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## PECULIARITIES OF BIMETAL MATERIAL QUALITY ESTIMATION

V.Ya. SAENKO, L.B. MEDOVAR, B.B. FEDOROVSKY, N.T. SHEVCHENKO, V.M. YAROSH, V.V. ZHUKOV, V.M. ZHURAVEL, V.A. ZAJTSEV, R.V. KOZIN and A.G. REMIZOV E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Standard methods of testing sheet hot-rolled double-layer corrosion-resistant steel, as well as procedures for evaluation of quality and strength of layer joining in round bimetal products used in their production and investigation, are considered.

**Keywords:** bimetal sheets and rods, shear, tear, bend, torsion test of bimetals, tensile, impact bending, corrosion tests, macro- and microanalysis

Bimetals are widely used in various fields of engineering. Although production of various types of bimetals is mastered long ago, there are no common methods for estimating their service properties and metallurgical qualities. Authors of this article made an attempt to find on the basis of analysis of works of various authors, requirements of standards, and own experience generalizing approaches, which would simplify estimation of quality of various bimetals and at the same time increase their authenticity.

Greater part of produced in this country and in the world bimetal materials is represented by hotrolled double-layer corrosion-resistant sheets. According to GOST 10885--85, produced double-layer sheets have thickness from 4 to 60 mm, whereby the base layer is made of carbon or low-alloy steel and the cladding layer consists of corrosion-resistant steels and alloys, nickel, and Monel metal. According to GOST 10885--85 (changes 1 of 01.07.89), on agreement between a manufacturer and a customer double-layer sheets of 120 mm thickness may be produced [1].

Thickness of the corrosion-resistant layer depends upon thickness of a bimetal sheet and should correspond to that indicated in Table 1. It is checked, according to GOST 10885--85, on two specimens, one of which is taken from middle of the sheet cross-sectional template, and the other near the edge. One side of a specimen is ground over its thickness. Thickness of a cladding layer is measured using a magnifying lens or a microscope with error 0.1 mm [2].

Macrostructure of the base layer steel should not have visible (without using magnifying instruments) laminations, accumulations of expanded blisters (separate blisters of maximum 15 mm length are allowed), and soiling. In fractures laminations over the base layer are possible, if their general length does not exceed 20 mm. On requirement of a customer, in the places of double-layer steel bending laminations and cracks should not occur when strength of layer joining and ductility of the base layer are tested.

Fracture tests for determining content of fiber and bend tests of wide specimens are performed according to GOST 5521--76.

Sheets with the base layer made of steel grades 09G2, 09G2S, and 10KhSND on requirement of a customer should correspond to conditions of GOST 5521--76 in bend tests of wide specimens.

According to GOST 10885-85, for determining properties of bimetal steel two test sheets are selected from each lot. Manufactured double-layer sheets are heat treated. Kind and conditions of heat treatment are established by the manufacturer. From each test sheet a strip of 100-200 mm width is cut out, from which specimens are made (1 for tensile strength; 3 for impact bend test for each temperature; 3 for impact bend after mechanical ageing; 2 for bend test, and 3 if thickness exceeds 30 mm; 4 for testing ductility of corrosion-resistant layer; 1 for bend test of wide specimens; 1 for fracture test; 1 for shear test; 1 for checking

Sheet thickness, mm	Thickness of corrosio	n-resistant layer, mm	Shoot thicknoss mm	Thickness of corrosion-resistant layer, mm			
Sheet thickness, him	Normal	Increased	Sheet thickness, him	Normal	Increased		
4	0.7-1.1		22, 2426	3-4			
5	0.8-1.2		28, 30	3.5 - 5.0			
6	1.01.6	Not onvice and					
7	1.2-1.8	Not envisaged	32, 34, 36, 38, 40,	46	Not envisaged		
8, 9	2.0-3.0		42, 45, 48, 50, 52,		not envisaged		
1015	2.0-3.0	34	55, 60				
1621	1621 2.5-3.5 34						

Table 1. Requirements to thickness of cladding layer of bimetal sheets

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Figure 1. Schemes of bend tests of bimetal specimens with cladding layer inside (a) and outside (b)

thickness of corrosion-resistant layer; 1 for checking microstructure; for intercrystalline corrosion test (ICC) number of specimens is established according to GOST 6032--84 from each melting of corrosion-resistant layer in a lot).

