitrogen, kinetics, reaction rate constant

Investigations of thermodynamic and kinetic parameters of the process of nitrogen absorption by highly reactive metals in conventional oscillation state (method of levitation melting) have been carried out [1, 2]. Study of nitrogen absorption by these metals in arc and plasma heating is of interest, because gas molecules, receiving additional energy from a concentrated heat source, will be in excited state, and character of their interaction may change.

Investigations were carried out on laboratory installation, developed in the E.O. Paton Electric Welding Institute, which allows controlling, in addition to parameters of the melting process, performed according to arc and plasma methods, temperature of molten metal by color pyrometers (Figure 1).

Temperature was measured through a hole in bottom part of the mould and an inspection window in the bottom of the water-cooled chamber. In this way, due to shielding of arc by the mould, influence of plume on the pyrometer readings was excluded.

Preliminary influence of the arc current on change of the melt temperature was studied (Figure 2).

Results of the experiments prove that it is possible to regulate rather smoothly metal temperature in melting for comparing data on absorption of excited and non-excited gas by molten metal.

Nitrogen absorption by highly reactive metals (niobium, vanadium, zirconium) in arc and plasma melting at temperature and partial pressure values of nitrogen, used in case of levitation melting [1], has been investigated in order to be able to compare the results.

Kinetics of nitrogen absorption by molten niobium in arc and plasma melting at temperature 2923 K and partial pressure of nitrogen 0.25–25 kPa has been studied.

Both in arc and plasma melting (Figure 3), as partial pressure of nitrogen in gas phase grows, its

equilibrium (threshold) concentration in the metal and rate of nitrogen absorption by niobium increases. It is necessary to pay attention at the fact that rate of nitrogen absorption in arc melting is higher than in levitation melting, but lower than in plasma heating (see Figure 3). This is explained by energetic state of nitrogen molecules, characterized by a certain reserve of non-relaxed oscillation energy. Their direct contact with the melt causes increase of nitrogen absorption reaction rate.

Kinetics of nitrogen absorption by molten vanadium was studied at temperature values 2273 and 2473 K and different levels of nitrogen partial pressure in gas phase. Results of the experiments prove that in arc and plasma melting growth of partial pressure of nitrogen in gas phase causes increase of its absorption by molten vanadium and its threshold concentration. Increase of the melt temperature at constant partial pressure of nitrogen, on one hand, increases rate of the molten metal saturation with nitrogen and, on the other hand, reduces its limit content in the metal (Figure 4). This does not contradict to general laws of thermodynamics, because as temperature increases, solubility of nitrogen in molten highly reactive metals reduces.

Kinetics of nitrogen absorption by pure zirconium has been also studied. Taking into account carried out similar investigations with application of melting in suspension state, which showed impossibility of achieving equilibrium in Zr–N system, such temperature, partial pressure of nitrogen, and duration of molten zirconium soaking in nitrogen were selected that formation of nitrides on the metal surface to be excluded. In this connection the experiments were carried out at temperature values 2273 and 2573 K and levels of nitrogen partial pressure 0.09 and 0.56 kPa. Rate of nitrogen absorption by zirconium grew as temperature and partial pressure of nitrogen increased and was significantly higher than in melting

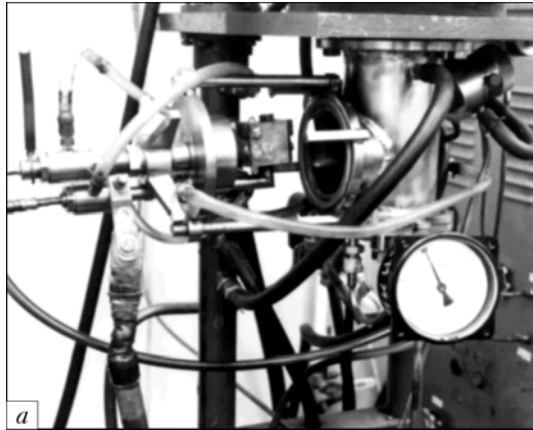
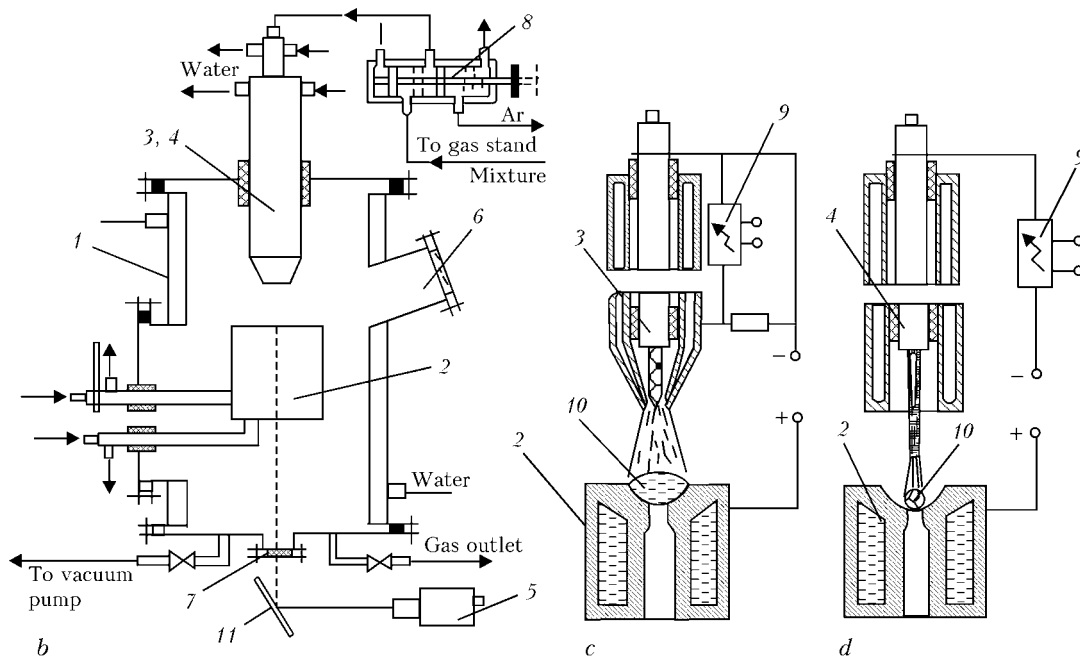


Figure 1. Appearance (a) and scheme (b) of installation for investigation of nitrogen absorption in plasma (c) and arc (d) melting of metals with direct measurement of temperature: 1, 2 — water-cooled chamber and mould, respectively; 3, 4 — plasma and arc torch, respectively; 5 — color pyrometer; 6, 7 — inspection window and window for measuring temperature, respectively; 8 — gas switch; 9 — oscillator; 10 — molten metal; 11 — mirror



of zirconium in conventional oscillation state (Figure 5) [2].

For comparing rates of nitrogen absorption by different metals in different methods of melting, coefficients of mass transfer were calculated using equations of first β order and second K_β order according to the methodology, published in [1, 2] (Table).

As one can see from the Table, the highest rate of nitrogen absorption is registered in niobium. In levitation

tation melting rate of nitrogen absorption by niobium is described by equation of second order, while in arc and plasma melting — by equation of first order. This is, evidently, connected with the fact that in melting of niobium by arc or plasma, energetic state of the metal atoms, which are located in adsorption layer, change. So, a limiting element of nitrogen absorption reaction becomes its diffusion in the metal (in the

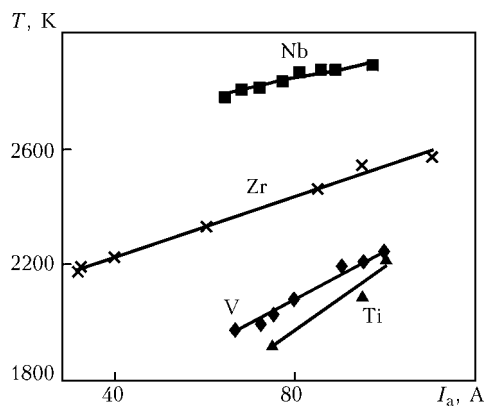


Figure 2. Dependence of metal temperature upon arc current in arc melting

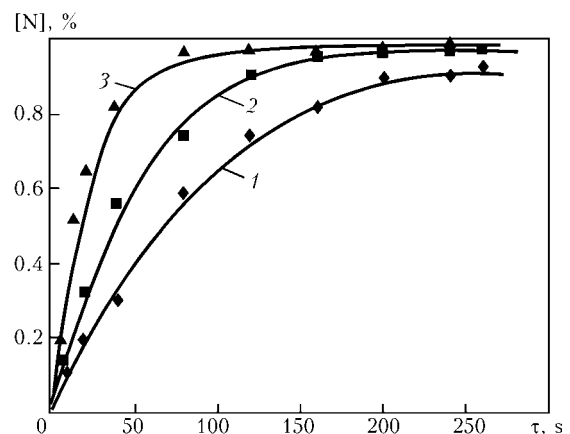


Figure 3. Kinetics of nitrogen absorption by molten niobium in different methods of melting ($T = 2923$ K, $P_{N_2} = 1$ kPa): 1 — levitation; 2 — arc; 3 — plasma

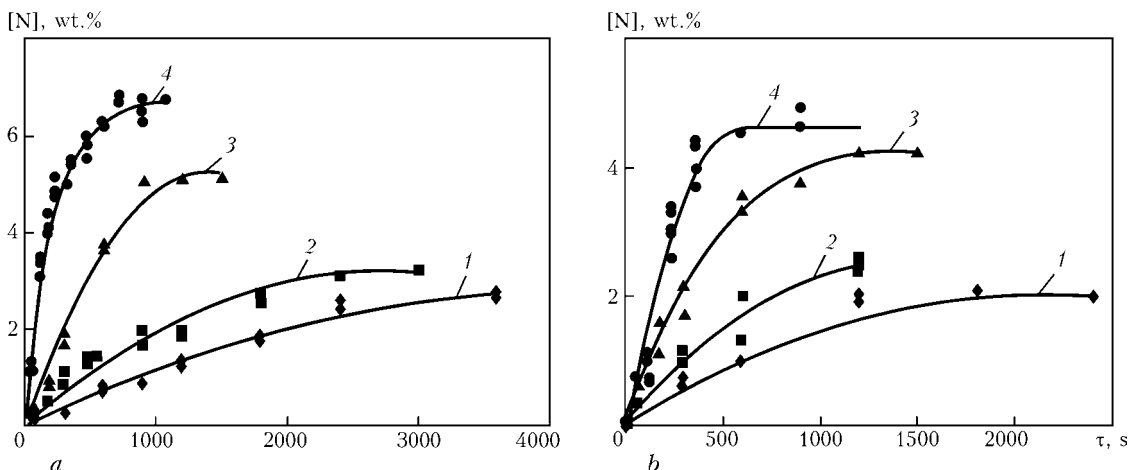


Figure 4. Kinetics of nitrogen absorption by molten vanadium in arc melting under conditions of temperature 2273 (a) and 2473 K (b) at P_{N_2} , kPa: 1 — 0.09; 2 — 0.25; 3 — 0.56; 4 — 1.0

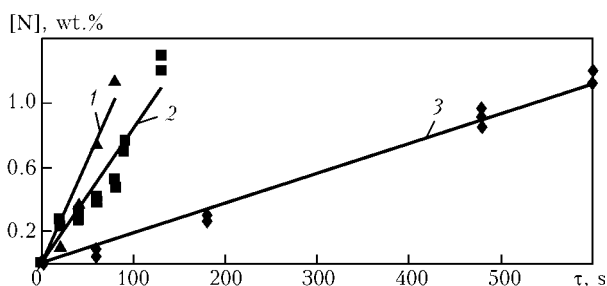


Figure 5. Kinetics of nitrogen absorption by zirconium in arc melting: 1 — $T = 2573$ K, $P_{N_2} = 0.56$ kPa; 2 — 2273 K, 0.56 kPa; 3 — 2273 K, 0.09 kPa

diffusion layer), but not chemical-adsorption element, as in levitation melting.

Comparison of values of mass transfer coefficients, which describe rate of nitrogen absorption by highly reactive metals when using levitation, arc and plasma methods, shows that application of concentrated melting sources enables increase of the rate of nitrogen absorption by these metals.

In addition, as a result of carried out investigations it was discovered for the first time that values of equilibrium concentrations of nitrogen within investigated range of its partial pressures in different melting methods are close to each other. In case of niobium (see Figure 3), they differ in levitation, arc and plasma melting by not more than 10 %. Value of equilibrium concentration of nitrogen in vanadium, achieved in arc melting (see Figure 4), for example, at temperature 2473 K and partial pressure of nitrogen 1.0 kPa, is 4.77 %, and at 2273 K and 0.56 kPa — 5.13 %. In levitation melting equilibrium concentrations of nitrogen under the same conditions are 5.0 and 5.6 %, respectively [2]. Difference between them does not exceed 7 %.

In case of absorption of nitrogen by such metals as iron, nickel and copper, energy of excited molecules of nitrogen has great significance, which allows increasing in plasma melting dozens (iron) and even hundreds (copper and nickel) times content of nitrogen in comparison with standard solubility [3, 4].

For highly reactive metals energy of excitation of nitrogen molecules practically does not exert signifi-

Metal	Method of melting	D_{N_2} , kPa	T , K	β , cm/s	K_β , cm/s
Nb	Levitation	1.0	2923	—	$1.48 \cdot 10^{-3}$
	Arc	—	—	$1.88 \cdot 10^{-3}$	—
	Plasma	—	—	$0.421 \cdot 10^{-2}$	—
V	Levitation	1.0	2273	—	$6.05 \cdot 10^{-5}$
	Arc	—	—	—	$1.68 \cdot 10^{-4}$
Zr	Levitation	0.09	2273	—	$2.78 \cdot 10^{-5}$
	Arc	—	—	—	$1.65 \cdot 10^{-4}$

cant influence on its equilibrium content in the metal, but just enables increase of the absorption rate. One of the explanations of noted peculiarities may be comparison of values of Gibbs energy, calculated in [5] for the reaction of nitrogen absorption by different molten metals in arc and plasma melting. For highly reactive metals their value is much lower (vanadium — 2.67, niobium — 8.9 kJ) than for the metals with low affinity to nitrogen (iron — 149.38, nickel — 147.08 kJ) [5].

So, one may draw conclusion that in metals with high absorption capacity (vanadium, niobium, etc.) in contrast to metals with low absorption capacity (iron, nickel, etc.) does not take place significant increase of nitrogen content due to additional energy of excited by arc molecules of gas, because process of nitrogen absorption by highly reactive metals is accompanied by release, but not absorption of heat.

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BEHAVIOR OF PHOSPHORUS IN LIQUID-PHASE REDUCTION MELTING

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Behavior of phosphorus in liquid-phase melting of dump electric steel melting slag has been studied. It is shown that combination of oxidizing and reduction periods in liquid-phase melting does not allow performing dephosphorization of the metal.

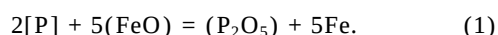
Key words: liquid-phase melting, heat exchange, dump electric steel melting slag, metal, phosphorus

Behavior of phases in liquid-phase melting of oxide-containing materials has its peculiarities, because proceeding of physical-chemical processes in the melting unit occurs in the foaming slag. Intensification of heat and mass transfer processes in the molten pool enables mixing and high temperature in the intensive heat exchange zone in arc furnace melting.

One of harmful impurities in steel is phosphorus. Brittle interlayers, enriched with phosphorus, are located in inter-grain space and reduce ductile properties of the metal. It manifests itself especially noticeably at low temperatures.

For oxidizing phosphorus it is necessary to perform melting under strongly oxidizing conditions on high-basicity slags [1].

Phosphorus is oxidized into phosphoric anhydride P_2O_5 according to the reaction



At high temperature P_2O_5 is easily reduced by carbon and iron up to elementary phosphorus, which is immediately dissolved in metal.

Phosphoric anhydride, which is characterized by rather strong acid properties at the temperature 1600 °C, easily couples with iron oxide FeO with formation of phosphate $3FeO \cdot P_2O_5$. At sufficient concentration of CaO in slag phosphoric anhydride is bound into strong compound $4CaO \cdot P_2O_5$. As a result, a mixture of ferrous and calcium phosphates forms in the slag. So, phosphoric anhydride is distributed among free bases of slag with prevalence in it of iron and calcium phosphates.

Presence of free silica in slags destroys tetracalcium phosphate $4CaO \cdot P_2O_5$, while carbon and manganese, present in the melt, reduce phosphoric anhydride. That's why change of the slag basicity in the direction of increase in it of SiO_2 content causes transition of phosphorus from the slag into the metal, because at high temperature SiO_2 displaces from $4CaO \cdot P_2O_5$ phosphorus pentoxide with formation of

the silicate ($4CaO \cdot P_2O_5 + SiO_2 \rightarrow P_2O_5 + 4CaO \cdot SiO_2$), and phosphorus of the anhydride is reduced by carbon or iron at slag-metal interface due to which it transits into the metal. That's why it is practically impossible to perform dephosphorization of metal in a furnace with acid lining.

Growth of temperature enables increased intensity of interaction between carbon of the metal and iron oxide FeO of the slag. That's why temperature increase is accompanied by reduction of iron oxide content in the slag, especially in the directly adjacent to the metal layer. At sufficiently high temperature dephosphorization of the metal proceeds very slowly, or does not proceed at all. At low content of carbon in the metal ($< 0.2\%$) temperature exerts just insignificant influence on oxidation of phosphorus [2].

In melting of metal in furnaces with basic lining conditions of dephosphorization are the most favorable within the period of the charge melting, which is characterized by low temperature of the metal and its high oxidation. Impurities, contained in the metal, exert significant influence on character of dephosphorization proceeding. So, manganese, silicon, chromium and other elements, which have high affinity to oxygen, noticeably retard rate of the metal dephosphorization.

Dephosphorization of the metal in the process of melting is more efficient if oxidizing atmosphere, high activity of iron oxides in the slag, sufficiently high basicity of the slag, presence of slags with insignificant content of phosphorus, replacement of the slag, and low temperature of the metal are ensured.

Results of investigation of phosphorus oxidation rate, depending upon its content in the metal, partial pressure of oxygen, and temperature are presented in [3]. It is established that kinetics of dephosphorization is determined by content of oxygen in boundary layers of the metal, degree of oxygen transition to the contact surface, on which phosphorus oxidation reaction takes place, degree of phosphorus transition to the same surface, and reaction proper of phosphorus oxidation with formation of phosphoric anhydride.

**Table 1.** Chemical composition of slags of reduction period of melting of different steels

Steel grade	Weight share of slag components, %								
	Na ₂ O	SiO ₂	MnO	Al ₂ O ₃	MgO	FeO	Fe ₂ O ₃	$\frac{CaO}{SiO_2}$	P
High-carbon	44.2	18.28	6.38	4.80	15.48	6.52	2.57	2.40	0.27
Medium-carbon	42.4	20.82	7.16	3.65	9.48	12.28	3.90	2.00	0.11
Low-carbon	37.2	16.50	6.71	4.01	10.12	20.30	4.80	2.30	0.14

Rate of dephosphorization is expressed by the following formula:

$$-\frac{dP}{d\tau} = ([O]_{\text{surf}} - [O]_l) D / \frac{A}{\delta} V, \quad (2)$$

where $dP / d\tau$ is the rate of dephosphorization, % / s; $[O]_{\text{surf}}$ is the content of oxygen on the contact surface metal–slag, %; $[O]_l$ is the content of oxygen at the time τ in the metal, %; D is the coefficient of oxygen diffusion to the contact surface, cm^2 / s ; V is the total volume of the molten metal, cm^3 ; A is the area of contact surface, on which the reaction takes place, cm^2 ; $\delta = 0.004 \text{ cm}$ is the thickness of the metal diffusion layer.

In the presented above formula $A / \delta = 1.91 \cdot 10^2 = \text{const}$.