Tensile test is carried out according to GOST 1497--73 on specimens with cladding layer or without it. Sheets of up to 15 mm thickness are tested on flat specimens; of 16--25 mm thickness ---- on flat and cylindrical specimens; above 25 mm ---- on cylindrical specimens. Mechanical properties of double-layer sheets should correspond to requirements of standards on a steel grade of the base layer.

Impact bend test of the base layer is performed at normal and reduced temperatures according to GOST 9454--78 on specimens with preliminary removed cladding layer, and after mechanical ageing ---- according to GOST 7268--82.

In the process of manufacturing equipment for petrochemical industry double-layer corrosion-resistant steel is subjected to various kinds of treatment (bending, forge-rolling, forming, drawing, etc.). That's why it should have sufficient ductility in cold state and be characterized by strong bond, which would ensure absence of the bimetal lamination in the process of technological operations.

Ductility of double-layer sheet steel is checked by cold bend tests carried out according to GOST 14019--80. Mandrel diameter should equal two, and for steel 10Kh2M1 ---- three thicknesses of a specimen. For sheets, having thickness above 30 mm, specimens for bend tests are brought to necessary thickness by machining, whereby one specimen is tested on the side of the cladding layer (for determining ductility of the base layer); two specimens on both sides at the depth proportional to the thickness of each layer (for determining ductility of the cladding layer). Ductility is determined with a tested layer of specimens bent outside.

Strength of joining of layers is determined with cladding layer of specimens bent inside and outside (Figure 1). In case of insufficiently high strength of bond (welding) of the layers, lamination takes place in the place of bend. However, bend tests allow obtaining only qualitative characteristic. Separation of the cladding layer from the base one usually takes place not at once over the whole length of a specimen, and it is difficult to determine the time, at which bond between layers in the bimetal is lost.

One of the most important characteristics of double-layer corrosion-resistant steel is resistance of the cladding layer metal against ICC. Manufacturing of specimens, preparation and performance of tests, estimation of propensity to ICC of the cladding layer from steel of all grades and alloy of the grade 06KhN28MDT are carried out according to GOST 6032--84, and from alloys of grades KhN65MV, KhN65MVU, and N70MFV-VI ---- according to GOST 24982--81.

For testing resistance against ICC specimens of 20 mm width and 80 mm length are manufactured from the cladding layer metal. Steel of the base layer as well as the boundary zone should be obligatory removed. After boiling specimens in 10 % solution of copper vitriol and sulfuric acid, specimens are bent at 90° in vice with radius of rounding of jaws or a mandrel not more than three-fold thickness of a specimen (but maximum 10 mm), whereby the side of a specimen adjacent to the removed base layer should be directed inside after bending. Quality of the bent specimen surface is estimated using a magnifying lens of 8and 10-magnification power. Formation of cross cracks after bending of specimens and loss of the metal sound prove propensity of the cladding layer metal to ICC.