Calculations, carried out by the authors, allowed drawing conclusion that the limiting stage of the metal dephosphorization is diffusion arrival of oxygen to the surface, on which the reaction proceeds. So, dephosphorization proceeds on occurring in volume of the metal contact surface metal–slag or on introduced into the metal particle of the slag-forming material. For example, in case of introduction into the metal of material particles by the carrier-gas dephosphorization should proceed at a higher rate, because the metal is vigorously mixed, and contact layers of the slag and the metal are intensively renovated, due to which products of the reaction are quickly removed from the reaction zone into the slag and dissolve in it.

It is established in [4, 5] that in liquid-phase melting processes of reduction and melting of pellets proceed in solid-liquid phase of the foamed slag. Intensive mixing of solid-liquid phase in melting stipulates significant increase of the rate of proceeding heat and

mass exchange processes. That's why there is a certain analogy between blowing of the melt pool by gas-reactant agents and liquid-phase melting. So, certain regularities of the metal dephosphorization in blowing of the molten pool by gas-reactant mixtures may be extended to the process of liquid-phase melting.

In Institute for Physics and Technology of Metal and Alloys of the NASU behavior of phosphorus was studied in remelting of the ferrosilicon manganese waste and dump electric steel melting slags in direct-current electric arc furnaces.

Chemical composition of dump slags was as follows, %: 7.16 FeO; 22.55 Cr_2O_3 ; 17.37 SiO_2 ; 15.21 MgO; 7.58 CaO; 2.31 CaF_2 ; 7.40 MnO; 7.80 Al_2O_3 ; 0.048 S; 0.0706 P.

Coke nut, limestone and fluorite were used as a reducer and flux-forming additives. Preliminary chemical composition of slags of oxidation period of melting of different steels was analyzed (Table 1) [6].

It follows from presented data that the highest content of phosphorus in the slag was discovered in melting of high-carbon steel. For medium- and low-carbon steels concentration of phosphorus in the slag is, approximately, the same and practically 2 times lower in comparison with high-carbon steel.

In Table 2 data are presented on influence of carbon on content of phosphorus in the alloy in remelting of ferrosilicon manganese waste.

Analysis of Table 2 shows that as amount of carbon in the alloy increases, intensive reduction of carbon by iron from the oxide takes place, which retards process of the alloy dephosphorization.

Of great interest are behavior of phosphorus in remelting of dump slag that contains metal oxides. In this case oxidation-reduction processes are combined and proceed in solid-liquid phase of the foamed slag, which exerts significant influence on behavior of the phases, in particular of phosphorus.

As it follows from analysis of the Table 3 data, the alloy, molten from dump electric steel melting slag, represents high-carbon ferrochromium with reduced content of chromium. Content of phosphorus in ferrochromium is 0.036–0.068 %.

It is established that basicity of the slag effects degree of assimilation by the metal of phosphorus and sulfur from charge materials in the process of reduction melting (Table 4).

Table 2. Dependence of phosphorus content in alloy upon content of carbon

Weight share of elements, %				
Na	Si	Mn	Fe	P
6.52	13.23	75.80	4.22	0.130
6.39	12.56	77.45	3.48	0.120
1.90	18.00	80.00	3.53	0.069
1.89	17.00	70.64	10.40	0.062
1.80	13.24	77.70	7.19	0.072
1.68	14.10	75.66	8.50	0.058

**Table 3.** Chemical composition of molten alloy

Melt No.	Weight share of elements, %							
	N	Si	Mn	Cr	Ni	Đ	S	Fe
4.11	7.61	0.60	1.92	35.40	1.28	0.065	0.018	50.50
4.12	6.70	0.093	1.48	29.20	2.15	0.068	0.020	59.40
4.13	5.74	0.20	1.78	34.47	2.45	0.057	0.020	55.28
4.14	6.96	0.10	2.08	35.00	2.05	0.054	0.019	53.74
4.15	6.07	0.20	1.77	34.40	1.98	0.043	0.019	54.10
4.17	7.16	0.30	1.85	36.70	1.30	0.036	0.029	52.60

Table 4. Influence of slag basicity on degree of assimilation by metal of phosphorus and sulfur from charge materials

Melt No.	Slag basicity $\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3}$	Weight share of elements, %	
		$\frac{G_m P_m}{G_s P_s} \cdot 100 \%$	$\frac{G_m S_m}{G_s S_s G_c S_c} \cdot 100 \%$
4.11	0.90	15.30	24.20
4.12	1.30	7.90	1.35
4.13	1.55	5.50	1.11
4.14	1.40	8.44	2.09
4.15	1.40	8.70	2.12
4.17	1.20	8.70	3.97

Note. Here G_m — amount of molten alloy, kg; G_s , G_c — consumption of dump slag and coke nut per melting, kg; P_m , P_s — content of phosphorus in molten metal and dump slag, respectively, %; S_m , S_s , S_c — content of sulfur in molten metal, dump slag and coke nut, respectively, %.

One can see from the data of Table 4 that carrying out of reduction process under acid slag is characterized by high degree of phosphorus and sulfur transition into the metal. As basicity of the slag increases, degree of assimilation by the metal of phosphorus and sulfur from dump slag and coke drastically reduces. So, at slag basicity 1.2 (melt 4.17) degree of assimilation by the metal of phosphorus from the charge materials reduces almost 1.75 times in comparison with similar index of melt 4.11, and of sulfur — 6 times. Increase of the slag basicity from 1.2 to 1.55 does not exert significant influence on coefficient of phosphorus and sulfur distribution between the metal and the slag.

For the purpose of studying efficiency of dephosphorization and desulfuration of a high-carbon melt by the refining slag a melting was carried out with application of the metal of melts 4.11–4.15 and the refining slag, containing 56 % CaO, 27 % FeO and 17 % CaF₂. The latter one was composed of limestone (56 % CaO), iron ore pellets of Komsomolsk Mining-and-Processing Works (2 % FeO; 87.3 % Fe₂O₃; 8.5 % SiO₂) and fluorite. Consumption of the slag constituted 6 % of the treated metal mass.

The metal was treated by two portions of the slag, each of which contained 66.4 % of limestone, 24.4 %

Table 5. Change of chemical composition of metal before and after its treatment by refining slag

Investigated metal	Weight share of elements, %*						
	N	Si	Mn	Cr	Ni	Đ	S
Initial	6.76	0.27	1.84	34.10	1.98	0.057	0.065
After melting and treatment by slag	5.32	0.056	0.823	35.94	—	0.068	0.016

*The rest is iron.

of pellets, and 11.2 % of fluorite. Duration of the metal treatment by the molten slag in both cases was 10 min.

In Table 5 change of chemical composition of the metal is shown before and after its treatment by the refining slag.

Presented data prove that after treatment of the molten metal by the refining slag content of carbon reduces 1.27, silicon 4.82, manganese 2.23, and sulfur 3.98 times. Content of phosphorus in the molten metal practically does not change, and insignificant increase of its weight share in the metal is stipulated by melting loss of carbon, silicon, and manganese.

So, carried out investigations allowed detecting certain peculiarities of phosphorus behavior in liquid-phase melting of dump electric steel melting slags. It is established that increased content of carbon in the charge and combination of oxidation and reduction periods in liquid-phase melting do not allow performing dephosphorization of the metal. Amount of phosphorus in the metal mainly depends upon content of P₂O₅ in initial charge.

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MELTING OF SILICON IN VERTICAL INDUCTION CRUCIBLE-FREE ZONAL MELTING

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Conditions of melting initial crystal of silicon in vertical induction crucible-free zonal melting are considered. It was established that for ensuring flowing off of the molten metal it is necessary to significantly increase radius of a drop contact area at minimum thickness of the melt layer on the surface of melting. Optimum conditions of melting are defined for effective flowing off of the molten metal, formed on a part of the initial crystal surface, into general zone.

Key words: crucible-free zonal melting, drop, melt, melting surface, melt cell, centrifugal force, angle of melting surface inclination

In growing of single crystals by the method of vertical crucible-free zonal melting (CFZM) different behavior of the melt in areas of melting and solidification of initial polycrystalline bar was registered. Influence of state and behavior of the melt on conditions of solidification and distribution of impurities has been studied in [1, 2]. Behavior of the melt in the area of melting requires for more detailed investigation. This is explained by the need to ensure melting by high-frequency current of the melting inductor of a portion of the initial single crystal surface and uniform timely flowing off of the formed drops into general zone of the melt. In addition, it is necessary to take into account influence of centrifugal force on flowing off of the melt drops, because in growing of single crystals of silicon by CFZM method rotation of initial polycrystalline bar and / or a single crystal occurs.

The goal of this work consisted in study and creation of optimum conditions for melting the initial polycrystal of silicon for ensuring efficient flowing off of drops into general melt zone.

In vertical CFZM in the melting chamber initial polycrystalline silicon bar is vertically fixed on the

upper rod. On the lower end a melt drop is created by means of induction heating, into which inoculation single crystal is introduced, which is attached to the lower rod, and then melt zone is created. The latter moves along initial silicon bar. On the side of the inoculation crystal growth of single crystal of silicon with assigned structure, and on the side of the initial crystal — melting of silicon take place (Figure 1), whereby both the initial silicon bar and single crystal can rotate. The main requirement in melting is stability of the melt zone, ensured by continuous and uniform flowing off of drops into general melt zone.

The main element of induction installation is inductor, by means of which energy is transferred into the bar and melting of the latter takes place. Electromagnetic field, created by the inductor, should ensure heating and melting of the initial bar, maintain optimum heat conditions in the melt zone, and assigned cooling of a single crystal, being grown from the molten zone.

Determining factor in development of induction systems for melting silicon crystals of different diameters are maximum allowable height of the melt zone and thermal conditions, which ensure reproducibility of the process of growing of non-dislocation single crystals. Theoretically maximum height of the melt zone of cylindrical shape is 1.5 cm [3]. That's why height of the inductor may not exceed the mentioned one.

In connection with the need in increasing diameter of single crystals to be grown, technological methods have been developed with application of an inductor, internal diameter of which is less than of a single crystal (Figure 1).

This allowed using instead of a cylindrical shape the melt zone of the «needle ear» type [4], in which melt is on the end of the crystal portion being solidified and connects with the initial bar by a transition section of 10–15 mm diameter. On the initial bar a small amount of flowing off melt is formed, which enters through a transition section into the melt on the end of a single crystal portion being solidified.

New methods of growing single crystals of more than 100 mm diameter allowed increasing distance

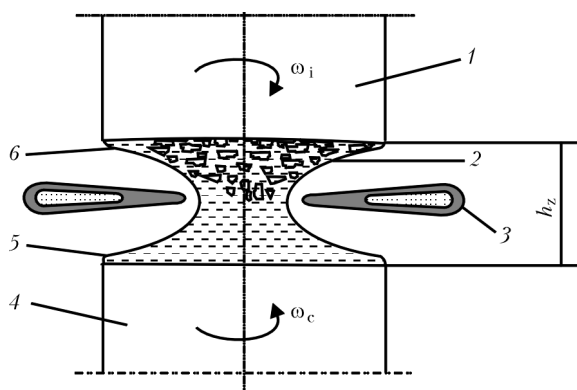


Figure 1. Scheme of CFZM process: 1 — initial crystal; 2 — melting; 3 — inductor; 4 — crystal being grown; 5 — melt; 6 — unmolten part; h_z — general height of melt zone; ω_i , ω_c — frequency of rotation of initial polycrystalline bar and crystal, respectively

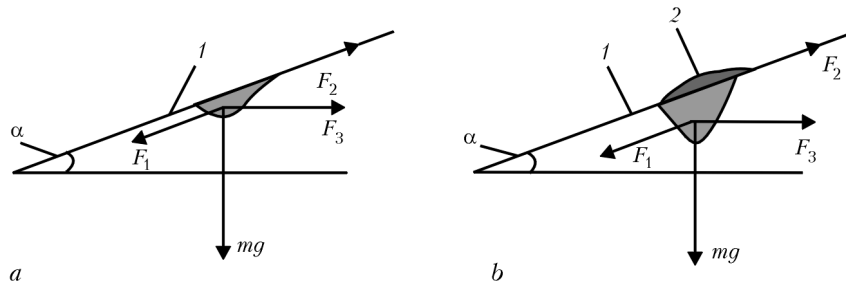


Figure 2. Scheme of melt drop on melting surface: *a* — flowing off of drop; *b* — flowing off of drop is complicated; 1 — melting surface; 2 — melt cell; α — angle of inclination of melting surface to horizontal; F_1 — force ensuring rolling down of drop; F_2 — force holding drop on melting surface; F_3 — centrifugal force

between melting portion of the initial bar and solidifying portion of a single crystal up to 25–27 mm [5].

In melting by an inductor with internal diameter smaller than that of a crystal (see Figure 1) an initial crystal forms in the area of melting so called cone of melting. On surface of the cone, directed at the inductor, maximum output of power and melting of the initial crystal take place. The drops flow off over the cone and get into the melt zone.

Conditions of the liquid flowing off over an inclined surface are considered in detail in [6]. In CFZM of silicon flowing off of the melt is characterized not just by forces of surface tension of silicon and mass of a formed melt drop, but also by acting on this drop centrifugal force (Figure 2).

According to [6], forces F_1 , which hold a drop on the melting surface, and F_2 , which ensure its flowing off, are equal

$$F_1 = mg \sin \alpha,$$

$$F_2 = 2R\Delta\sigma,$$

where R is the radius of area of a drop contact with the melting surface; $\Delta\sigma$ is the surface tension at the interface of phases; $\Delta\sigma = \sigma_{s-g} + \sigma_{l-g} - \sigma_{l-s}$; $\sigma_{s-g} = 1.617 \cdot 10^{-6}$ N/m is the surface tension in system solid body–gas; $\sigma_{l-g} = 0.720 \cdot 10^{-6}$ N/m is the surface tension in system liquid–gas; $\sigma_{l-s} = 0.210 \cdot 10^{-6}$ N/m is the surface tension in system liquid–solid body; m is the melt drop mass, kg.

During rotation centrifugal force acts on a drop

$$F_3 = m\omega^2 r,$$

where ω is the frequency of the initial bar rotation; s^{-1} ; r is the distance from axis of rotation to center of the drop gravity, m.

So, conditions of a drop flowing off over melting surface, taking into account acting on the drop centrifugal force, are observed at $F_1 > (F_2 + F_3)$, i.e. $mg \sin \alpha > (2R\Delta\sigma + m\omega^2 r)$. Analyzing obtained ratio one may draw conclusion that under conditions of the initial bar rotation flowing off of the melt drop is determined by frequency of the bar rotation and location of a drop relative axis of rotation. At the given frequency of rotation drops in central area flow off into the melt zone quicker (low r value) than in peripheral area (r value approaches radius of the bar).

In real melting processes observance of the condition $mg \sin \alpha > (2R\Delta\sigma + m\omega^2 r)$ is complicated in

connection with the fact that initial bars of silicon are characterized by structural and impurity inhomogeneity. Areas with increased concentration of impurities and density of structural defects enable significantly higher absorption of high-frequency energy, radiated by the inductor, than areas with low amount of impurities and low density of defects. During formation of the melt specific electric resistance of such areas drastically reduces, and release of energy in them causes intensive melting.

On the melting surface melt cells may be formed with radius of the drop contact area R equal, approximately, to 3–5 mm (see Figure 2, *b*). For fulfillment of the condition of a drop flowing off it is necessary to ensure angle of the melting surface inclination much higher (Figure 3) than the angle, created by maximum possible height of the inductor (see Figure 1). Flowing off of a drop is possible only after accumulation of a certain mass of the melt, which causes deepening of a cell.

In case of formation of several adjacent cells and flowing off of the melt from them between them occur sharp edges, which are transparent for adopted working frequencies of the inductor. Edges are the places of intensive heat removal and do not ensure melting of adjacent areas of the initial silicon bar.

At constant movement of the initial bar during melting, quantity of the non-molten material increases with formation of sharp protrusions on the melting surface, called spurs. After achievement by the protrusions of the inductor surface short circuit and emergency cessation of the melting process occur.

Simultaneously with formation of protrusions another unfavorable for the process of growing single crystals effect is detected, the essence of which consists in the following. For flowing off of the melt

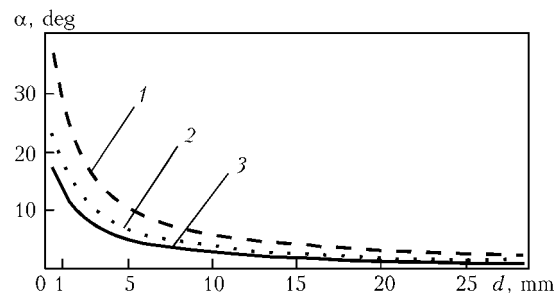


Figure 3. Dependence of angle of melting surface inclination upon diameter of area of melt drop contact at different values of melt layer thickness, μm : 1 — 100; 2 — 150; 3 — 200



drop from a formed cell at maximum angle of the melt surface inclination, limited by maximum height of the inductor, increase of the melt mass is necessary, which causes, if there is no flowing off, increase of the drop size and violation of uniformity of its inflow into the melt zone.

Having achieved critical size, the melt drop quickly flows off (breaks), frequently merging with drops from adjacent cells. A broken away drop may get on the inductor, having created conditions for short circuit, or into the melt zone, having drastically changed volume of the zone, which causes violation of its geometric shape and optimum conditions for single crystal solidification, or to break of the melt, i.e. to emergency cessation of the process of a single crystal growing.

CONCLUSIONS

1. It is established that at a certain frequency of the initial bar rotation it is possible to hold a drop without its flowing off into the melt zone.

2. It is shown that as radius of the bar increases, it becomes more difficult to hold drops because of

different speed of flowing off in central and peripheral areas.

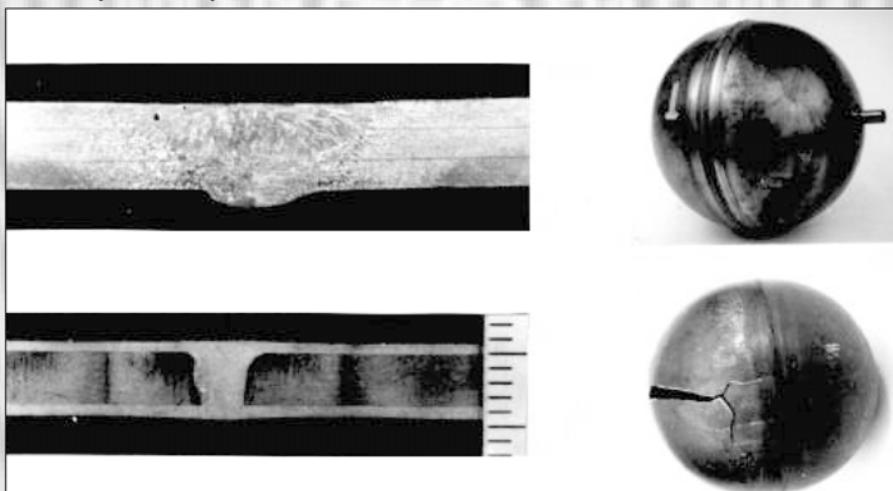
3. It is determined that one of the ways of uniform melting of the initial bar and flowing off of the melt into the general zone is formation of cells of unmolten initial material on the melting surface at minimum thickness of the melt.

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ARGON-ARC WELDING OF JOINTS OF HIGH-STRENGTH MULTI-LAYER STEELS IN SIMILAR AND DISSIMILAR VERSIONS

The high-strength multi-layer steels in similar and dissimilar version of 3–12 mm thickness consist of two and more layers, joined between each other in planes. The high strength is provided by layers of maraging steels and corrosion resistance is provided by external layers of high-alloy chromium-containing steels. The strength of multi-layer corrosion-resistant steels is 1200–2000 MPa depending on the combination of materials and ratio of thicknesses of the layers. The strength of the welded joint of the multi-layer steel made by the offered argon-arc method, reaches 0.87–1 of strength of the parent metal depending on used welding consumables and technological process of welding.

Application. For manufacture of high-pressure vessels and containers, operating under conditions of high loads and corrosion action. Its application is possible in aerospace industry, chemical machine building, for manufacture of navy machinery.



Proposals for co-operation. Creation of multi-layer steels, development of technologies of manufacture and welding, production of experimental batches of these steels and products on contract base.

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SHORT-TERM STRENGTH OF BRAZED JOINTS OF NICKEL ALLOY VJL12U AT TEMPERATURES 20 AND 950 °C

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Effect of chemical composition of composite brazing filler alloys, used in high-temperature resistance brazing, on strength of brazed joints of casting alloy VJL12U at temperatures 20 and 950 °C has been considered. Application of isothermal brazing with low-melting brazing alloy Ni-Co-Cr-Al-2.5 % B in mixture with a filler from powders of alloys Rene-142 and JS6U (up to 50 wt.%) within temperature range 1215–1220 °C (15–10 min) made it possible to produce brazed joints of strength, constituting 90–95 % of the base metal strength at room temperature and 70–85 % at 950 °C. Microstructural peculiarities of brazed joints after different kinds of heat treatment are considered.

Key words: alloy VJL12U, high-temperature brazing, vacuum, boron-containing brazing filler alloy, powder filler, heat treatment, tensile strength, seam metal, structure

Stationary components of hot duct of gas turbines, made of cast nickel alloys, are subjected in the process of operation to heat-fatigue cracking because of cyclic change of the surface temperature and occurrence of gradients of thermal stresses in the volume of components [1]. For items with disturbed critical dimensions, when width of a crack in its mouth exceeds 0.5 mm, renovation repair is required, which in recent years is performed by application of high-temperature brazing [2–5] and multi-component brazing filler alloys (BFA), containing boron and silicon (and iron for improving spreading of the BFA) as depressants, and efficient wetting of the area being repaired [6–7].

Nozzle vanes of II stage of a turbine may be manufactured from low-tungsten alloy VJL12U that allows saving on one item up to 75 % W and reduce mass of the machine by 7.3 %. Reduction of the weight of rotor blades allows reducing level of stresses in the disks and their mass and, as a result, mass of the item [8].

Some data on properties of alloy VJL12U are given in [8–10].

Metallurgical features of high-temperature isothermal brazing of high-temperature nickel alloys are considered below. The main requirement to the material of a composite BFA consists in achievement of satisfactory toughness of the melt, which ensures flowing in and filling of microcracks and voids in the item being renovated. Ratio of volume shares of a BFA (a low-melting component) and a filler without boron and iron ensures required toughness of the melt at a specific temperature of brazing.

The main goal of technological process of brazing and subsequent heat treatment of the item being renovated is to bring structure of the brazed seam metal

nearer to the base alloy structure due to activated diffusion interaction. Temperature of a component annealing before repair brazing should achieve temperature of the isothermal brazing process.

In case of a repair brazing it is advisable to use a BFA with maximum possible correspondence of its composition, in particular of the filler, to content of components in the item to be renovated.

Availability of tungsten and molybdenum in the BFA is important, because these refractory components enable solid-solution hardening of the seam metal and obtaining of necessary level of the joint strength. Chromium and aluminum ensure protection of a brazed joint (BJ) against oxidation; titanium, aluminum and tantalum define formation of γ' -phase, which hardens matrix of nickel alloy; carbon, zirconium and boron enable precipitation of hardening phases over grain boundaries.

Increased content of aluminum in powder mixtures is necessary for producing a more heat-resistant joint, and increase of tantalum content in the mixture of powders is necessary for improving its mechanical properties. Addition of tantalum increases parameters of γ - and γ' -phases due to reduction of discrepancy of parameters of their crystal lattices. At the same time resistance to oxidation increases. Tantalum, dissolving in γ' -phase, increases temperature of full dissolution (solvus) of the latter and limit temperature of the alloy serviceability.

Cobalt exerts positive influence on high-temperature strength and adaptability to manufacture (processibility), which is especially useful, when alloys are doped by titanium, tungsten, molybdenum and aluminum, and boron is present. Cobalt effects more efficiently creep resistance than aluminum, provided titanium is present [11].

A hardening phase in nickel alloys, containing more than 10 % Co, is γ' -phase (Ni, Co)₃(Ti, Al),



whereby its highest amount was registered, when content of cobalt did not exceed 15 wt.%. At higher weight shares of cobalt amount of γ -phase in nickel alloys reduces, which is connected with its favorable influence on heat resistance of solid solution and hardening phase.

Cobalt exerts positive influence on increase of impact toughness and elongation values, but insignificantly effects short- and long-term strength of the alloy.

Introduction of hafnium into the BFA causes certain strengthening of γ -phase. Hafnium reduces temperature, at which starts melting of the melt, and increases temperature of γ -phase melting, thus hindering homogenization of a BJ. At the same time hafnium increases resistance to oxidation, whereby it behaves similar to such chemically active elements as yttrium, cesium, lanthanum, etc.

Brazing alloy and filler powders are mixed on an organic binder. Binder Contronics 4B [4], produced by foreign industry, is environmentally safe and ensures reliable cohesion between a brazing alloy and a filler particles in composite brazing mixtures before brazing. Twenty minutes of the isothermal brazing process are sufficient for complete evaporation of the binder, flowing of the BFA into all cracks and formation of the seam structure, equivalent to that of the base metal. The BFA melts at a lower temperature and dissolves filler powders, creating bi-phase mixture, and then forms seam skeleton. Then annealing at 1135–1165 °C (better at 1150 °C) within 0.5–4.0 h (optimum time is 2 h) ensures inter-diffusion of components of the alloy being brazed and the composite BFA.

An important parameter is rate of the item cooling after annealing up to 650 °C. It is best of all to use rate up to 30 °C / min. In this case a network of globular carbide particles forms over grain boundaries. Lower rates or longer soaking within temperature range 1150–815 °C cause coarsening of carbide particles and reduction of ductility and fatigue resistance.

An important instant in brazing is occurrence in the seam metal of chromium- (molybdenum, tungsten) base embrittlement phases of the «china font» type, containing boron, silicon and carbon, volume share of which defines resistance of brazed parts to impact loads.

Composition of high-temperature part of the brazing alloy (the filler) must be close to that of metal of the part being renovated. Melting point of the BFA turns out to be significantly lower than that of the base alloy due to application of boron (and silicon) as a depressant.

High amount of the filler in the brazing alloy ensures better mechanical properties of a BJ due to reduction of relative concentration of boron and silicon in the seam metal. At the same time sufficient amount of a low-melting component ensures better spreading of the BFA.

According to patent [4], it is necessary to select melting point of the BFA lower than temperature, at which starts growth of grain of the alloy being renovated, and melting of the grain boundaries. For example, optimum composition of the BFA in repair of the parts, made of alloys GTD-222 and IN-939, should be as follows, wt.%: Ni10–19Cr3–10.5Co1.75–4.9Ti0.75–3.4Al1.25– 4.0W1.25–4.1Mo<1.5Fe0.025–0.225C0.005–0.15Zr 0.5–2.6B. Here carbon acts in composition of hardening carbide phases, while boron — as a depressant.

In this work alloy VJL12U, which is analogue of alloy JS6K, was used as the base one. The main peculiarity of the former is higher content of cobalt (14.5 against 5 %), titanium (4.5 against 3 %), and lower content of tungsten (1.4 against 5 %). Amount of the rest components of the alloy is similar, technological approaches to repair brazing of these materials are identical.

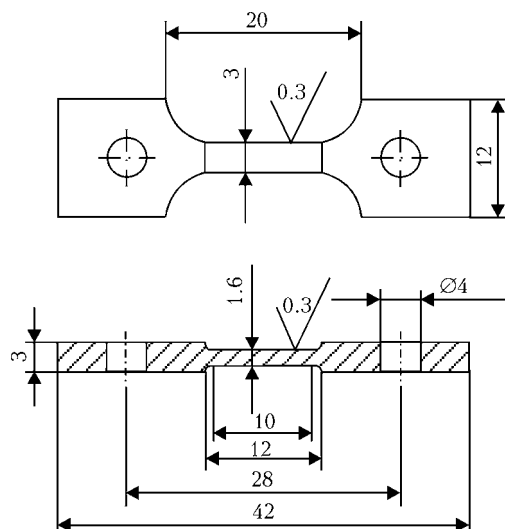
Molten BFA in capillary gap is intensively saturated by components of the part being brazed that causes loss of the melt fluidity. Processes of the gap filling with the BFA are effected by presence in the melt of separate crystal formations (chemical compounds), that's why filling of micro-loosenesses in the parts being brazed with application of multi-component fillers becomes problematic. During interaction of solid and liquid phases, contacting with solid phase volumes of the molten BFA and the base being brazed have similar structural state, but are characterized by a higher mobility of atoms, enabled by processes of surface diffusion.

Flowing in of the BFA into vertical gaps from above is possible only in case of its active interaction with the metal being brazed. Formation of a joint occurs from the very beginning due to interatomic interaction of the molten BFA and solid surface of the base being renovated, for intensification of which it is advisable to apply to the surfaces being joined a certain pressure in the form of static or alternating loading, for example ultrasonic oscillation.

In brazing by a composite BFA with a filler in the form of a powder of the metal being brazed (30–60 wt.%) primary liquid (BFA) is distributed mainly over boundaries of the powder particles and the contact surface filler–metal being brazed, due to which occurs process of contact-reaction sintering (brazing), connected with penetration of liquid phase, in particular depressant, over grain boundaries both into the base metal and into the filler material. In heating of parts in the process of isothermal brazing above solidus temperature of the BFA contact melting of the material depends upon rate of the depressant diffusion into liquid and solid phases of a joint. Increase of soaking time in isothermal brazing determines growth of the seam metal grain and expands area of solution-diffusion junction (along fusion line). The latter is rational from the position of technological ductility of joints.

Limitations in performance of tensile tests are connected with possibilities of the machine R-05 strain-measuring device, calibrated at maximum force 5 kN.

Heating of specimens in vacuum furnace SNV was performed stepwise. Brazing was performed at 1210–1220 °C within 10–15 min. Cooling of the specimens was performed after complete disengagement of the



ADVANCES IN ELECTROMETALLURGY

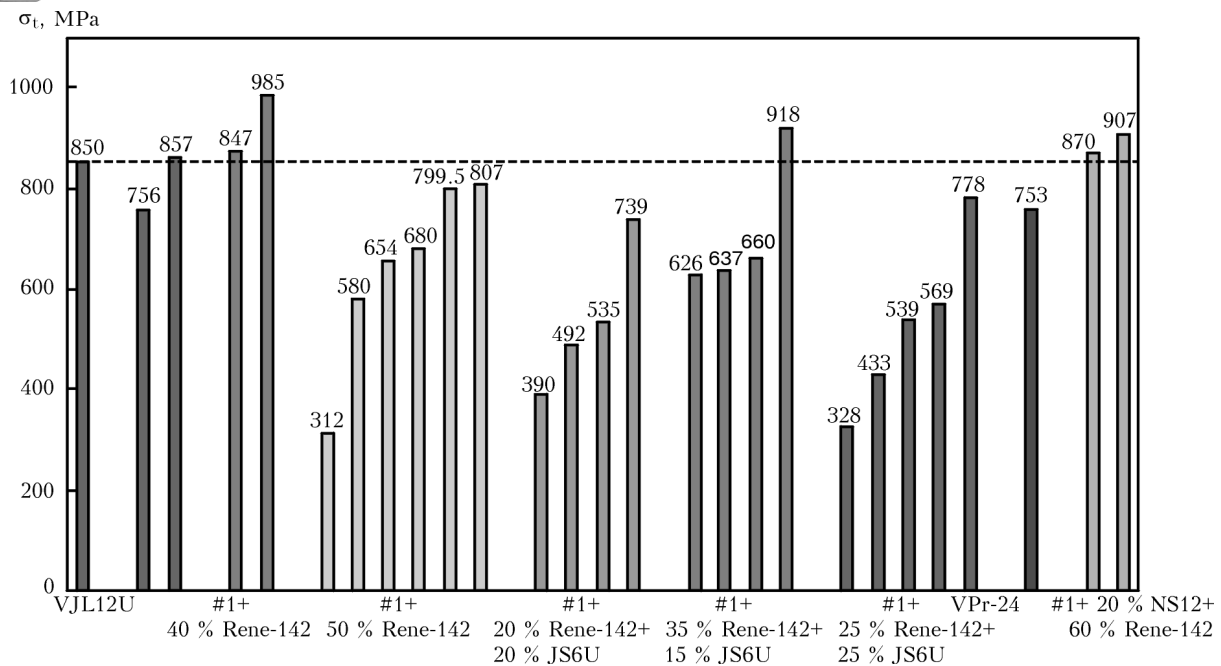


Figure 2. Strength level of the alloy VJL12U BJ produced with application of composite brazing alloys, consisting of #1 and fillers (alloys Rene-142 and JS6U), depending upon kind and weight share of filler; standard tensile strength of base metal VJL12U (850 MPa) is marked by dash line

furnace heaters. This ensured rate of cooling of the objects 18–20 °C / min in high-temperature area of 1200–900 °C.

Short-term strength of brazed joints at 20 °C. In Figure 2 results of mechanical tests of BJ of alloy VJL12U are generalized. In composite BFA different quantity of powder Rene-142 was used. Alloy Rene-142 is high-alloy system with temperature of complete dissolution of γ -phase in matrix of $T > 1240$ °C. Presence of tantalum, rhenium and hafnium in composition of the brazing alloy filler makes metal of the joint high-strength, scale-resistant, and ensures increased creep resistance of the BJ.

On the abscissa (Figure 2) phase composition of the brazing mixture from low-melting boron-containing nickel brazing alloy and the filler either in the form of powder of pure Rene-142 or in combination with powder of alloy JS6U is shown. The most stable results concerning BJ strength were obtained in brazing of VJL12U plates by composite BFA of two types — with fillers from 50 wt.% of Rene-142 and with a binary filler (35 wt.% of Rene-142 + 15 wt.% of JS6U). Minimum level of strength in this case con-

stituted 580–680 and 626–662 MPa, respectively, and maximum level — 800–918 MPa, respectively, when quality factor of BJ exceeded 100 %.

The highest values of BJ strength were obtained in case of using binary systems of brazing alloys, when 40 wt.% of powder Rene-142 were used as the filler: tensile strength was 874 MPa. At 50 wt.% of the filler from pure Rene-142 strength characteristics of joints turned out to be lower: 565, 580 and 680 MPa, maximum value of tensile strength being 807 MPa.

Statistical processing of data on tensile mechanical tests of BJ showed that area of the most probable strength values constituted 65 % of all results obtained, whereby strength level corresponded to 550–800 MPa (Figure 3). Strength of 40 % of specimens was 650–700 MPa.

Strength of alloy VJL12U (according to the certificate) equaled 850 MPa, while quality factor of BJ, obtained in three different experiments on isothermal brazing in vacuum at $T_{\max} = 1210$ °C (10 min), was 65, 84, 92 % (see Figure 2).

Absence of pronounced maximum on the curve (see Figure 3) proves existence of several dominant technological factors in brazing of billets VJL12U, which may effect strength level of investigated BJ.

Variation of phase composition (ratio of components in the composite BFA) has great significance in the level of BJ short-term strength, which may be achieved. Temperature and duration of brazing determine intensity of thermal diffusion interaction on surfaces of plates being mated and grain size in the seam metal.

Selection of the brazing alloy system with increased low-melting component for better flowing of melt into the gap was compensated by application of not less than 40 wt.% of the filler-powder from alloy

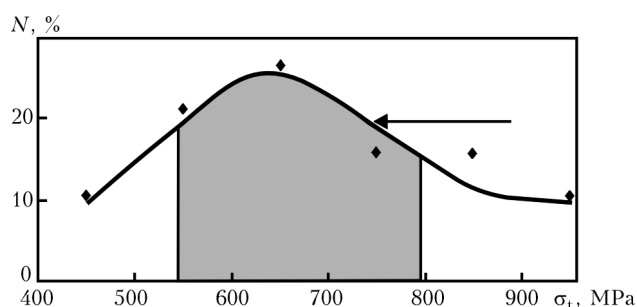


Figure 3. Statistic curve of strength distribution of the alloy VJL12U BJ (19 specimens) at 20 °C produced with application of boron-containing BFA; N — number of specimens; arrow shows area of most probable values



Rene-142. This allowed increasing quality factor of joints up to 102–115 % in comparison with alloy VJL12U being brazed. Application of the brazing alloy system 60 wt.% of #1 + 40 wt.% of Rene-142 made it possible to get one of the highest strength values of BJ.

Refractory components of alloy Rene-142, which played role of the filler in brazing mixtures, were modifiers for the metal of seams being formed due to refining of its grain, which enabled reduction of specific concentration of boride phases over interfaces. At the same time in test of BJ specimens on long-term strength fine-grain structure of the seam metal and concomitant microporosity were reasons of unsatisfactory creep resistance of BJ.

For improving wettability and changing morphology of eutectic phases in the seam metal a small amount of brazing alloy NS12, containing silicon, was introduced into composition of the brazing mixture. Silicon significantly improves penetration of BFA into capillaries (cracks), which occur in metal in thermal cyclic loading [6].

Two specimens of BJ, manufactured with application of triple composition (NS12 + #1) + 60 % of Rene-142 at $T_m = 1215^\circ\text{C}$ (15 min) had high values of not just yield and tensile strength, but also of relative elongation — 4–9 %.

Brazing by binary system #1 + 50 wt.% of Rene-142 according to mentioned conditions guaranteed stable level of strength (650–800 MPa) at insignificant ductility ($\epsilon = 0.5\text{--}1.6\%$).

In BJ metal with residual ductility deformation of a joint was ensured at the expense of the base metal, which had after two-stage heat treatment yield strength of 700–773 MPa. Results of different tests of specimens were close, which confirmed stability of the material properties after selected conditions of BJ heat treatment.

High-temperature annealing of BJ, used for equalizing microstructure of the base and seam metal, did not enable obtaining high level of creep resistance, because it caused coarsening of $\gamma\text{-Ni}_3(\text{Al}, \text{Ti})$ -phase particles of the base metal and γ -grain boundary phase in the seam metal. That's why it is advisable to perform additionally BJ ageing.

Strength of the BJ metal in case of using composite brazing alloy from 60 % of low-melting component and 40 % of the filler Rene-142 (in one experiment) after high-temperature annealing achieved 874 MPa, and after additional ageing at 1050°C for 2 h — 985 MPa.

In case of using brazing alloy 50 wt.% of #1 + 25 wt.% of Rene-142 + 25 wt.% of JS6U in primary experiments under the same conditions of brazing (1220°C , 10 min) tensile strength after high-temperature annealing was 327.6–415.0 MPa, and after ageing — 568.7 MPa.

Figure 4 illustrates high-temperature strength of alloy VJL12U and its brazed joints. Averaged strength of the base metal at 950°C after single-stage

annealing in vacuum was 530 MPa. Tensile strength of the metal, aged at 1050°C for 2 h, was 504 MPa.

The highest strength had BJ, produced with application of a composite brazing alloy, 40 % of filler of which consisted of equal parts of powder of alloys Rene-142 and JS6U. In this case quality factor of joints was 87 %. Further replacement of powder of alloy Rene-142 for powder of alloy JS6U increased spreading of the BFA, that's why contact interaction of the brazing mixture with the base metal strengthened. While at room temperature this increased propensity to embrittlement and reduced strength of metal of brazed specimens, at 950°C strength level of respective BJ was the highest. Quality factor of a joint, produced with application of the binary brazing alloy 50 wt.% of #1 + 50 wt.% of Rene-142 at 950°C , achieved 70 %.