Continuity and guaranteed strength of bond of the base and the cladding layers in a double-layer sheet are characteristics peculiar only to bimetals as structural materials. In case of the bond disturbance each layer works independently and structural properties of the bimetal change. Continuity of bonding of layers, i.e. absence of laminations in the double-layer sheet steel, is checked by the ultrasonic test method according to GOST 22727--88. Check of bond continuity of the double-layer steel of 4--7 mm thickness and steel produced without ultrasonic test is performed on each sheet. Continuity of bonding of sheets of 8 mm and higher thickness has to correspond to requirements presented in Table 2 (GOST 10855--85, change 1 of 01.07.89). ELECTROSLAG TECHNOLOGY

Class of	Condition: discontinu	al area of ities, cm <sup>2</sup>	Conditional area of maximum allowable zone	Relative co all account	onditional maximum area of ed metal discontinuities, %, not more than	Maximum allowable length of discontinuities mm <sup>2</sup>
Sileets	Minimum accounted	Maximum allowable	of discontinuities, m2	Per 1 m <sup>2</sup>	Per unit of rolled sheet area	uiscontinuities, min
01			On agreement b	etween mar	ufacturer and a customer	
0	5	20	1	1	0.3	30 (for rolled sheet of up to 60 mm thickness), 50 (for rolled sheet of above 60 mm thickness)
1	10	50	2	2	0.5	50
2	20	100	2	3	1	100
3	50	250		5	2	200

**Table 2.** Requirements to allowable area of bimetal sheet discontinuities

Joining of layers in the bimetal is quantitatively characterized by bonding strength along boundary plane of joining of the base and the cladding layers and perpendicular to it. According to GOST 10855--85, quantitative estimation of the layer joining strength of double-layer sheets is performed by shearing test with determination of shear strength over the contact plane of the base and corrosion-resistant layers. Shear strength, when determining on requirement of a customer strength of joining steel layers, having cladding coating 2 mm and more, should be at least 147 N/mm<sup>2</sup> (15 kgf/mm<sup>2</sup>).

Schemes of a specimen and a shearing test of double-layer sheets in correspondence with compulsory supplement to GOST 10885--85 are given in Figure 2. Application of other schemes of specimens is allowed, provided their width and size *b* are preserved (see Figure 2). Specimens are selected equal to the sheet thickness, allowing for machining on the base layer side. Machining of sheets above 50 mm thickness is performed on the side of the base layer till the thickness achieves 50 mm. When manufacturing specimens, it is necessary to preserve parallelism of machined surfaces for them to be able freely move without jamming in parallel guides, and in case of pressure applied from above downwards shear of the site to take place simultaneously over the whole cross-section.

For estimating quality of bimetal materials other specimens are also used in shearing tests (Figure 3). Special tear tests are envisaged for testing bond (welding) strength by applying load across the plane of joining of layers in bimetal [3, 4]. Schemes of typical specimens and tear tests of bimetal are given in Figure 4.

Quantitative estimation of bonding strength of layers in bimetal may be performed not only by mechanical separation of bimetal components over the contact surface. For quantitative estimation of quality of bond of layers in auto-vacuum pressure welding, methodology is proposed in [5] based on correlation of the degree of contamination by non-metal inclusions of the boundary zone in laminated metal with data on standard tear tests of these layers. When using such methodology for specific laminated steel, the degree of the layer joint zone purity in regard to the content of non-metallic inclusions has to be compared just ones with tear strength of joined layers. Manufacturing and testing of specimens for tear is not needed.

The main requirement to bimetal rods and rolled round bimetal billets, except guaranteed strength of the core and the cladding layer joining, is production of assigned size of the core of round or close to round form.

In ship-building industry round double-layer rods with the core from high-strength steel and cladding layer from austenite stainless steel are used for manufacturing propeller shafts of high speed ships [6]. As far as it is impossible to get strictly round form of the core in cross section of a rolled double-layer rod, its size in circle may be characterized by diameter of a circumference described around the bimetal rod core,



**Figure 2.** Scheme of specimen (a) for shearing test of bimetal sheet cladding layer and scheme for its test (b): 1 — base layer; 2 — cladding layer; S, b — thickness and width (1.5S), respectively; h = H - S

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**Figure 3.** Schemes (*a*, *b*) of bimetal specimens loaded along plane of joining for shearing tests

the biggest size of which is determined by assigned diameter of a shaft and minimum allowable thickness of the cladding layer, and diameter of the rod core circumference  $d_r$ , the smallest value of which is calculated proceeding from the necessary strength. Circumference diameter is calculated by formula  $d_r = 1.128\sqrt{s}$ , where *s* is the core section area (it is determined by planimetry of area or some other method).