Metallographic investigations. According to the delivery certificate, low-melting brazing alloy #1 (Ni-CoCrAl–2.5 % B) contains 13–14 wt.% Cr and does not contain refractory alloying additives. Approaching of averaged chemical composition of the seam metal to the base alloy turned out to be possible due to introduction of the filler into the brazing alloy. Metal of the seam, in comparison with the base alloy, represented a more alloyed system with insignificantly reduced content of aluminum and titanium — to 2.3–3.2 wt.% (Table).

Higher amount of the filler in the brazing alloy enables achievement of higher toughness of the melt in brazing of a joint and, respectively, smaller halo around the BFA bead, weaker flowing through the gap, and lower bellying of the bead on bottom surface of the billet. The more complete was coverage by the BFA melt on end surfaces of BJ, the better quality of joints was obtained. High quantity of the alloy JS6U powder in composition of the filler ensured better flowing through the gap and spreading of the BFA into its environs. Respectively, a wider halo along bead of the brazing alloy after its hardening was registered.

After hardening of the BFA and cooling of the billet BJ was heat treated.

Macrostructure of joints in cross section after heat treatment is presented in Figure 5. Such structure had specimens, designed for mechanical tensile tests. Final heat treatment (annealing at 1050°C , 2 h) of ready BJ specimens enabled vacuum etching of their working part surface, which made it possible to determine macrostructure of the seam and near-seam zone metal. Due to presence of the BFA beads and bellying in rear part of specimens, in the process of first annealing solid-phase interaction between the BFA material and alloy VJL12U was registered, which has in section of the specimen form of bilateral dovetail (see Figure 5).

Increase of brazing time at certain reduction of the process temperature enabled structure equalization of the seam metal, which guaranteed satisfactory level of strength in BJ test on single-axis tension at room temperature and 950°C .

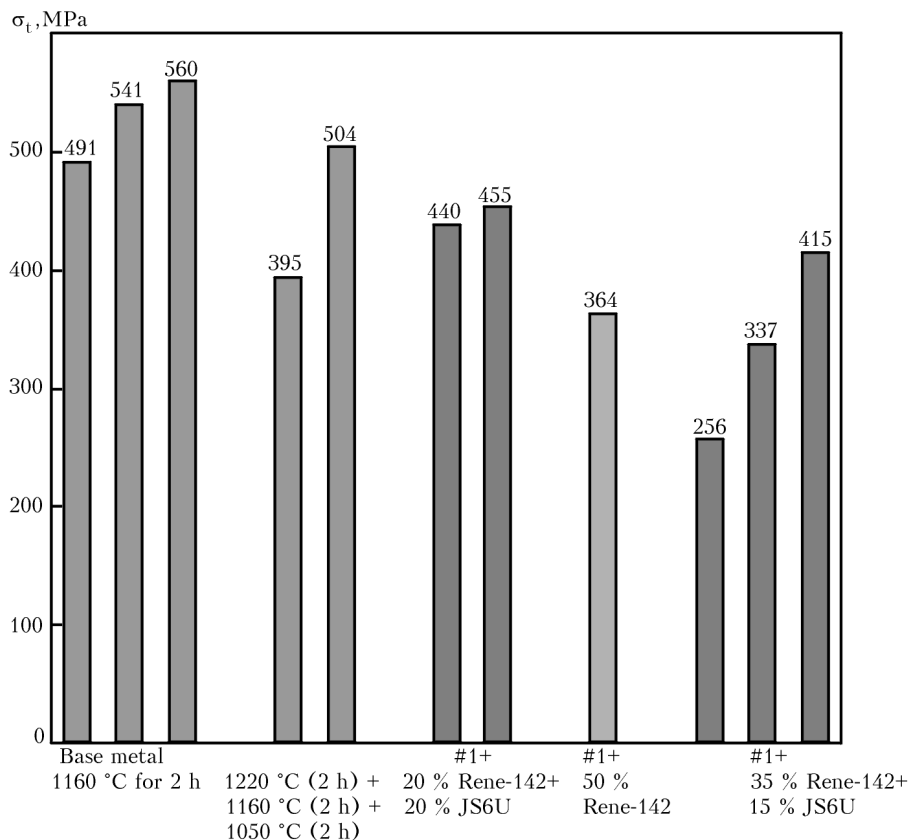


Figure 4. Strength of alloy VJL12U and its BJ produced with composite BFA of different chemical composition at 950 °C in air

Brazed joints, produced with application of binary brazing alloys #1 + Rene-142 in ratio 60:40 and 50:50 had width of in middle section 350–400 μm. At lower quantity of the filler (40 %) boron-containing brazing alloy interacted with the base and formed a diffusion

zone, which had depth up to 500 μm (Figure 6, *a*, *b*). Application after brazing of annealing at 1160 °C for 2 h, enabled diffusion interaction and equalizing of structure between the seam and the base metal (Figure 6), whereby dissolution of course carbide phases and their transformation into globular and polyhedral precipitates over grain boundaries took place. These phases represented double carbides of Me₆C type (on the basis of tungsten, molybdenum, chromium and rhenium) and discrete carbides MeC (on the basis of titanium, tantalum and niobium) (Figure 7, *a*, *b*).

Application of composite brazing alloy of system 50 % of #1 + 35 % of Rene-142 + 15 % of JS6U allowed obtaining relatively stable strength results — 626, 637, and 918 MPa. Joints, formed at 1220 °C for 10 min, were characterized by good spreading of the BFA over surface and completely filled the gap. However, on microstructures insignificant microporosity was detected, distributed near rear part of the specimen, connected with partial «sweating» of the BFA on ceramic support in the furnace (see Figure 6, *d*).

After introduction of alloy JS6U into composition of the BFA equalization of structure between the seam and the base metal was registered. Number of phase components reduced in structure of the solidified metal (Figures 6, *c*, *d*; 7, *c*, *d*). High-temperature annealing enabled dissolution of course carbide phases and eutectics of the seam, creating structure close to that of the base metal (Figure 8, *a*, *b*; Table). In

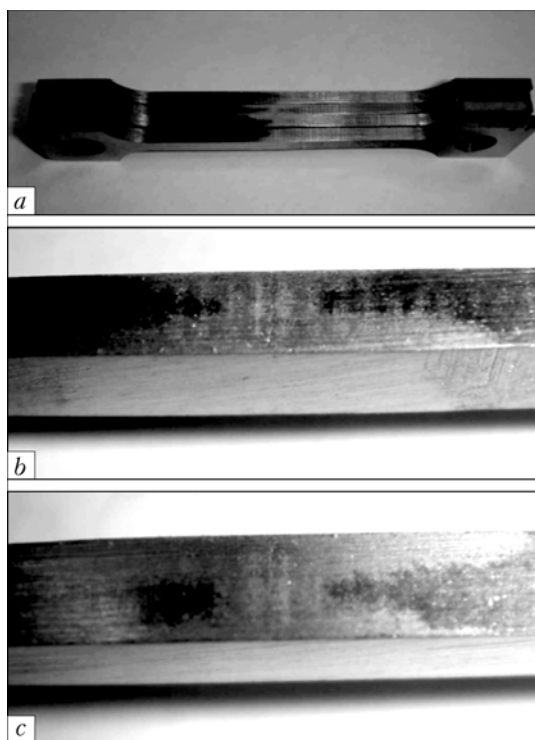


Figure 5. General view (*a*) and macrostructure of end surface of working part of brazed specimens (*b*, *c*)

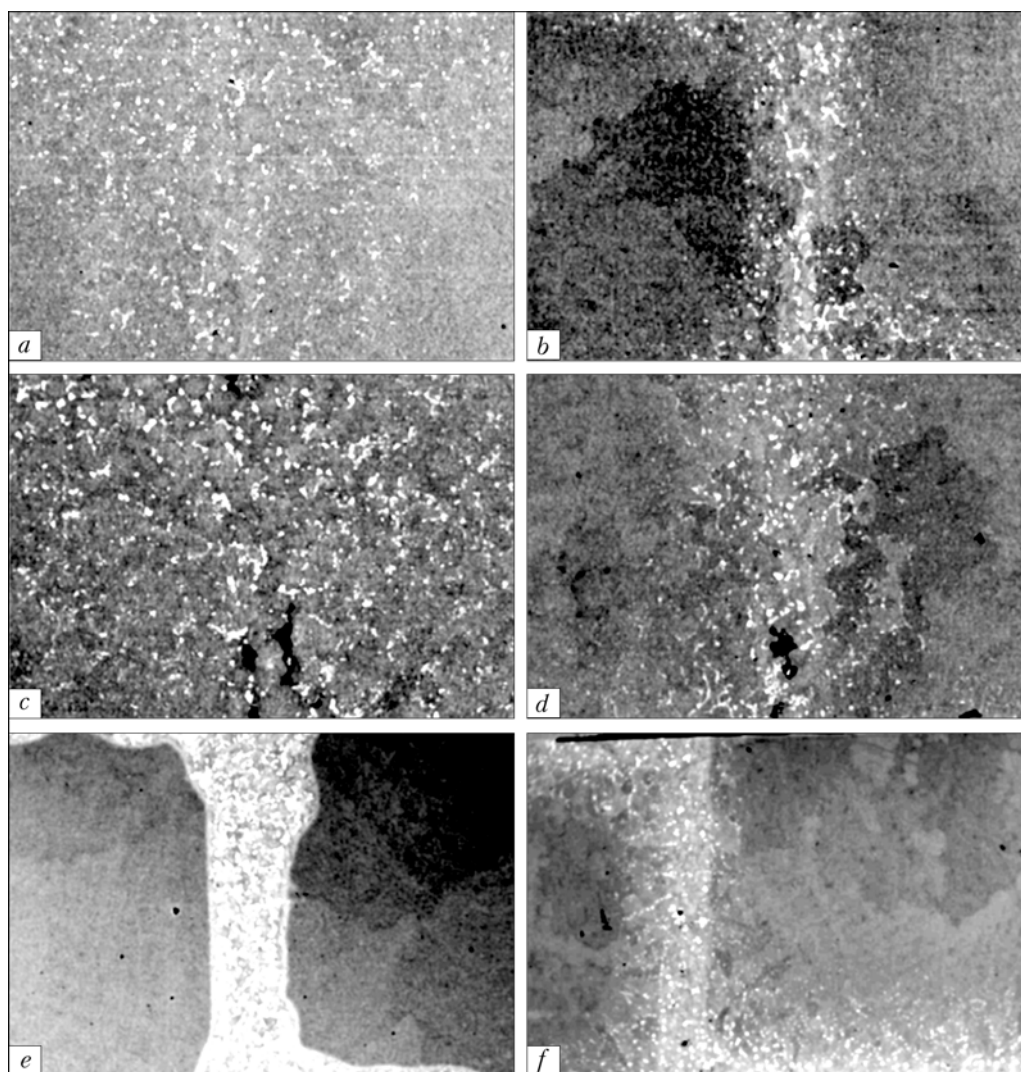


Figure 6. Microstructure of the alloy VJL12U BJ specimens formed at 1220 °C (10 min) with application of different composite BFA after two-stage heat treatment: *a* — 60 wt.% #1:40 wt.% Rene-142; *b* — 50 wt.% #1:50 wt.% Rene-142; *c* — 50 wt.% #1:(25 wt.% Rene-142 + 25 wt.% JS6U); *d* — 50 wt.% #1:(35 wt.% Rene-142 + 15 wt.% JS6U); *e* — VPr-24; *f* — 40 wt.% (NS12 + #1):60 wt.% Rene-142

fracture of the specimen, which demonstrated high tensile strength ($\sigma_t = 918$ MPa), tough component prevailed (Figure 8, *c*, *d*).

Increase of the powder content of alloy JS6U in the filler up to 25 % caused strong spreading of the brazing alloy over surface and intensified interaction of the brazing alloy with the base in subsequent high-temperature annealing (Figure 6, *c*). «Sweating» of the BFA weakened total contact area in the seam metal, which caused early fracture ($\sigma_t = 328$ MPa).

Alloy VJL12U is a material with relatively low stability of structure. In the process of isothermal brazing and high-temperature heat treatment between the melt and the base metal mutual diffusion of components occurs. Application of the alloy JS6U powder with 0.17–0.20 wt.% C as a filler and increase of its weight share enables formation of developed seams with maximum width of diffusion zone. Diffusion processes proceed, first of all, over grain boundaries, that's why presence of «brooks» of thin carbide phases over grain boundaries of the occurring diffusion zone

or acicular carbide phases Me_6C in it causes early fracture in the process of loading.

Presence in the BFA of the alloy Rene-142 powder, containing carbide-forming elements (rhenium, tantalum, hafnium, tungsten) as a filler, enables formation in solidified metal of the seam of great amount of carbides. In two-stage heat treatment after brazing carbides mainly represented polyhedral precipitates MeC (on the basis of titanium, niobium and tantalum). At the boundary with the base metal, containing up to 0.2 % C, carbide phases precipitated in the form of disperse particles over grain boundaries. Exactly they created barrier for further diffusion of low-melting components, for example boron, and «erosion» of the base. In its turn mentioned carbide phases together with precipitating from high-alloy solid solution γ' -phase increased strength of BJ.

Correctly selected heat treatment for the specimens with application of composite brazing alloy #1 + Rene-142 + JS6U enabled producing of BJ with quality factor 51–78 %, and of the system #1 + Rene-142 — with quality factor 80–115 % of the base alloy.

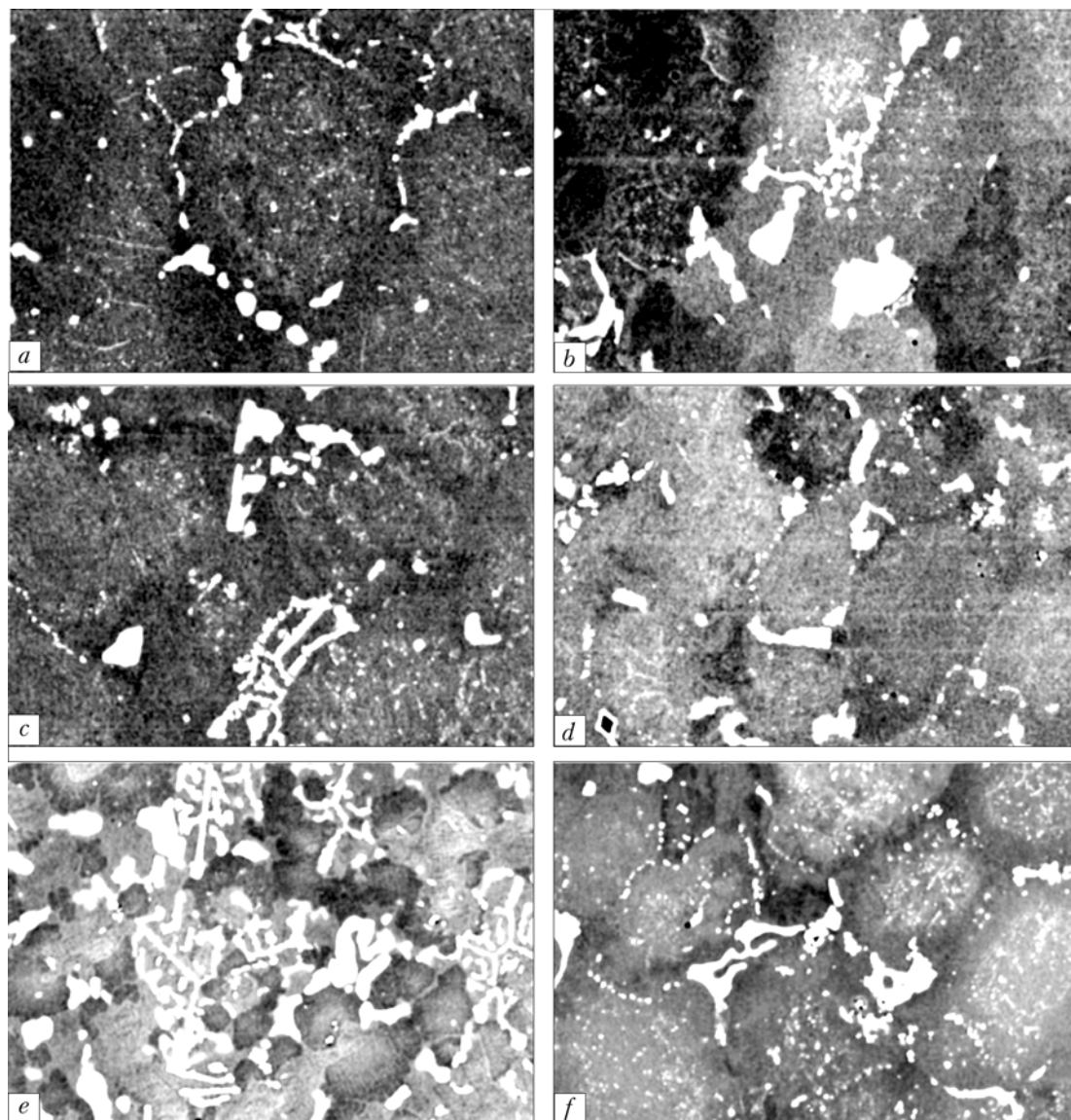


Figure 7. Peculiarities of microstructure ($\times 430$) of solidified seam metal depending upon type of used brazing filler alloy: *a* — 60 wt.% #1:40 wt.% Rene-142; *b* — 50 wt.% #1:50 wt.% Rene-142; *c* — 50 wt.% #1:(25 wt.% Rene-142 + 25 wt.% JS6U); *d* — 50 wt.% #1:(35 wt.% Rene-142 + 15 wt.% JS6U); *e* — VPr-24; *f* — 40 wt.% (NS12 + #1):60 wt.% Rene-142

In addition to good strength properties, some investigated specimens of BJ had small elongation (approximately up to 1.6 %). Fine structure of the base, diffusion zones and seam metal contained both primary coarsened and secondary disperse hardening γ -phase (Figure 9).

Fractography of fractures of the specimens after tensile tests was characterized by combination of fracture toughness and intergrain fracture with prevalence of the tough component (see Figure 8).

Application of high-alloy BFA VPr-24 with 3 % Si as a depressant allowed ensuring formation as a result of brazing and annealing of a seam 400 μm width with clear outline of the base metal–BFA fusion line (see Figure 6, *e*). Exactly silicon, which almost completely dissolved in the matrix, limited penetration of boron (up to 0.3 %) into the base metal. Width of mutual diffusion zone constituted in this case only 50 μm .

Presence in brazing alloy VPr-24 of 10 % Nb caused formation of coarse carbide phases of particles MeC in the volume of grains, while increase of silicon content caused formation of nickel and niobium carbosilicides in inter-dendrite areas (see Figure 7, *e*). Precipitated phases were rather stable at temperature of annealing 1160 $^{\circ}\text{C}$ (2 h), and participated in origination of cracks in mechanical tests. On fracture fractogram of such BJ transcrystalline fracture prevailed (Figure 8, *e*, *f*).