In machine-building industry bimetal rods of 20--30 mm diameter with wear-resistant cladding layer from steel Kh12 or 200Kh4F of 3.5--5.0 mm thickness are used for manufacturing caterpillar pins of powerful tractors [7]. It is established that service life of bimetal pins is 7--10 times longer than that of the pins made of steel 50. Application of bimetal rods, manufactured from the compound high-speed steel R6M5 + carbon steel, for example for manufacturing taps, allows increasing their wear resistance 2--3 times and at the same time saving steel R6M5.

In contrast to rolling, deformation in hot extrusion of round bimetal profiles is axisymmetrical, due to which disturbance of the round core form does not occur. That's why hot-pressing dominates till nowadays in production of bimetal rods.

As far as because of the layer surface curvature in hot-extruded bimetal rods application of standard specimens for sheet bimetal is difficult, special specimens were developed for estimating shearing (impactpuncture) and torsion bond strength of layers [8]. Design of a specimen for shearing (impact-puncture) test is given in Figure 5. During puncturing of the core on a test machine shear of a bimetal specimen over bond surface of the components takes place. Shear strength  $\tau_{sh,p}$  may be determined as

$$\tau_{\rm sh.p} = P_{\rm p}/F_{\rm sh} \ [N/m^2],$$

where  $P_p$  is the core puncturing force, N;  $F_{sh}$  is the shear area, m<sup>2</sup>.

$$F_{\rm sh} = \pi d_{\rm c} t_{\rm b}$$

where  $t_b$  is the bond zone width, m.



Figure 4. Scheme for tear testing of bimetal specimens



**Figure 5.** Scheme of puncturing shear test of bimetal specimens:  $d_c$  — core diameter;  $d_r$  — rod diameter;  $t_{sh}$  — shearing zone width

It should be noted that technical requirements to quality of bimetal rods were developed taking into account technological peculiarities of their production.

So, according to TU 14-3-1222--83 requirements, in bimetal rods manufactured by the method of hot extrusion of hollow centrifugally cast bimetal billets, stipulated by the manufacturing technology transition zone between the cladding layer and the core is allowed, in which number of elements changes within their content in the cladding layer and the core [9]. In measurements of a cladding layer thickness, transition zone is included into the core and its thickness should no exceed 3 mm on each side. In addition, chemical composition of the core metal may have increased content of carbon (up to 0.7 %), chromium (up to 3.0 %), and vanadium (up to 0.3 %) because of partial mixing of metals during pouring of the second layer (the core metal). In connection with this acceptance of bimetal rods is performed according to the results of chemical analysis: for external (cladding) layer ---- of a ladle sample; for the core (base --- of chips taken from the middle of internal metal) layer of transverse macrosection.

Macrostructure of cladding and base layers of a bimetal rod should have dense homogeneous structure. At the same time, over the axis of a bimetal rod, produced by the method of hot-pressing of hollow centrifugally cast bimetal billets, a hole of maximum 6 mm diameter (on edges of the biggest rays) is allowed, inside which non-metallic inclusions may be.



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Figure 7. Scheme of bend tests (a) and specimen of corrosion-resistant bimetal reinforcement of 16 mm diameter after bending (b)

It should be noted that this centering hole does not worsen operation properties of bimetal rods [9].

Transversal macrosections are used for estimating thicknesses of cladding and transition layers and centering hole. Measurements are carried out on toolmaker's microscope. Thickness of cladding layer and allowances are stipulated by respective specifications (for the rods of 25 mm diameter they are  $4^{+1.0}_{-0.5}$  mm).