For improvement of fluidity of relatively tough composite brazing alloy #1 + Rene-142, good filling of the gap without formation of micropores and weakening of reaction capacity of boron-containing brazing alloy #1, a small amount of commercial brazing alloy NS12 ($T_m = 1180$ $^{\circ}\text{C}$) with 12 % Si as a depressant was introduced into it. Silicon partially neutralizes harmful role of boron. Produced seam in BJ had width



Chemical composition of the BJ seam metal formed in the process of high-temperature brazing of alloy VJL12U with application of different composite BFA

Type of brazing alloys	Weight share of components, %											
	Ni	Cr	Co	Mo	W	Ta	Nb	Al	Ti	Re	Hf	Si
Alloy VJL12U	Base	8.5–10.5	12.0–15.0	2.7–3.4	1.0–1.8	–	0.5–1.0	5.0–5.7	4.2–4.7	–	–	–
60 % #1 + 40 % Rene-142	60.69	10.20	14.12	1.50	2.02	1.58	0.48	5.47	2.62	0.80	0.50	–
50 % #1 + 50 % Rene-142	62.83	9.33	12.24	1.90	2.82	1.15	0.80	5.03	2.24	0.78	0.90	–
40 % #1 + 60 % Rene-142	59.80	9.70	11.20	2.46	5.00	2.38	2.75	3.80	2.85	0.62	0.13	–
50 % #1 + 35 % Rene-142 + 15 % JS6U	64.55	9.50	12.62	2.61	1.80	1.40	0.65	4.34	2.74	1.13	–	–
50 % #1 + 25 % Rene-142 + 25 % JS6U	59.97	8.87	13.22	2.85	3.23	1.86	0.67	5.36	3.20	0.77	–	–
VPr-24	59.75	7.81	10.14	1.86	6.21	–	4.20	5.45	2.84	0.49Fe	–	1.26
20 % #1 + 60 % Rene-142 + NS12	62.19	9.00	12.75	2.20	1.60	2.22	0.46	4.28	2.00	0.80	0.95	1.57

not more than 300 μm , diffusion zone being not more than 100 μm (see Figure 6, *f*).

After high-temperature heat treatment the solidified seam had dendrite structure with size of a cell 30 μm and represented high-alloy matrix solution with precipitates of carbide phases. Up to 1.5 wt.% Si dissolved over dendrite axis and up to 2.5 wt.% in inter-dendrite areas. Detected carbide phases were of two types: disperse boundary ones of Me_{23}C_6 type (on the basis of chromium, tungsten, molybdenum, rhenium), and more course globular ones of MeC type, into composition of which, in addition to usually present tantalum, hafnium and titanium, entered 8 % of nickel and silicon (see Figure 7, *f*).

Carbide phases in the seam metal of globular configuration did not negatively effect strength of the joints; correctly selected heat treatment allowed producing BJ with quality factor 102–107 %.

Pattern of the specimen tensile fracture represented combination of tough and transcrystalline fracture. Coagulated carbide particles MeC, which were present in microstructure of the seam metal, were clearly registered. Fracture in the test proceeded over grain boundaries of the base metal (see Figure 8). Strength of BJ with silicon turned out to be sufficiently high ($\sigma_{0.2} = 717.8 \text{ MPa}$, $\sigma_t = 907.5 \text{ MPa}$). There was only local lamination over contact lines of brazed plates in longitudinal structure of the tested specimen.

Discussion of the results obtained. Different ratios of low-melting boron-containing component and a filler from powders of nickel refractory alloys JS6U and Rene-142 allows achieving not just optimum fluidity of a BFA (its spreading over adjacent to a defect surface), but also penetration of the brazing melt into gaps (capillaries) both of model specimens and of real parts with thermal fatigue cracks.

Saturation of the seam metal by alloying additives at the expense of a «noble filler», to which relates powder of alloy Rene-142, ensures achievement of high level of short-term strength of BJ at 20 and 950 °C. Quality factor of BJ, which characterizes ratio of values of tensile strength of the brazed seam metal and the base metal under similar conditions of tests, constituted 65–100 %.

We did not manage to get satisfactory creep resistance (long-term strength) of BJ of alloy VJL12U in case of using conditions of final heat treatment in vacuum (conditions of thermofixation of flaps). Not just low creep resistance of the BJ metal was noted, but also of the base metal due to presence in internal volumes of the metal of dissipated microporosity, which did not manifest itself outside. Reason of this negative result has not been completely found out; may be it is connected with conditions of casting of respective parts [9]. Fracture of brazed specimens occurred over seam metal. Presence of fine grain in the seam metal partially explains weak creep resistance of the joints, produced by the resistance brazing method.

Analysis of the process of brazing of the alloy VJL12U plates carried out under different conditions, showed that the best brazing mixtures from nickel alloy powders are brazing alloy #1 with 40–50 wt.% of Rene-142 and with 35 wt.% of Rene-142 and 15 wt.% of JS6U as fillers of the brazing alloy.

Optimum brazing temperature of the VJL12U alloy plates is within 1210–1220 °C range, duration of brazing is 15–10 min.

Introduction of silicon into composition of the brazing mixture, in addition to improvement of fluxing capacity of the brazing alloy, ensures stable strength of the seam metal and allows obtaining due

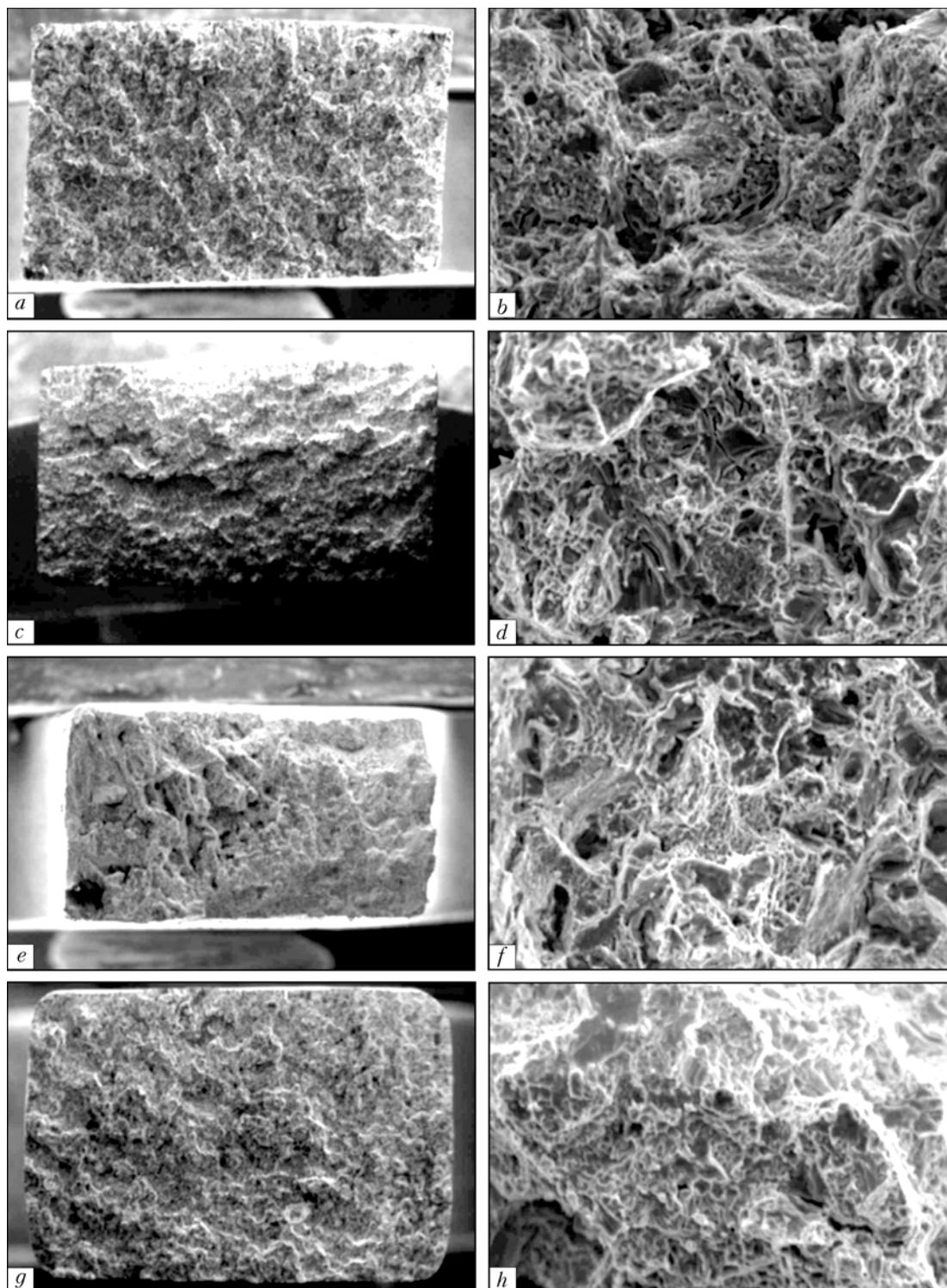


Figure 8. Pattern of fracture of BJ specimens produced with application of composite BFA in case of single-axis tension: *a, b* — 50 % #1 + 50 % Rene-142 ($Q = 80\%$); *c, d* — 50 % #1 + 35 % Rene-142 + 15 % JS6U ($Q = 108\%$); *e, f* — VPr-24 ($Q = 88.6\%$); *g, h* — 40 wt.% (NS12 + #1) + 60 % Rene-142 ($Q = 97\%$); *a, c, e, g* — $\times 23$; *b, d, f, h* — $\times 450$

to deformation of the base alloy relative elongation of BJ within 4–5 %.

Presence of insignificant amount of silicon in the brazing mixture is favorable due to increased efficiency of the brazing process at BJ formation. All specimens have satisfactory level of strength (more than 800 MPa), brittle intergrain fracture in seam metal is absent.

On gasdynamic stand of Institute for Problems of Strength, NASU, thermal-cycle burn-through tests of flap fragments were carried out, brazed by composite BFA in products of kerosene combustion at $T_{\max} = 1000\text{ }^{\circ}\text{C}$. Heat fatigue fractures in the base metal and in the area of brazing after 100 thermal cycles were not detected, which confirmed efficiency of developed repair brazing technology.

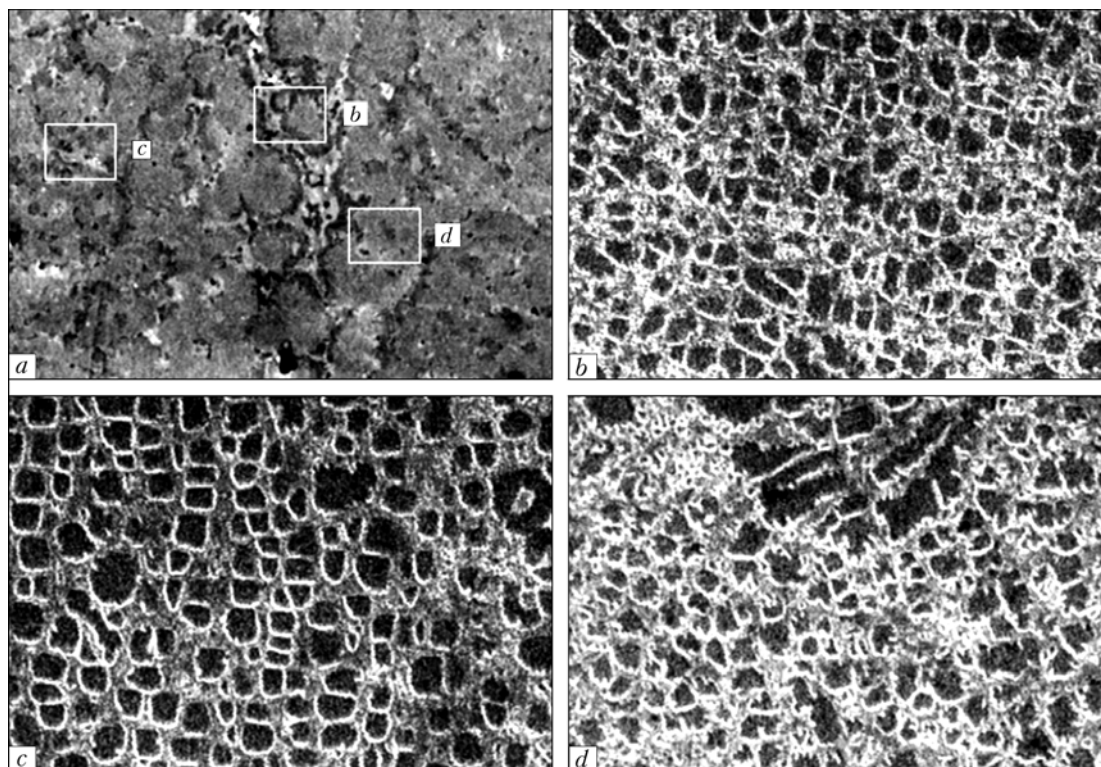


Figure 9. Fine (γ - γ') structure of brazed seam metal VJL12U / 60 % #1 + 40 % Rene-142 / VJL12U (a) on BJ specimen produced at 1220 °C for 10 min after two-stage heat treatment in different zones, and γ -phase in seam (b), base metal (c) and diffusion zone (e); a — $\times 140$; b–d — $\times 5000$

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DIFFUSION TITANIZING OF TUNGSTEN-FREE HARD ALLOYS TN20 and KKhN15

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Effect of technological parameters of diffusion metallization by titanium in close reaction space in chlorine on phase composition, structure and certain properties of coatings on tungsten-free hard alloys TN20 and KKhN15 was studied. Nickel participation as the basis in formation of diffusion zone of layers of intermetallics TiNi₃ and TiNi is shown. It was established that microhardness of TiC layers on investigated alloys is 19–24 GPa, Ni₃Ti — 6–12.5 GPa, dependence of thickness of carbide and intermetallic layers on temperature and time of saturation is of complex nature.

Key words: *titanizing, hard alloys, carbides, intermetallics, stability*

In connection with deficiency of tungsten, cobalt and some other elements, traditionally used for manufacturing tool and structural materials, new tungsten-free alloys TN20 and KKhN15 have been developed [1, 2]. Alloys TN20 supersede traditional W–Ti–Co alloys of TK type in finish and semi-finish machining operations [2]. Alloys KKhN15 are used as structural ones.

Tools and parts of machines operate under conditions of complex action of high contact loads and temperatures, whereby surface of items is intensively worn. So, increase of serviceability of tools and parts of machines by means of improvement of their stability is the main factor of production efficiency increase, which may be achieved by application of hard protection coatings with participation of carbides, nitrides and borides of transition metals [2–4], technology of production of which constantly improves.

Methods of producing protection coatings may be divided into two groups — physical and chemical ones. To the latter also relate methods of chemical heat treatment (CHT), characterized by simplicity of technological equipment and high quality of coatings [5, 6].

Peculiar feature of coatings, produced by CHT, is presence of a developed transition zone between the coating and the base, which predetermines rather strong adhesion between them.

It should be noted that investigations of the process of coating application on tungsten-free hard alloys are incomplete [7–9], and insufficient amount of experimental data on the method of diffusion metallization of tungsten-free hard alloys does not allow correct approaching to optimization of its technical parameters.

So, work connected with investigation of structure and properties of coatings, in which participates titanium, on alloys TN20 and KKhN15 is of actual character. Composition of alloys is given in Table 1.

Titanizing of alloys TN20 and KKhN15 was performed in close reaction space at reduced pressure [5]. Powders of titanium, carbon tetrachloride and charcoal were used as initial components. Coatings were applied within temperature range 1173–1373 K and soaking time 2–6 h.

Specimens of alloys with coatings were investigated using methods of physical materials science. It was established as a result of layer-by-layer X-ray diffraction analysis that in titanizing of tungsten-free hard alloy TN20 form, depending upon temperature-time conditions of saturation, multilayer coatings, consisting of the following phases: titanium carbide TiC, and nickel intermetallics TiNi₃ and TiNi (Table 2).

TiC carbide layer adjoins directly the base. Period of TiC crystal lattice is 0.4284–0.4288 nm, which is less than period of TiC base crystal lattice — 0.4289–0.4291 nm. The latter may be connected both with deficit of carbon in the area of homogeneity of TiC

Table 1. Composition and some properties of hard alloys TN20 and KKhN15

Grade of alloy	Weight share of main components in mixture of powders, %				Ultimate bending strength σ_b , MPa	Density, $\rho \cdot 10^3$ kg / m ³	Hardness $\bar{H}RA$
	TiC	Cr ₃ C ₂	Ni	Mo			
TN20	79	—	15	6	> 1050	5.5–6	> 90
KKhN15	—	85	15	—	> 1050	5.5–6	> 90

Note. Composition of alloys is determined without taking into account impurities.

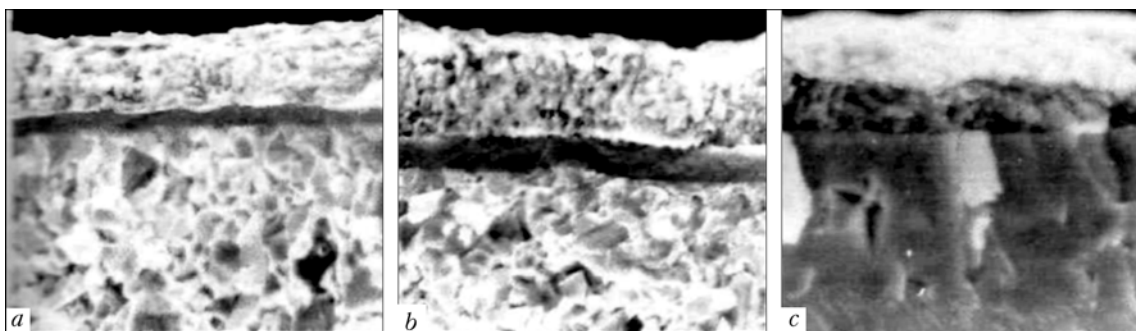


Figure 1. Fractograms of titanized alloys TN20 (a, b) and KKhN15 (c) at T , K: a — 1223, 2 h; b — 1273, 4 h; c — 1373, 2 h

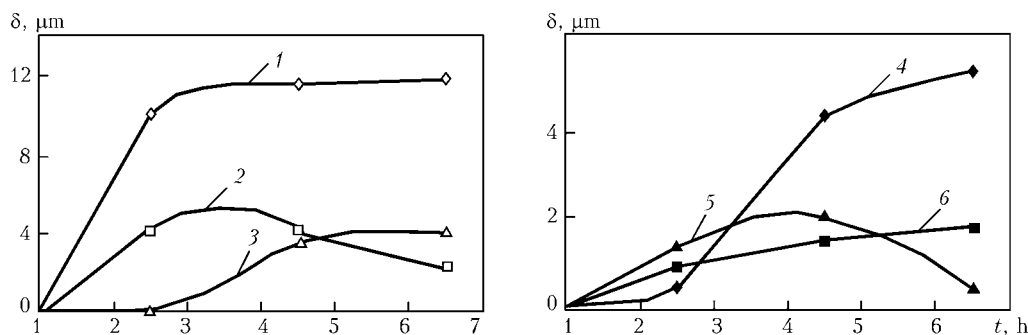


Figure 2. Growth kinetics of titanium coatings on alloys TN20 at $T = 1223$ K (a) and KKhN15 at $T = 1273$ K (b): 1 — TiNi_3 ; 2, 6 — TiC ; 3, 4 — TiNi ; 5 — Cr_7C_3

carbide coating and with dissolution in TiC of the base of the binder elements, first of all molybdenum [10, 11]. The TiC layer is followed by intermetallics TiNi_3 and TiNi . Formation of zone of intermetallics on external side of TiC coatings was detected in titanizing of steels [5, 6].

On alloy KKhN15, in addition to multilayer zone with participation of titanium and nickel (TiC , TiNi), forms zone of carbide Cr_7C_3 . In formation of carbide TiC insufficient amount of free carbon is compensated by carbon, formed in dissociation of the base carbide according to the reaction $\text{Cr}_3\text{C}_2 \rightarrow \text{Cr}_7\text{C}_3 + \text{C}$.

Analysis of distribution of chemical elements over the diffusion zone thickness showed that the nickel base metal actively interacts with titanium, forming respective phases. At the same time titanium penetrates into the base of hard alloys TN20 and KKhN15 and ensures high adhesion of the coating to the base.

In Figure 1 typical microstructures of alloys TN20 and KKhN15 after diffusion titanizing are shown. The coating proper consists of separate layers of carbides and intermetallics of light tincture, having clear interface with the base. At a certain distance from the coating in the base on non-etched sections a zone of dark-grey color — a zone of increased microporosity manifested itself, which formed in the process of saturation due to diffusion of nickel from the base into the coating.