Strength of the bond between the cladding layer and the core is estimated by the shearing test. It should be at least 180 MPa. The test is carried out on heat treated specimens manufactured on a turning lathe. Cold hardening of the metal should be prevented. Geometrical size of a specimen is selected proceeding from the allowance on external diameter  $d_{\rm e}$  and cladding layer thickness  $t_{cl}$  according to the expression (Figure 6)

$$D_1 = d_{e \min} - (2t_{cl \max} + 2 \text{ mm});$$
  

$$D_2 = d_{e \max} - (2t_{cl \min} - 2 \text{ mm}).$$

Specimens are tested on test machines, which meet requirements of GOST 7855--74 and ensure loading of a specimen by compression force between planeparallel stops at a speed 2 mm/min. In test of specimens maximum force P is determined, which corresponds to the moment of the specimen fracture with error up to 9.8 N. Shear strength of the layer bond is calculated by formula  $\tau_{sh} = P_{sh} / F_{sh} [N/m^2], F_{sh} =$ =  $\pi D_s h$ , where *h* is the height of cylindrical belt of a shear surface equal to 2.5 mm;  $D_s$  is the separation diameter. Bond strength is calculated with error up to 1 MPa.

High prospects for expansion of production of bimetal round profile are opened in using method of electroslag cladding with liquid metal (ESC LM) of bimetal billets and their subsequent hot deformation (rolling, pressing, etc.) [10, 11].

Length of transition zone in bimetal corrosion-resistant reinforcement profile of 16 mm diameter, rolled from bimetal billet 20GS +316L of 350 mm



Figure 8. Microstructure of bimetal (×320) and its microhardness (a), distribution of Cr and Ni (b) in metal of transition zone of steels 20GS + 316L of bimetal reinforcement of 16 mm diameter; 1 --- length of studied zone; A --- content of elements: 1 --- Cr; 2 ---- Ni

diameter clad by ESC LM method, is only 6--12 µm and does not depend upon thickness of the cladding layer [12].

Quality of the cladding layer and the core bond in bimetal profile of 16 mm diameter was estimated by cold bend test of special specimens. Longitudinal macrosections having thickness equal to half diameter of bimetal profile were used. Bending was performed on a mandrel, diameter of which equaled two diameters of the profile, whereby surface of the macrosection was bent outside (Figure 7). Separations of cladding layer in the specimen after bending was not detected. Study of transition zone microstructure of bimetal profile (Figure 8) also showed high quality of the bimetal.

For wide introduction of bimetal reinforcement with corrosion-resistant cladding layer it is necessary to develop special specifications, which would regulate test of not only a bimetal profile, but also of its welded joints.

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## DEPOSITION OF COATINGS, CONTAINING REFRACTORY ELEMENTS, BY ELECTRON BEAM EVAPORATION USING «FLASH» METHOD

**K.Yu. YAKOVCHUK, V.V. SKRYABINSKY** and **L.A. KRUSHINSKAYA** E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

The process of coating deposition by EB evaporation using «flash» method is considered. Mechanism and kinetics of processes proceeding on the surface of an overheated pool and in vapor flow are described. Results of investigations of chemical composition and structure of titanium coatings containing in addition to refractory elements molybdenum, vanadium and aluminium, are presented.

**Keywords:** EB evaporation and deposition, evaporation by «flash» method, high-temperature alloys, titanium-base coatings

For state-of-the-art gas turbine building industry, in which metal multicomponent complex-alloyed alloys of wide spectrum are used, especially actual is development of new technological processes for application of protection coatings and renovation of worn components of complex configuration, for example turbine blades.

For the purpose of applying of protection coatings of various designation on gas turbine blades vacuum deposition is widely used, including EB evaporation from one evaporator (crucible) of high-temperature alloys of Ni--Co--Cr--Al--Y type with subsequent condensation of vapor flow on subject to protection components. One of the shortcomings of this method is impossibility of depositing coatings, into composition of which would be included chemical elements with big variation in values of vapor pressure in vacuum, for example, W, Mo, Ta, and Re.

For producing mentioned coatings method of EB evaporation of complex-alloyed alloys from one source is proposed, which allows depositing on a substrate coatings, which contain refractory elements [1].

Such process of vacuum evaporation of complex compounds received the name evaporation by «flash» method [2, 3], the essence of which consists in use of one evaporator with hard surface heated up to the temperature above 2000 °C, which is sufficient for complete evaporation of supplied to this surface complex alloy in the form of granules or powder.

In proposed in [1] method of evaporation in copper water-cooled evaporator with application of EB heating a molten pool from refractory metal with low vapor pressure is formed (for example, molybdenum and niobium), and evaporated alloy is supplied by separate portions in the form of little pieces or granules on the pool surface, from where it is evaporated. Melting, mixing, instantaneous overheating, and evaporation of all components of the supplied alloy take place in the evaporator. First metals with high vapor pressure get into vapor flow, then, by means of their reduction in the melt, concentration of more refractory metals increases in the vapor flow. Evaporation of refractory metal, from which evaporator pool is formed, evidently takes place continuously at constant rate.

It is convenient to study processes of evaporation of complex-alloyed alloys using mathematical models constructed similar to those described in [4--6].

Technology of evaporation by «flash» method of the alloys containing refractory elements has the following peculiarities. Firstly, mass of one portion of evaporating alloy is less than the pool metal mass to such degree that temperature, volume, and density of the pool metal in the process of dissolution and evaporation of such portion may be considered constant. Secondly, time interval from beginning of evaporation of one portion of alloy till delivery of the next one should be sufficient for necessary amount of refractory metal to pass over into the vapor flow.

Let us determine dependence of concentration of the *i*-th component of alloy in the evaporator pool  $C_i$ upon time. Rate of concentration change of the *i*-th component depends upon rate of its evaporation  $\Pi_i$ , area of the melt surface *S*, volume *V* and density  $\rho$ of the pool melt. Then, allowing for made assumptions, one may write

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = -\frac{\Pi_i S}{V\rho}.$$
 (1)

Sign minus shows that as time passes, concentration of the *i*-th component of alloy in the melt reduces.

In case of metal evaporation in high vacuum, its rate is determined by the Lengmur relation, i.e. rate of evaporation of the *i*-th component from the melt will be equal to

$$\Pi_i = \alpha_i P_i^0 f_i C_i \sqrt{\frac{M_i}{2\pi R T}}$$

where  $\alpha_i$  is the accommodation factor;  $P_i^0$  is the vapor pressure of the *i*-th component of the alloy at the melt surface temperature *T*;  $f_i$  is the activity coefficient;  $M_i$  is the molecular mass of the *i*-th component; *R* is the universal gas constant.

In such case equation (1) acquires the form

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \frac{K_i S}{V \rho} C_i, \qquad (2)$$

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**Figure 1.** Dependence of Al, Ti, V and Mo content in vapor flow upon time t in case of dumping into Mo molten pool a portion of alloy VT14 of 1.2 g mass

where  $K_i = \alpha_i P_i^0 f_i \sqrt{\frac{M_i}{2\pi RT}}$ .

At the beginning of evaporation of the next in turn portion of the melt concentration of the *i*-th component of alloy in the melt equals  $C_i^0$ . Solution of equation (2) in this case will have the form

$$C_{i}(t) = C_{0i} \exp\left(\frac{K_{i}S}{V\rho}t\right)$$
(3)

Concentration of refractory metal in the evaporator pool  $C_T(t)$  may be determined from the expression, %:

$$C_T(t) = 100 - \sum_{i=1}^{N-1} C_i(t),$$
(4)

where N is the number of the alloy components.