Analysis of fractograms showed that for the investigated coatings brittle trans- and intercrystalline fractures are characteristic. Separate layers of intermetallics do not have pronounced boundary TiNi – TiNi_3 .

Peculiar feature of growth kinetics of coatings on alloys TN20 and KKhN15 is reduction of TiC thickness

at temperatures 1223–1273 K and duration of treatment of the layers $t = 4$ –6 h (Figure 2).

It should be noted that formation of zone of carbides in the coatings in the process of saturation and their subsequent dissolution in intermetallics have been also registered in metallization of steels [5, 6, 12].

Some data on investigation of microhardness of diffusion coatings on alloys TN20 and KKhN15 are presented in Table 2. Maximum level of microhardness have titanium carbide (TiC) base layers, which constitutes 24.0–28.5 GPa for selected temperature-time conditions of CHT.

Microhardness of layers of intermetallics TiNi and TiNi_3 turned out to be higher than that of cast materials, which is, most probably, connected with their composition and structure [13] and is stipulated by dissolution of carbides in layers of intermetallics. It

Table 2. Phase composition, characteristics and properties of coatings with participation of titanium on alloys TN20 and KKhN15

Grade of alloy	Temperature, K	Duration of titanizing, h	Phase composition of coating	Thickness, μm	Microhardness, GPa
TN20	1223	4	TiNi_3	4.0	17.5
			TiNi_3	19.0	6.0
			TiNi	3.0	7.0
KKhN15	1223	4	Cr_7C_3	4.0	14.5
			TiC	3.0	22.0
			TiNi	8.0	4.5
TN20	1273	4	TiC	4.5	22.5
			TiNi_3	18.5	7.5
			TiNi	7.0	8.0
TN20	1273	6	TiNi_3	19.5	7.5
			TiNi	9.5	7.0



is confirmed to a certain degree by hardness increase of layers TiNi_3 and TiN as CHT temperature increases (see Table 2).

The authors carried out commercial tests of stability of hard alloys with coatings. Stability of the titanized alloy TN20 increased in processing of steel 30KhGSA in comparison with initial alloy and alloy T15K6 4.8 and 4 times, respectively.

CONCLUSIONS

1. It is shown that in case of diffusion titanizing within temperature range 1173–1373 K for 2–6 h of tungsten-free hard alloys TN20 and KKhN15 coatings on the basis of titanium carbide TiC and intermetallics TiNi_3 and TiNi form.

2. It is determined that microhardness depends upon phase composition of the coating and conditions of saturation: for carbide TiC — 24.0–28.5 GPa, for intermetallics TiNi and TiNi_3 — 6.0–12.5 GPa.

3. It is established that titanizing increases stability of cutting plates TN20 in cutting processing of steel 30KhGSA in comparison with initial plates and plates from alloy T15K6 4.8 and 4 times, respectively.

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FLUX-CORED WIRE AND TECHNOLOGY FOR ARC SURFACING OF RAILROAD FROGS OF HADFIELD STEEL 110G13L

Technology of semiautomatic arc surfacing and self-shielding flux-cored wire PP-AN105 were developed for reconditioning of parts from Hadfield steel 110G13L (railroad frogs, components of crushing-milling equipment) and repair of casting defects. Metal deposited with this wire is characterised by high ductility and toughness. Its hardness after deposition amounts to HB 180–200, and after cold working — to HB 350–400. In the cold worked state, the deposited metal has very high wear resistance under conditions where wear is accompanied by heavy impacts or high contact pressure.

Semiautomatic devices PSh-107, PDO-517, etc., providing feed of flux-cored wire with a diameter of up to 3 mm and equipped with power supply VDU-506 or other type having similar characteristics, are used for surfacing railroad frogs. The frogs are prepared for surfacing by removing films, metal rolls and upper layer with microcracks from wing rails and cores using abrasive wheels. The layer deposited in one pass is 4–5 mm thick. In multilayer surfacing, it is necessary to apply forging for each deposited layer. Treated frogs are subjected to grinding using a suspended rail grinding machine tool.

The developed technology provides high-quality deposited layers in repair of frogs with a vertical wear of wing rails and cores down to 25 mm (allowing for removal of cracks, spallings and other defects). The experience shows that it is possible to successfully deposit frogs with individual defects removed to a depth of down to 40 mm. Depending upon the depth of wear, the frogs repaired by surfacing can be used in main, approach and other tracks.

Other parts of Hadfield steel can be repaired by the similar technology.

Application. Surfacing of railroad frogs, components of crushing-milling equipment, recovery of sizes and repair of casting defects.

Proposals for co-operation. Supply of flux-cored wire on a contract base, application of the surfacing technology.

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INNOVATION TECHNOLOGICAL PROCESSES OF ELECTRIC FURNACE FERRONICKEL REFINING BY PROGRESSIVE INDUSTRIAL METHODS

Part 3. Processes and technology for refining ferronickel in acid and basic oxygen converters

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Results of thermodynamic investigation of reactions of oxidizing of dissolved in ferronickel silicon and chromium by oxygen in the converter with silica brick lining, as well as carbon, phosphorus and sulfur in the converter with periclase-carbon lining are described. Technological conditions of ferronickel blowing by oxygen using single-nozzle lances, chemical compositions of slag phases, and behavior of impurity elements are shown. Processes of deoxidizing after oxygen refining of ferronickel by silicon and aluminum and principles of mechanized casting technology are considered.

Keywords: ferronickel, out-of-furnace refining, silicon, chromium, carbon, impurities, converter, acid lining, blowing by oxygen, technological conditions, phosphorus, carbon, sulfur, converter, basic lining, parameters of blowing by oxygen, slag mode, deoxidizing of ferronickel by silicon and aluminum, casting, ingot quality

In [1, 2] thermodynamic properties of binary systems nickel–iron, oxygen, silicon, sulfur and phosphorus elements, as well as physical-chemical premises and technology of out-of-furnace (ladle) desulfuration of electric furnace ferronickel by soda are presented.

In this article results of thermodynamic analysis and technology of subsequent, third stage, of ferronickel refining by oxygen first in the acid converter for the purpose of reducing content of silicon, chrome and partially carbon and then in the basic converter for removal of phosphorus, carbon and sulfur up to the limit values in correspondence with requirements of TU U 27.3-31076956-009:2005 are generalized.

Processes of ferronickel refining in acid converter. Crude ferronickel from New Caledonia ore is an iron- and nickel-base (from 15 to 17 %) multicomponent system with the following content of impurity elements: 0.3–0.4 Co; 0.5–5.0 Si; 0.5–2.0 Cr; 1.8–2.5 C; 0.013–0.020 Cu; 0.2–0.4 S; 0.01–0.02 P. That's why one has to take into account in thermodynamic analysis of oxidizing-reduction processes of ferronickel production and refining that the system metal (ferronickel)–slag (furnace and converter acid and basic ones)–gas phase can not be in equilibrium only on the basis of one component (for example, chrome or silicon), but must simultaneously achieve equilibrium in relation to the content of all components. If reaction proceeds at different rates, the slowest of them determines state of the whole system.

In [3] process of chrome distribution between metal and slag in melts, saturated with carbon, was experimentally investigated. Although in this work in the slag–metal system nickel is absent, general principles of chrome distribution between the metal and the slag, depending upon activity of silicon in the metal and different basicity of slag, is of interest for acid process of ferronickel refining as well. The slag contained 30–44 % CaO, 37–53 % SiO₂, 15.5–16.5 % Al₂O₃, whereby weight share of chrome oxides recalculated into chrome varied from 2.33 to 3.74 %, and ratio $Cr^{2+} / \Sigma Cr$ equaled 0.96, i.e. practically the whole chrome in the slag was represented by ($Cr^{2+}O$).

Content of chrome in iron-chromic melt achieved 14 %. Results of experiments are presented graphically in coordinates $(\% Cr)_m / [\% Cr]_{sl} - (SiO_2)_{sl}$ in Figure 1, from which it follows that index of chrome distribution has a very low value at slag basicity above 1.2, and increases up to 0.04 as basicity reduces down to 0.6. This index is not very sensitive to the tem-

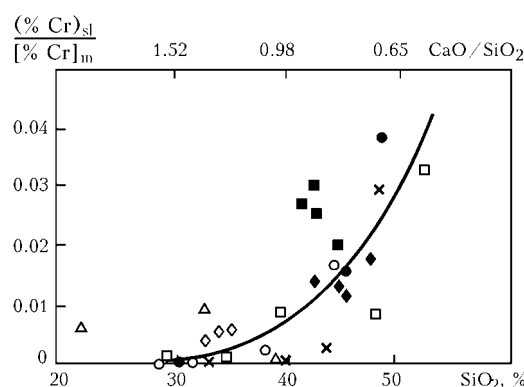
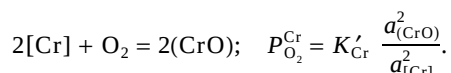
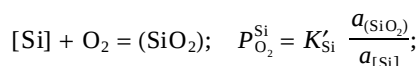


Figure 1. Connection between ratio of slag chrome to metal chrome and SiO₂ content in slag Al₂O₃ / CaO = 0.53 at $T = 1500\text{--}1600\text{ }^{\circ}\text{C}$ [3]

perature change, because points both for 1500 and for 1600 °C get into the same area.

Goal of work [3] consisted in investigation of possibility of more complete reduction of chrome from slag into the metal, i.e. determination of necessary conditions, under which distribution coefficient $L_{Cr} = (\% Cr_2O_3) / [Cr]$ would be the least. One of the tasks of this article consists in the opposite — determination of conditions, under which transition of chrome from ferronickel into the slag would be more complete, and coefficient L_{Cr} would have a high value. Slag of acid process at the end of ferronickel refining has the following composition, %: 45–60 SiO_2 ; 2.7–5.0 CaO ; 10–32 Fe (12.86–41.14 FeO), and 10–14 Cr (12.91–18.01 CrO). Ferronickel after oxidizing refining in acid converter consists of the following elements, %: 0.8 Si ; 1.0–1.5 Cr ; 15–20 Ni . For determining conditions of the most complete transition of chrome from ferronickel into acid slag we shall write down reactions of silicon and chrome oxidizing in the following form:



Under conditions of equilibrium of these reactions $P_{O_2}^{Si} = P_{O_2}^{Cr}$, the ratio

$$\frac{a_{(CrO)}^2}{a_{[Cr]}^2} = K_{Si, Cr}' \frac{a_{(SiO_2)}}{a_{[Si]}}$$

is fair, from which it follows that the higher is content of $a_{(SiO_2)}$ and the lower is content of $a_{[Si]}$, the lower should be content of chrome in ferronickel.

In work [4] equilibrium of slag of the $CaO-SiO_2-Al_2O_3-CrO-FeO$ system with $Fe-Cr-Si$ metal at 1600 °C was studied. Content of chrome in the metal varied from 5 to 30 %, silicon up to 2.5 %, ratio $(\% CaO) / (\% SiO_2)$ varied from 0 to 2, and amount of Al_2O_3 varied from 0 to saturation. In this work participation of (FeO) in equilibrium of the reactions, which cause oxidizing of chrome and silicon, is analyzed.

As it is noted in [5], the main primary act of blowing of iron-carbon melts and, evidently, of the system $Fe-C-Ni$ [6] is oxidizing of iron according to the reactions



$$\Delta G_{298}^0 = -237950 + 50T \text{ [J/mol]}.$$

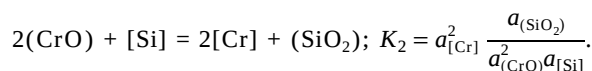
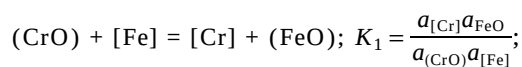
Heat effect of this process and degree of iron evaporation

$$\lg P_{Fe} = -\frac{18500}{T} + 5.90 \text{ [Pa]}$$

exert decisive influence on overheating and mean temperature of the reaction zone under conventional con-

ditions of blowing, when lance is located over the pool.

We shall present equilibriums in the metal-slag system by reactions and constants of equilibrium:



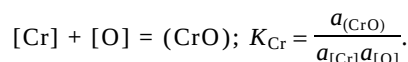
Dependences $\lg \frac{(\% Cr)}{[\% Cr]}$ upon content of (FeO) and activity a_{Si} are expressed in [4] in the following way:

$$\lg \frac{(\% Cr)}{[\% Cr]} = \lg \frac{(\% FeO)}{[\% Fe]} + \lg \left[\frac{\gamma_{FeO}\gamma_{[Cr]}C_1}{\gamma_{[Fe]}\gamma_{(CrO)}K_1} \right];$$

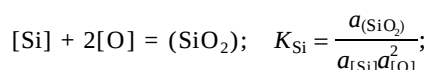
$$\lg \frac{(\% Cr)}{[\% Cr]} = -0.535 \lg a_{Si} + 1/2 \lg \left[\frac{a_{(SiO_2)}\gamma_{[Cr]}C_2}{\gamma_{(CrO)}^2 K_2} \right],$$

where C_1 and C_2 are the coefficients of proportionality.

When analyzing processes of chromium oxidizing, one has also to take into account reaction of chromium interaction with oxygen dissolved in molten ferronickel:

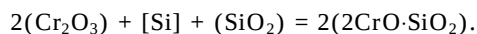


For reducing content of chromium in ferronickel it is necessary to determine two variables — $a_{[O]}$ and $\gamma_{(CrO)}$. Activity $a_{[O]}$ increases by means of oxidizing of silicon and reduction of its content in ferronickel:



$$a_{[O]} = \sqrt{\frac{a_{(SiO_2)}}{K_{Si} [\% Si] \gamma_{[Si]}}}.$$

Chromium oxidizing may be described by ratios, obtained for the case of the oxidizing period of electric melting of chrome-containing steels. Chrome oxidizing at the expense of oxygen and iron protoxide may proceed, depending upon chemical composition of the metal, with formation of chromite $FeO \cdot Cr_2O_3$, Cr_2O_3 , Cr_3O_4 and CrO . At temperature values 1550–1650 °C and $[\% Cr] = 0-3$ chrome is oxidized with formation of $FeO \cdot Cr_2O_3$, and at $[\% Cr] = 9-21$ with formation of oxide Cr_2O_3 . In acid slag chrome is mainly in the form of (CrO) [7]. At higher weight share of SiO_2 in slag (at saturated concentration of SiO_2) chrome is contained in groups, corresponding to orthosilicate $2CrO \cdot SiO_2$. Presence of silicon in ferronickel during its blowing by oxygen enables formation of $2CrO \cdot SiO_2$ according to the reaction



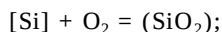
In the $\text{CrO}-\text{SiO}_2$ system there is eutectic with melting point 1400°C . Coefficient of chrome distribution between the slag and the metal depends upon temperature and amount of iron oxide in the slag. This connection is described by the ratio

$$\lg L_{\text{Cr}} = \lg \frac{(\% \text{Cr})}{[\% \text{Cr}]} = \frac{900}{T} - 5.14 + \lg (\Sigma \% \text{FeO}).$$

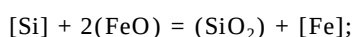
After termination of oxygen refining of ferronickel in acid converter the slag contains the following components, %: 45–60 SiO_2 , 10–14 Cr (12.90–18.07 CrO) and 10–32 Fe (12.86–41.14 FeO), and ferronickel 1.0–1.5 Cr and $[\text{Si}] < 0.7$ (12.90–18.07 CrO) 12.86–40.40 (FeO).

Having assumed for calculation composition of the slag 10 % (Cr) and 14 % (Cr), 1% [Cr] and 2 % [Cr], 12 % (FeO) and 32 % (FeO), we shall determine, using expression $\lg L_{\text{Cr}} = f \left[\frac{(\% \text{Cr})}{[\% \text{Cr}]}; (\% \text{FeO}), T \right]$ and the temperature, values of temperature of ferronickel refining process. Calculations show that at 10 % (Cr) and 12 % (FeO) equilibrium temperature of the process is 1785 K (1512°C); for second version of the slag 14 % (Cr), 1 % [Cr], 32 % (FeO) it equals 1764 K (1491°C). Obtained calculated values of temperature are close to those, determined as a result of measurements in conversion of ferronickel ($1480\text{--}1520^\circ\text{C}$) in acid converter.

When oxygen is fed on molten slag and metal, silicon, dissolved in ferronickel, may be oxidized according to the reactions



$$\Delta G_T^0 = -827730 + 228T \text{ [J / mol]};$$



$$\Delta G_T^0 = -351710 + 128T \text{ [J / mol]}.$$

After achievement of temperature $1450\text{--}1500^\circ\text{C}$ oxidizing of carbon starts, intensity of which increases with temperature increase. As a result of exothermic nature of the reactions of oxidizing of impurities, temperature of the process, as a rule, exceeds rational limits, which negatively effects stability of silica brick lining. That's why in the course of blowing temperature of ferronickel refining process is reduced by additives of nickel-containing waste, less frequently — of iron ore.

Oxidizing of impurities by oxygen is performed at intensive flow of oxygen $120\text{--}140 \text{ nm}^3 / \text{min}$ and its pressure $1.0\text{--}1.2 \text{ MPa}$. Blowing is performed by single-nozzle single-circuit lance with critical diameter of nozzle 38.3 mm and its section at outlet 51.2 mm (Figure 2). The lance is water-cooled, flow of cooling water is $60\text{--}70 \text{ m}^3 / \text{h}$, pressure is $0.7\text{--}0.9 \text{ MPa}$. The lance is mounted above pool surface at the level $0.8\text{--}2.0 \text{ m}$, depending upon chemical composition of ferronickel, temperature conditions and period of melting.

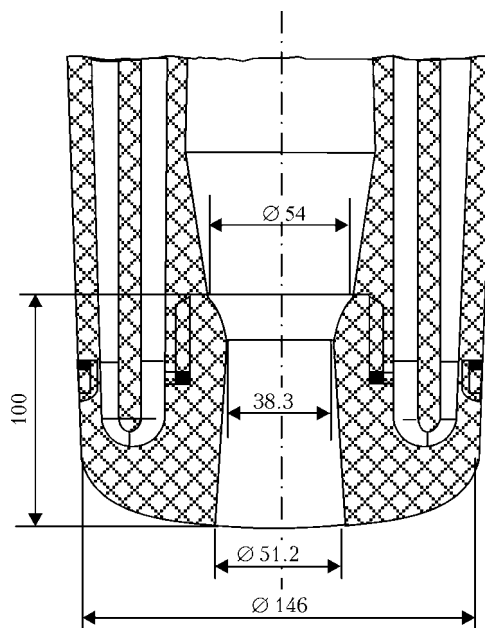


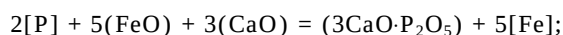
Figure 2. Single-nozzle single-circuit lance for oxygen refining of ferronickel in converter with acid (silica brick) lining for oxidizing of chromium, silicon and carbon

As weight share of silicon in ferronickel reduces, probability of iron oxidizing as the base component of metal melt increases. Formed low-melting iron silicates $\text{FeO} \cdot \text{SiO}_2$, $2\text{FeO} \cdot \text{SiO}_2$ intensively react with lining, destroying it. That's why it is recommended to stop blowing by oxygen after achievement of 0.8 % Si.

Processes of ferronickel refining in basic converter. Because of increased erosion of silica brick lining in acid converter only a part of silicon and carbon are oxidized. The rest amount of these impurities is removed in oxygen conversion in basic converter. The main task of the process of ferronickel refining in basic converter is its dephosphorization, whereby one has to keep in mind that in melting of lean ferronickel (5–7 % Ni) with application of lean (0.9–1 % Ni) Pobuzhskaya ore content of phosphorus in the former achieves 0.15 %. So, dephosphorization of ferronickel is a necessary technological operation, because in commercial ferronickel weight share of phosphorus should not exceed 0.02 %.