When analyzing equations (3) and (4) one may notice that concentration of the alloy components in the refractory metal melt exponentially reduces to zero as time passes. Within this time content of refractory metal in the evaporator pool respectively increases and approaches 100 %.

Change of concentration of the alloy components in vapor phase depending upon time may be determined as ratio of the amount of evaporated *i*-th component of the alloy to general amount of evaporated metal:

$$\left\{E_{i}(t)\right\} = \frac{K_{i}C_{i}(t)}{\sum_{i=1}^{N} K_{i}C_{i}(t)} 100 \ [\%].$$
(5)

Regularities of evaporation of alloys by «flash» method were studied on evaporation of titanium alloy VT14, which has the following chemical composition, %: Ti ---- base, 3.5--6.3 Al, 2.5--3.8 Mo, 0.9--1.9 V.

Dependences of content of the alloy elements in vapor flow upon time were determined by equation (5) under the following conditions of evaporation. As an evaporator molybdenum pool of 70 mm diameter and 5 mm depth was used. It is assumed that pool overheating above molybdenum melting point is 100 °C. In calculations activity and accommodation coefficients were assumed equal 1. Mass of a portion of evaporated alloy equaled 1.2 g (Figure 1).

One can see from the Figure that at initial moment of the alloy portion evaporation content of aluminium in vapor flow was about 80 %, and titanium about 20 %. Within 1 s the whole aluminium manages to evaporate, while content of molybdenum in vapor flow increases, and of titanium increases up to 90 %. Then titanium content exponentially reduces down to zero, while molybdenum content respectively increases up to 100 %. As far as vanadium vapor pressure at evaporation temperature is close to titanium vapor pressure, its evaporation from the melt proceeds in similar way, but vanadium content in the alloy is 60 times lower. In our case evaporation of aluminium, titanium and vanadium from liquid molybdenum finishes in 6 s after beginning of the evaporation process.

Experiments connected with study of evaporation of alloy VT14 were carried out on EB unit UE-150 equipped with a mechanism for discrete supply of alloy portions into the evaporator. Mass of a portion was controlled with an error  $\pm 5$  %. Vapor flow was deposited on titanium substrate, which was preliminarily heated up to 650 °C. At the beginning of the experiment molybdenum molten pool was formed in copper water-cooled evaporator, and then portions of alloy VT14 were dumped into it in equal time intervals. Thickness of deposited coating was 80--100  $\mu$ m.

For chemical composition of vapor flow and, therefore, of the condensate to correspond to chemical composition of the alloy being evaporated, time interval between supply of the alloy portions into the evaporator should be selected in such way that within one cycle necessary amount of refractory metal be evaporated.

The experiments showed that for selected power of the evaporation EB gun beam average content of molybdenum in coating 2.9–3.2 % may be achieved if time interval between dumping of 1.2 and 0.2 g portions of alloy VT14 is 6 and 1 s, respectively.

Change of intensity of vapor flow from the evaporator may be assessed by change of pressure in the vacuum chamber during evaporation process. In Figure 2 curves of residual gas pressure values in the evaporator chamber are given during dumping into the molybdenum pool of the alloy VT14 portions of 1.2 (Figure 2, a) and 0.2 g mass (Figure 2, b).

Presented curves have saw-tooth shape. Frequency of peaks corresponds to frequency of dumping of the alloy portions into molybdenum pool. Sharp reduction of vacuum level after beginning of evaporation of next in turn portion is stipulated by maximum intensity of vapor flow at the time when, simultaneously with Ti, V and Mo, Al is evaporated at high rate. In 1 s (Figure 2, *a*) vacuum improves, which corresponds to termination of the aluminium evaporation process.

Then within 4 s pressure curve gently slopes, which is, evidently, connected with evaporation of Ti, V, and Mo. Before next in turn peak fall of 1 s duration is seen, during which vapor flow mainly consists of evaporating at low rate molybdenum. Such explanation of behavior of the curve in Figure 2, a matches well results of calculations presented in Figure 1.