Since 2002 melting of ferronickel at Pobuzhsky ferronickel plant is performed using imported New Caledonian rich (2.9–2.6 % Ni) ore with low (0.018 %) content of phosphorus, that's why in electric furnace (crude) ferronickel content of phosphorus does not exceed 0.012–0.015 %. New Caledonian ore contains up to 23 % MgO , due to which form slags with high melting point ($> 1460^\circ\text{C}$). For reducing melting point of the slag down to $1300\text{--}1350^\circ\text{C}$ Pobuzhskaya nickel ore, in which MgO does not exceed 4–6 %, is added into the charge.

Process of ferronickel dephosphorization in basic converter during its blowing by oxygen under high-basicity slag with high content of (FeO) may be presented in general form by the following summarized reaction [5, 8]:



$$K_p = \frac{(\% \text{ 3CaO} \cdot \text{P}_2\text{O}_5)}{[\% \text{ P}]^2 f_{[\text{P}]}^2 (\% \text{ FeO})^5 f_{(\text{FeO})}^5 (\% \text{ CaO})^3 f_{(\text{CaO})}^3};$$

$$\Delta G_T^0 = -1372830 + 550T \text{ [J / mol]}.$$

Impurity elements effect in different way activity coefficient of phosphorus and, therefore, activity of phosphorus in ferronickel. This influence of impurity elements is quantitatively estimated by signs and numeric values of Wagner's interaction parameters [9, 10]:

Element, <i>j</i>	C	O	P	S	Si	Ni	Cr
$e_{\text{P}(1873)}^j = \frac{\partial \ln f}{\partial [\% j]} \cdot 100$	13	13	6.2	2.8	12	0.02	-3

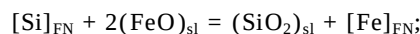
It follows from presented data that chrome reduces, while the rest elements increase activity coefficient of phosphorus in ferronickel.

Ferronickel refining in basic converter of up to 50 t capacity (mass of the metal being processed is 33–35 t) is performed under slag, which by the end of the process has the following composition, %: 0.2–0.3 Ni; 20–30 CaO; 5–15 SiO₂; 45–51 (57–64) Fe (FeO); 7–20 (9–26) Cr (CrO).

Oxygen is fed through a single-nozzle two-circuit lance, designed at Dneprodzerzhinsk Metallurgical Works Ltd., with diameter of external nozzle 32.5 mm. Working pressure of oxygen is 1.0–1.2 MPa, oxygen flow is 100–120 nm³ / min. For cooling of oxygen lance 60–70 m³ / h water and pressure 0.7–0.9 MPa are required. The lance is mounted at the level 0.8–2.0 m above surface of the pool of 0.9–1.0 m depth. Position of the lance changes depending upon chemical composition and temperature of ferronickel. Durability of the lance tips achieves 1000 and more melts.

Both in acid and basic processes of ferronickel conversion nickel is distributed between the metal and the slag. As weight share of nickel in the metal increases due to oxidizing of not just silicon and chrome, but also of iron, equilibrium content of nickel in the slag increases. In addition to oxidized form of ferronickel, fine reguluses of ferronickel are contained in the slag, that's why slag of the basic refining process is subjected to enrichment.

As amount of impurity elements in ferronickel in the course of its refining reduces, solubility of oxygen in it increases. That's why before casting ferronickel is deoxidized by ferrosilicon (aluminum) during its pouring from the basic converter into the ladle. For producing well deoxidized ferronickel 5.8–7.3 kg / t of ferrosilicon (FS45) and 0.7–0.8 kg / t of aluminum are consumed. Process of ferronickel and converter slag deoxidizing in a ladle by silicon is described by the reactions



Constant of ferronickel deoxidizing by silicon has the following form:

$$K'_{\text{Si}} = \frac{a_{[\text{Si}]} a_{[\text{O}]}^2}{a_{(\text{SiO}_2)}} = \frac{[\% \text{ Si}][\% \text{ O}]^2 f_{(\text{Si})} f_{[\text{O}]}^2}{a_{(\text{SiO}_2)}}.$$

For the case of iron deoxidizing by silicon dependence of $\lg K'_{\text{Si}}$ upon temperature is as follows:

$$\lg K'_{\text{Si}} = \lg \frac{[\% \text{ Si}][\% \text{ O}]^2}{a_{(\text{SiO}_2)}} = -\frac{31000}{T} + 12.$$

Equilibrium content of oxygen in iron (approximately the same is in ferronickel) depends upon weight share of silicon and temperature; the lower is temperature the higher is deoxidizing capacity of silicon because of exothermic nature of reactions of interaction of silicon with oxygen.

Deoxidizing of ferronickel by aluminum may be presented by the reaction:



$$K'_{\text{Al}} = \frac{a_{[\text{Al}]}^2 a_{[\text{O}]}^3}{a_{(\text{Al}_2\text{O}_3)}} = \frac{[\% \text{ Al}]^2 [\% \text{ O}]^3 f_{(\text{Al})}^2 f_{[\text{O}]}^3}{a_{(\text{Al}_2\text{O}_3)}}.$$

At small concentrations of aluminum in molten iron (ferronickel) product $f_{(\text{Al})}^2 f_{[\text{O}]}^3$ is assumed equal 1. Then

$$K'_{\text{Al}} = \frac{[\% \text{ Al}]^2 [\% \text{ O}]^3}{a_{(\text{Al}_2\text{O}_3)}};$$

$$\lg K'_{\text{Si}} = -\frac{39284}{T} + 11.05.$$

Ingots of sufficiently deoxidized ferronickel have dense structure and good commercial appearance.

So, oxygen refining of ferronickel under basic ferrous slag in the converter with periclase-carbon (periclase-graphite) lining after previous stage of oxygen blowing in acid converter allows producing commercial ferronickel with increased content (20–23 %) of nickel in comparison with crude ferronickel (15–17 %), chemical composition, weighing, and quality of ingots of which meet to full degree norms, regulated by TU U 27.3-31076956-009:2005.

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PECULIARITIES OF PRODUCING INTERMEDIATE PRODUCT FOR MANUFACTURING ESPECIALLY LOW-CARBON STEEL IN ELECTRIC ARC FURNACE

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Specifics of steel production under conditions of Moldavian Metallurgical Works are considered. Feasibility of producing ultra-low amounts of carbon using arc steel-melting furnace–evacuator–ladle-furnace scheme is shown.

Key words: arc steel-melting furnace, intermediate product, ladle-furnace, evacuator, lance, oxidation degree, deoxidation, IF-steel, wire

At present production of steels with especially low content of carbon and other impurities, characterized by high ductility properties (IF-steels), which are widely used in production of thin sheets for their subsequent deep (super-deep) drawing and application of coatings by hot method, is widely used in the world. At the same time steels, composition of which is close to that of IF-steels, due to low value of their tensile strength (less than 300–340 N / mm²) represent interest as super-ductile rolled wire for production of thin wires. Due to low content of carbon, alloying elements and impurities conversion of such rolled wire is possible by drawing without intermediate annealing, which allows significant reducing of hardware production cost.

All IF-steels are molten in converters with combined blowing by oxygen and argon [1]. Present trends in development of state-of-the-art steel making industry is bringing nearer possibilities of the main steel-melting units of ferrous metallurgy-oxygen converters and arc steel-melting furnaces (ASMF) and even development of a kind of the arc steel-melting converter [2]. In state-of-the-art ASMFs, which operate with blowing of significant amount of oxygen, in technological chain of the ladle-furnace and evacuator units steels of the whole assortment are molten, which were previously produced only in oxygen converters, including those with low content of carbon.

Assortment of profiled rolled stock produced by Company «Moldavian Metallurgical Works» (MMW) is extraordinary wide and includes both

high-carbon grades of steel for metal cord and low-carbon ones for manufacturing wire and reinforcement bars. Wide technological possibilities and high culture of production of MMW allowed setting task to melt especially low-carbon steel for producing high-ductility rolled wire from electric furnace intermediate product.

Technological possibilities of MMW in producing low-carbon steels. Electric arc furnace of MMW DSP-2 has rated capacity 120 t and power 95 MV·A (in standby 80 + 12 %). Technology of production envisages feeding into the furnace for heating of the metal rather high amount of carbon-containing materials (coke, natural gas) and blowing of oxygen for combustion and oxidizing of metal charge impurities by means of several kinds of burners and lances. So, on the DSP-2 furnace the following equipment is used:

- a system of wall gas-oxygen burners (4–6 single-type jet burners of 3.6 MW power with flow of oxygen 4800 m³ / h), ensuring production of strong flame, which allows efficient heating and cutting of metal charge and burning up of CO and CO₂ in working space of the furnace);

- manipulator «Palmur» for blowing of oxygen and powder-like coke for the purpose of acceleration of the metal charge melting in cold zone of the furnace, mixing of molten metal due to high rate of oxygen injection (flow of oxygen is up to 3000 m³ / h and of powder-like coke — up to 40 kg / min), decarbonization of molten steel pool by oxygen, burning up of CO by injection of gaseous oxygen, and formation and maintaining of foamed slag;

- MMW manipulator for acceleration of the melting process and improving metal quality due to melt-



Main technological parameters of melting in DSP-2 furnace

Specific consumption of electric power, (kW·h) / t	Flow of oxygen, m ³ / t				
	Manipulator «Palmur»	Side lances	MMW manipulator	Stein Lang oxygen lance	Oxygen tube
430	13.35	1.4	5.9	4.20	1.27
344	1.90	0.7	2.7	2.05	0.10
639	23.10	4.2	12.0	6.95	3.50

Note. Mean, minimum and maximum data of 200 melts are presented.

ing of metal charge in the area of the ASMF working window by gas-oxygen burner and controlled decarbonization of the melt by powerful and compact jet of oxygen (flow of oxygen in oxygen lance is up to 3000 m³ / h, in gas-oxygen burner of 7.3 or 10 MW power — up to 2200 m³ / h, flow of natural gas is up to 1100 m³ / h) and saving of electric power due to inclusion of additional alternative power source and reduction of the furnace operation period under current;

- oxygen lance of the Stein Lange company for producing additional thermal energy by feeding into the furnace of natural gas and oxygen (the power is 3.2 MW, flow of natural gas is up to 350 m³ / h, flow of oxygen per a lance is up to 2000 m³ / h and per a burner — up to 700 m³ / h) which allows increasing productivity of a steel making unit, reducing consumption of electric power and graphitized electrodes, and increasing general power;

- system of side oxygen lances for ensuring supply of gaseous oxygen in the pool through two lances in the area of the fifth and the seventh water-cooled panels of the furnace, which ensures intensification of the process of the metal charge melting in the zones that are not affected by direct action of electric arcs or gas-oxygen burners, mixing of the melt in the process of steel melting, oxidation of carbon, and burning up of CO in working space of the furnace.

If necessary, application of oxygen tube is allowed in technology of steel production.

Lining of the furnace working layer is made of high-resistant periclase-carbonaceous refractory materials (more than 700 melts).

Mentioned possibilities allow melting in the electric arc furnace of intermediate products with different content of carbon, including low one (less than 0.03 %), which significantly simplifies in further out-of-furnace processing production of especially low-carbon steel.

Technological possibilities of production allow performing further out-of-furnace processing of an intermediate product in the evacuator and the ladle-furnace unit according to the schemes: ASMF–ladle-furnace–evacuator–CCM (a direct one) and ASMF–evacuator–ladle-furnace–CCM (a reverse one).

The goal of this investigation consisted in development of technology for producing a low-carbon intermediate product in electric arc furnace DSP-2 of MMW for manufacturing especially low-carbon steel for ductile rolled wire. Maximum allowable content of carbon in steel was up to 0.01 %, silicon and manganese — up to 0.01 and 0.12 %.

Statistical analysis of technology for production of low-carbon intermediate product in electric arc furnace. For the purpose of substantiating rational parameters of technology for producing especially low-carbon steels statistical analysis of parameters of more than 200 melts of current production was carried out.

For determining efficiency of carbon oxidation in the DSP-2 pool by different blowing devices dependences of its final content in the intermediate product upon specific consumption of oxygen in these devices were established (Table).

It was established that consumption of oxygen in fuel devices («Palmur» and Stein Lange oxygen lance) insignificantly effected content of carbon in metal at the outlet; influence of oxygen consumption in «non-fuel» devices — its supply to bottom lances and oxygen tube that was used not in all melts (40.43 and 30.85 % of general number of the sampling), was appreciable, which is a reserve for obtaining low content of carbon at the outlet.

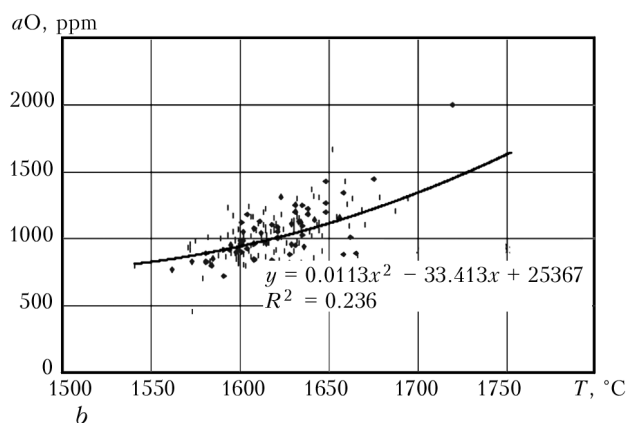
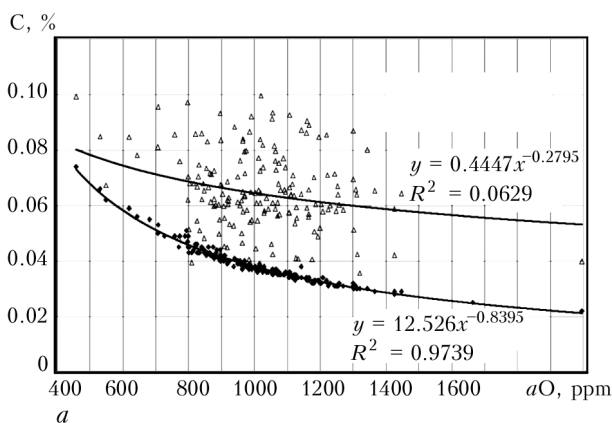


Figure 1. Dependence of carbon content and oxidation degree aO of steel at outlet (a), and influence of temperature on oxidation (b):
 ◆ — according to oxidation degree; Δ — according to chemical analysis

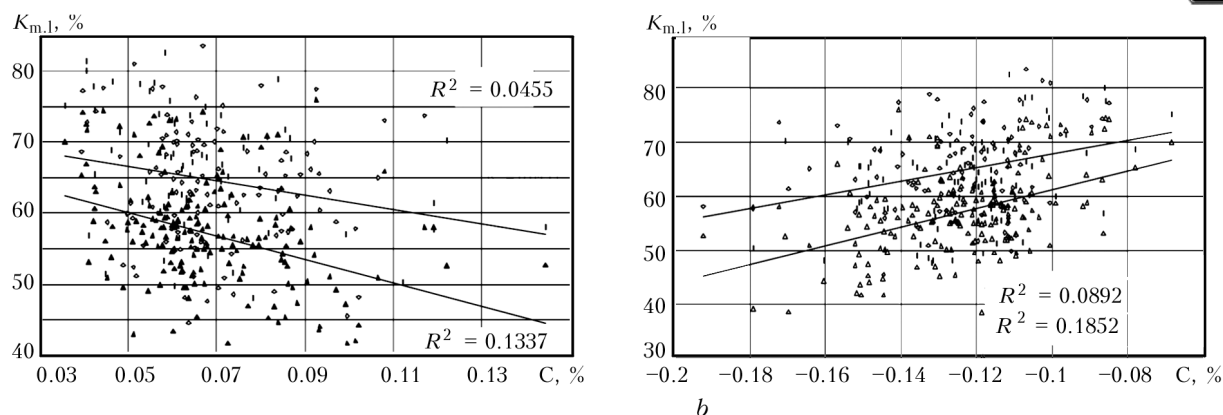


Figure 2. Influence of weight share of carbon at outlet (a) and change of its content in ladle-furnace (b) on amount of melting loss of deoxidizers: $\blacklozenge$ — silicon; $\triangle$ — manganese

Slag conditions of the pool heating during the last period of melting, which excludes transition of carbon into the metal from electrodes of electric arc furnace, may enable obtaining of low carbon content in the metal at the outlet.

Oxidation degree of the metal (measured by CELOX sensors) at the outlet was determined by weight share of carbon in the metal (Figure 1, a) and depended upon temperature of the metal (Figure 1, b).

Significant scatter of values of the metal oxidation degree, depending upon carbon content, should be noted, which was determined by chemical analysis, whereby in majority of cases actual values of oxidation degree exceeded those determined by measurements. Mentioned differences may be stipulated by the time of sampling and oxidation measurement.

As a whole, possibility of producing low content of carbon at the outlet was statistically authentically established. Weight share of carbon in the intermediate product varied, according to chemical analysis data, within 0.025–0.095 %, and measured oxidation — within 0.025–0.038 %. Oxidation degree and temperature of metal at the outlet (1100–2100 ppm, 1653–1741 °C) significantly exceeded usual values in converter processes of steel production.

Content of carbon and active oxygen in initial metal before ladle-furnace significantly effected melting loss of deoxidizer-elements (directly proportionally and inversely proportionally). Dependences of silicon and manganese melting loss upon content of carbon at the furnace outlet (Figure 2, a) and changes of carbon content in the ladle-furnace (Figure 2, b) showed that the fuller was decarbonization of metal in the ladle-furnace, the lower was melting loss of deoxidizers.

Analysis of data on content of sulfur in intermediate product at the DSP-2 outlet showed that it was significantly higher than average in the metal charge, even if one assumes the content to be at the level of upper limit for common grades of steel (0.04 % S). In the furnace increase of weight share of sulfur due to injection of carbon-containing materials was registered.

At the same time in steel melting processes sulfur was partially removed into gaseous phase, provided blowing by oxygen and high values of temperature and degree of metal oxidation were ensured. So, in [3] data are presented that during oxidation period of melting in electric arc furnace 36–50 % S, carried in by all charge materials, are removed from the furnace with furnace gases. Connection between concentration of sulfur in the intermediate product at outlet and oxidation degree of the metal was also detected in considered melting processes (Figure 3).

Essential dependence between content of sulfur in the intermediate product and metal temperature at the outlet was not established that proves prevailing influence of oxygen injection into the furnace and degree of metal oxidation on sulfur removal into gas phase.

As far as content of sulfur at outlet from the furnace is significantly higher than it is required by the standards, it is evident that desulphurization of the metal is performed in the course of out-of-furnace processing. Naturally, lower content of sulfur in the metal at outlet enables better proceeding of further desulphurization process, reduction of consumption of slag-forming components and desulfurizers.

Substantiation and experimental check of technological peculiarities of low carbon intermediate product production. Main thermodynamic parameters of steel desulphurization reaction, presented in literature sources, were calculated for the temperature 1600 °C. However, real temperature at outlet from ASMF is significantly higher. That's why it was interesting to estimate equilibrium values of oxygen content in the metal at 0.002–0.016 % C for temperature range 1550–1750 °C (Figure 4).

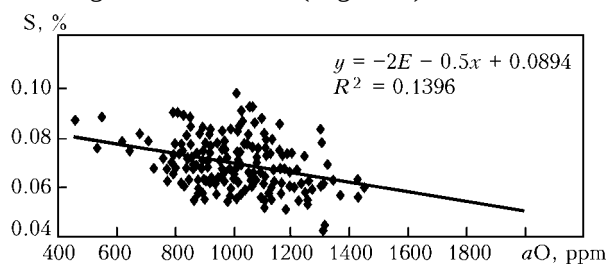


Figure 3. Metal oxidation at outlet and sulfur content in intermediate product

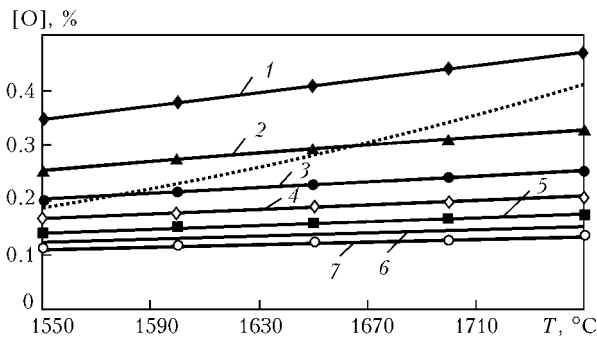


Figure 4. Dependence of equilibrium content of oxygen in iron upon temperature at different contents of carbon, %; 1 — 0.004; 2 — 0.006; 3 — 0.008; 4 — 0.010; 5 — 0.012; 6 — 0.014; 7 — 0.016; dot line shows solubility of oxygen in iron

Results of the calculation showed that as weight share of carbon in the metal reduced, equilibrium content of oxygen in iron increased, and at weight share below 0.004 % C and temperature 1750 °C exceeded oxygen solubility range in iron.

As temperature reduces to evacuation level and beginning of refining, in the ladle-furnace conditions are created for removal of carbon due to super-equilibrium (at these temperatures) amount of oxygen in the metal (presence of FeO in the form of a separate phase).

So, oxidation of the intermediate product when producing especially low-carbon steel should be sufficient for ensuring removal of carbon from initial intermediate product up to the assigned limit, carbon coming from ferroalloys (in steel deoxidation) and electrodes (in heating of steel in the ladle-furnace), and from periclase-carbonaceous lining of the steel-teeming ladle (content of carbon in the area of slag zone is 10–12 %, and in lining of walls and bottom — 6 %).

Minimum necessary amount of active oxygen for obtaining in steel 0.005 % C, its initial content in the intermediate product being different, was determined by calculation (Figure 5).

Comparison of calculated and statistical data analysis shows that real oxidation of the intermediate product at outlet from DSP-2 fluctuates within 458–1997 ppm (mean value of 200 melts is 1015 ppm).

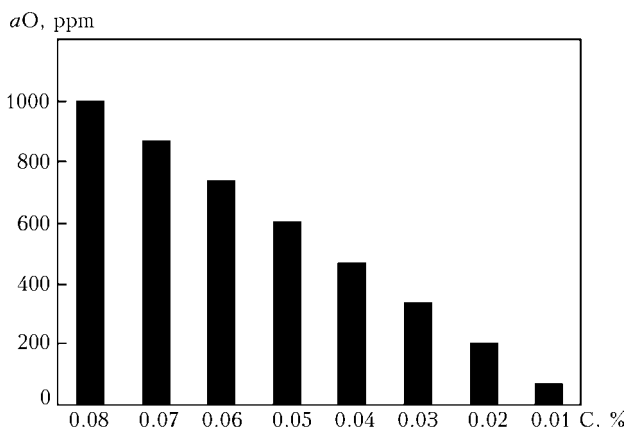


Figure 5. Necessary level of oxidation for decarbonization of steel down to 0.005 % at different initial contents of carbon

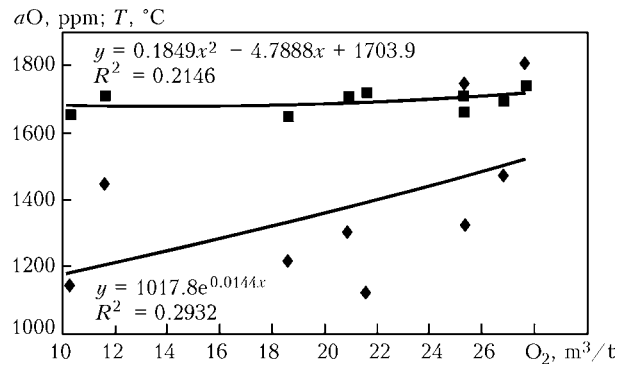


Figure 6. Dependence of temperature and degree of metal oxidation at outlet upon calculated amount of oxygen supplied for oxidation of impurities: ■ — temperature; ◆ — aO

It was experimentally established that in case of out-of-furnace processing of the intermediate product (evacuation and refining in the ladle-furnace) final content of carbon in the metal below 0.01 % was achieved, even when its initial content was 0.07–0.08 % and oxidation of the metal at outlet from the furnace was above 1100 ppm. Such oxidation of the metal at the outlet ensured as well oxidation of additional amount of carbon, which entered into the metal.

So, degree of oxidation at the outlet is sufficient (and frequently excessive) for removal of carbon in further out-of-furnace processing of the metal.

In this connection experimental melts were carried out, for which amount of oxygen necessary for oxidation of impurities was calculated, constituting difference between general consumption of oxygen in the furnace and that used for combustion of coke (content of carbon is assumed equal 95 %) and methane.

Experimental data prove that there is close inter-connection between consumption of oxygen above stoichiometry of fuel combustion reactions, oxidation, produced at the outlet, and temperature of the metal (Figure 6). It is evident that for getting high level of the metal oxidation at the outlet it is necessary to increase flow of oxygen injected into ASMF for oxidation of steel impurities (in addition to oxygen necessary for combustion of fuel).

High degree of the metal oxidation at outlet was registered in those cases, when flow of oxygen, in-

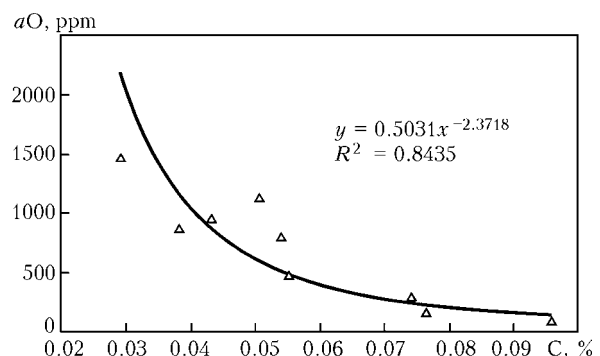


Figure 7. Level of steel overoxidation in trial melts



jected into ASMF, exceeded the one necessary according to stoichiometry of fuel combustion reactions.

Due to the amount of oxygen, which exceeds stoichiometric level, oxidation of carbon and other impurities of the metal charge occurs. At the same time achievement of a very high oxidation is undesirable because of reduction of the efficient metal yield (melting loss of iron) and reduction of the lining resistance.

So, results of the trial confirm dependences, produced by statistical processing of parameters of current production melts.

Level of the metal overoxidation was estimated (Figure 7), which was determined as difference between measured oxidation degree of the intermediate product and minimum content of oxygen necessary for decarbonization.

It is rational to remove metal overoxidation by introduction of aluminium (it is envisaged by technical instructions) or carbon-containing materials, whereby level of addition of materials for removal of oxidation should be determined by degree of the metal overoxidation. So, in case of aluminium overconsumption, potential possibility of carbon removal in evacuation is reduced (additional introduction of oxygen in one or another form is necessary), while in case of lack of aluminium excessive melting loss of silicon manganese occurs.

Theoretical and experimental investigations showed that possibilities of electric arc furnace of MMW company allow producing intermediate product fit for melting of especially low-carbon steel. It is established that for producing steel of a targeted composition oxidation degree of the intermediate

product should ensure completeness of the metal vacuum-carbon deoxidation and approach the minimum one. Possible entry of carbon into metal in ladle-furnace with ferroalloys and as a result its transition from graphitized electrodes and refractory lining of the steel-teeming ladle should be taken into account.

The results obtained were used by the authors in development of technology for further out-of-furnace processing (evacuation, deoxidation, and heating in the ladle-furnace) of the intermediate product for producing especially low-carbon steel.

CONCLUSIONS

1. It is shown that for obtaining especially low content of carbon in ready steel the intermediate product at the DSP-2 melt outlet should have high values of oxidation and temperatures.

2. It is established that for achieving low carbon content in the metal at outlet one may recommend slag conditions of the pool heating during the last period of melting and increased flow of oxygen in non-fuel ejection devices.

3. Results of experimental-commercial trial proved possibility of producing especially low-carbon steel (weight share of carbon in the metal is less than 0.01 %) under conditions of the complex ASMF-evacuator-ladle-furnace without using oxygen in out-of-furnace processing of the intermediate product.

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TECHNOLOGY OF MANUFACTURING LIGHT-WEIGHT WELDED CYLINDERS

The technology was developed at the E.O. Paton Electric Welding Institute and is aimed at solving two priority problems, namely lowering the specific weight and increasing the operating reliability. The novelty consists in the laminated structure of the cylinder wall and a rational combination of metals with different physico-mechanical properties.

The new approach to the technology of cylinder manufacturing allows using metals with a high specific strength, and, therefore, reducing the item weight by 30 to 50 %; increasing the operating reliability by minimizing the structure imperfections associated with the welds located on the cylindrical part and the nozzle; making the technology simple and accessible for implementation under the factory conditions.

There are no foreign analogs.

Pilot production batches have been made of cylinders of small and medium volume for the working pressure of 14.7 MPa (150 kg/cm²) with the strength margin of 2.6 according to the DNAOP 0.00-1.07-94 Rules. Technical documentation for cylinders manufacture has been developed.

Application. Storage and transportation of pressurized gases.

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POWER CONSUMPTION OF LIQUID-PHASE REDUCTION MELTING PROCESS

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Calculation was used to estimate power consumption in liquid-phase melting of metal oxides. It is shown that in steel melting power consumption depends upon type of metal oxides and their content in the charge.

Key words: metal oxides, melting, arc, slags, refining

One of promising directions in the field of remelting of waste metal, which forms in metallurgy and machine-building industries in production of metal products, is liquid-phase reduction melting, based on the principle of metal reduction in the molten pool [1].

At present intensive works have been carried out, directed at development of technology for producing metals and alloys from oxide materials, using method of liquid-phase reduction of oxides. Rather convincing data that confirm its efficiency were obtained [2–5].

In a number of publications [6–8] peculiarities of liquid-phase melting, interaction of phases in its process, methods of calculation of parameters, etc. are considered. At the same time issues of power consumption in this process dropped out from field of view of researchers.

The goal of this work consisted in an attempt to establish main parameters of liquid-phase melting, which exert decisive influence on power consumption.

Task of melting of any kind consists in transition of the whole processed charge into molten or gaseous state for producing metal and slag and separation thereof. Significant difference of physical-chemical properties of chemical compounds, which constitute the charge, first of all temperature of their melting, cause gradual formation of the melt.

Slag formation starts, as a rule, after melting of metal component of the charge and proceeds slower, because in majority of oxides, which constitute the charge, melting point is higher than that of iron.

Period of the charge melting is characterized by diversity of mass and heat transfer processes, stipulated by action of both heat engineering and technological factors. The former ones imply combination of physical-chemical processes that accompany melting (thermal decomposition of complex compounds; reduction of metal oxides; melting of charge and formation of liquid phases; separation of metal and slag phases). All these processes proceed in separate periods.

Peculiar feature of liquid-phase melting is combination of the processes of charge melting and reduction of metal oxides. That's why in liquid-phase reduction melting two following periods may be singled out:

- reduction period;
- soaking of metal in the course of reduction.

During reduction period processes of thermal decomposition of compounds, reduction of oxides, oxidation of impurities and carbon, and melting of the charge take place. So, duration of this period of melting is longer, due to which it exerts essential influence on power consumption.

Because of different conditions of heating and needs in power, power consumption conditions have to be determined by separate periods.

Liquid-phase melting may be performed on molten «bog» of metal and slag. These conditions exert significant influence on energy processes [9].

As a rule, one judges about economic efficiency of any melting by specific power consumption per melting of metal. In case of liquid-phase reduction method specific power consumption may be expressed in the following way:

$$q_{l-ph} = q_c + \sum_{i=n}^n \frac{G_i}{G_m} \varphi_i q_i,$$

where q_c is the specific power consumption in conventional melting, (kW·h) / kg; q_i is the specific power consumption in reduction of metal oxide, contained in the charge, (kW·h) / kg; G_i , G_m is the amount of metal oxide and metal, respectively, in the charge, kg; φ_i is the degree of oxide reduction.

It follows from this expression that power consumption of the liquid-phase melting process depends upon kind and amount of oxide-containing materials in the charge, determined by simplex $(G_i / G_m) \varphi_i q_i$. It will be always higher in comparison with conven-

Specific power consumption in reduction of different elements

Reduction reaction	Specific power consumption	
	(kW·h) / kg	kJ / kg
$Fe_2O_3 + 3C = 2Fe + 3CO$	0.856	3082
$FeO + C = Fe + CO$	0.600	2174
$Cr_2O_3 + 3C = 2Cr + 3CO$	1.479	5327
$Cr_2O_3 + 27 / 7 C = 2 / 7 Cr_7C_3 + CO$	1.386	4992
$NiO + C = Ni + CO$	0.480	1731
$MoO_3 + 3C = Mo + 3CO$	0.816	2938
$WO_3 + 3C = W + 3CO$	0.600	2160
$CuO + C = Cu + CO$	0.162	583

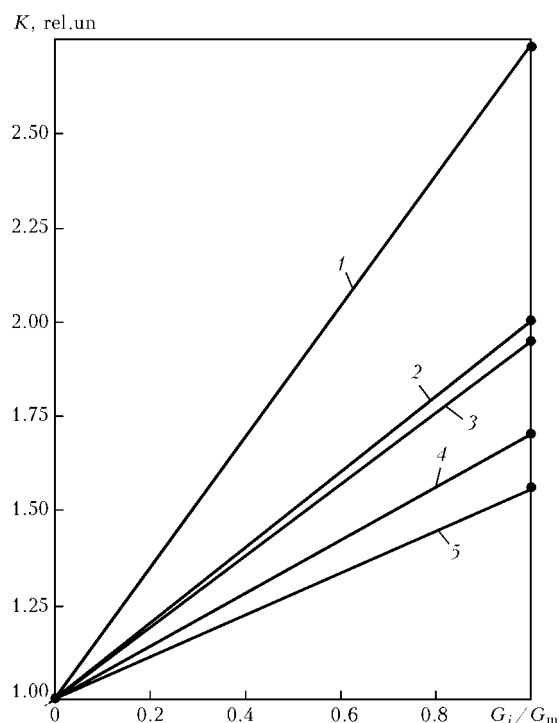


Figure 1. Dependence of change of relative power consumption increase upon content of metal oxides in charge: 1 — Cr_2O_3 ; 2 — Fe_2O_3 ; 3 — MoO_3 ; 4 — WO_3 ; 5 — NiO

tional melting due to power consumption needed for reduction of metal oxides (Table).

Analysis of the Table data shows that higher power is consumed for reduction of metal oxides, which exerts significant influence on power consumption of the melting process. For mentioned metal oxides specific power consumption varies from 0.162 to 0.1479 (kW·h) / kg. The highest specific power consumption is characteristic of chromium oxide. For the most applicable iron oxides (iron ore, scale, metallurgical slag and sludge, etc.) specific power consumption makes up 0.856 (kW·h) / kg, which exceeds the level, necessary for melting of steel in arc electric furnaces [10].

Specific power consumption in reduction of metal oxides, content of the latter in the charge being different, was calculated for the process of liquid-phase melting, allowing for a number of assumptions and data of the Table. Calculated data are presented in Figure 1. It follows from them that increase of content of oxides in the charge in liquid-phase melting increases power consumption of the process in comparison with conventional (open-hearth, electric arc, etc.) melting, whereby relative increase of energy is expressed in the form of coefficient K , equal to the ratio of power consumption in liquid-phase and conventional melting ($K = q_{l-ph} / q_c$).

The most significant power consumption is inherent to chromium and molybdenum oxides, which may be used for producing charge, containing alloying elements chromium and molybdenum. So, for example, introduction into the charge of 30 % Cr_2O_3 or NO increases power consumption of liquid-phase melting 1.52 and 1.17 times, respectively.

In Figure 2 change of power consumption in melting of alloyed steels by the method of melting in molten pool with application of metal oxides as alloying elements is shown.

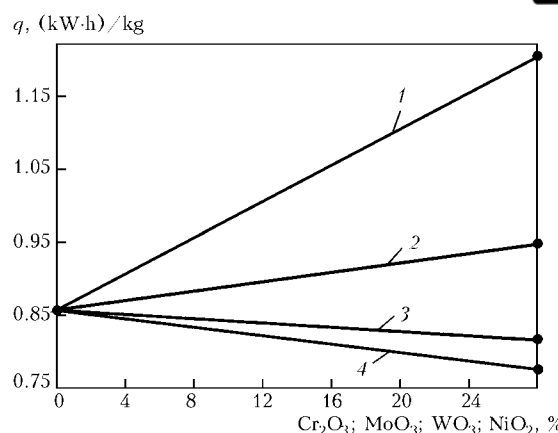


Figure 2. Dependence of power consumption in melting of steel upon content of alloying elements: 1 — Cr_2O_3 ; 2 — MoO_3 ; 3 — WO_3 ; 4 — NiO

Analysis of presented data shows that alloying of conventional steel by small additives of chromium, nickel, molybdenum and tungsten practically does not effect power consumption. In melting of steel with high weight share of chromium application of chromium oxide significantly increases power consumption of the melting process.

For example, power consumption in melting of stainless steel Kh18N10 from the charge, containing carbon steel and chromium and nickel oxides increases, in comparison with conventional melting, by 23 %. Melting of steel, containing 30 % Cr, increases power consumption of the melting process by 45 %.

It should be noted that power consumption of liquid-phase reduction melting will be always higher in comparison with conventional one. However, significant difference in cost of alloying elements in the form of ferroalloys and oxides completely covers additional power expenses in liquid-phase melting.

So, proposed dependence and data on analytical calculations allow estimating power consumption in liquid-phase melting of alloyed cast iron and steel from oxide-containing materials (primary raw materials, metallurgical sludge and slag, scale, galvanic sludge, etc.) and determining economic aspects of its application.

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THESIS FOR A SCIENTIFIC DEGREE



Shapovalov E.V. Means of Technical Vision as Feedback Element in Arc Welding Tracking Systems: Thesis on scientific degree of candidate of technical sciences in speciality «Automation of Technological Processes».

E.O. Paton Electric Welding Institute, NASU, Kiev, 2006. Date of defending is 14th of June 2006.

Thesis is devoted to development of technical vision means for systems, designed for tracking square groove butt joints. For solution of this issue TV method was proposed, based on computer processing of video images of the butt joint line, simultaneously illuminated by sources of structured and dissipated light. When a butt, with groove close to zero, is illuminated by the source of dissipated light, rays, which got into the gap between parts being welded, are practically completely absorbed. A butt joint line has on the video image a shape of a dark elongated strip. Computer processing of such video image allows getting direction of the butt joint line. Distance to the parts being welded is determined using method

of light section. Developed method allows calculating direct deviation of a welding tool from the butt joint line.

Method for selection of laser radiation, diffusely reflected from the metal surfaces being welded, is proposed, which allows normalizing bar graphs of video images of the butt joint line. It is shown that diffusely reflected laser radiation would be depolarized significantly stronger than a mirror one, which will make it possible to blank by means of polarization filter getting of mirror component into objective of a video camera.

On the basis of experimental and theoretical investigations of argon arc spectra, optical ranges of wavelengths of visible and near infrared spectrum were proposed, which are the most acceptable for operation of technical vision means of argon-arc welding ACS TP.

For the first time polarization light filter, established on the objective of video camera in optical channel of technical vision systems, based on laser location methods, was proposed for increasing signal noise ratio. Polarization plane of light filter must coincide with laser polarization plane, which allows increasing in practice signal / noise ratio.

Mathematical model for butt image recognition on video images with possibility of automatic training has been developed. It is shown that application in the model of step-by-step method for making decision on belonging of objects to the classes allows significant reducing volume of computations and using developed model in real-time systems. Peculiar feature of developed mathematical model is possibility to forecast coordinates of the butt line directly under a welding torch.