Fluctuations of pressure in the evaporator chamber in Figure 2, *b* have the same character as in Figure 2, *a*, but differ in frequency and amplitude. Frequency of peaks on the curve in Figure 2, *b* is 6 times higher than in Figure 2, *a*, which corresponds to 6-fold frequency increase of dumping of the alloy portions. Amplitude of pressure fluctuation of residual gases in

ADVANCES IN LECTROMETALLURGY the evaporator chamber on the opposite reduces due to reduction of mass of the evaporated alloy portion.

Microstructure and chemical composition of coatings were studied on cross-sections using scanning microscope CamScan4D equipped with attachment INCA 200 for X-ray spectral microanalysis. Chemical composition was determined both locally (size of the probe was approximately  $1-2 \mu m$ ) and in scanning mode over thickness of the coating.

Fragment of the microstructure and change of chemical composition over thickness of coatings are shown in Figure 3. As one can see from Figure 3, a, coating produced in explosion evaporation of the alloy VT14 portions of 1.2 g mass have lamellar structure in the form of alternating light and dark strips of about 2 µm thickness, whereby light layers are characterized by increased content of elements with higher atomic number, in this case molybdenum, mass share of which in light layers achieves 4.5 %, with minimum 1.5 % in dark layers. Amount of aluminium varies from 2.0 to 7.5 wt.% in dark layers. To reduction in the coating of the amount of aluminium and molybdenum corresponds increase of titanium from 75 to 90 wt.%. Mass share of vanadium makes up about 1 % over the whole coating thickness.

On the basis of microstructure analysis and distribution of elements over thickness of the coating, process



**Figure 2.** Dependence of pressure P values of residual gases in vacuum chamber upon time in case of dumping into molybdenum molten pool of alloy VT14 portions of 1.2 (a) and 0.2 (b) g mass

of evaporation of the alloy VT14 portion by «flash» method may be presented as follows. Beginning of the alloy portion evaporation should be considered the point, at which starts to increase content of aluminium in the coating. It is the darkest strip in the microstructure. At this time sharp reduction of molybdenum content takes place. Then, by means of reduction of mass share of aluminium in vapor flow its amount in the coating reduces, while titanium



**Figure 3.** Fragment of coating cross-section microstructure (*a*) and change of chemical composition over thickness  $\delta$  of coating (*b*) deposited by dumping into molybdenum molten pool of alloy VT14 portions of 1.2 g mass



**Figure 4.** Fragment of coating cross-section microstructure (a) and change of chemical composition over thickness of coating (b) deposited by dumping into molybdenum molten pool of VT14 alloy portions of 0.2 g mass

content at the same time increases, whereby microstructure in Figure 3, *a* gradually gets lighter. At last, when evaporation of a portion of the alloy approaches its end, content of molybdenum in the vapor flow and, respectively, in the coating increases. One can see well Mo-enriched light strips on the microstructure.

Obviously, it is possible to ensure deposition of coatings with «quasimicrostratified» structure, in which distribution of chemical elements will be practically homogeneous, by reduction of the alloy portion mass, evaporated using «flash» method, and by variation of substrate temperature in the process of deposition (and temperature of subsequent heat treatment).

In Figure 4, a fragment of microstructure and distribution of chemical elements in the coating deposited by evaporation of the alloy VT14 portions of 0.2 g mass are shown. 6-fold reduction of the portion mass in comparison with previous experiment, results of which are presented in Figure 3, ensured deposition of the coating layer with composition, which corresponds to chemical composition of alloy VT14, whereby microstructure and distribution of chemical elements look rather homogeneous.

### CONCLUSIONS

1. Main regularities of evaporation by «flash» method of multicomponent alloys, containing low-melting

and refractory elements with different vapor pressure in vacuum, are studied using calculation and experimental methods.

2. Evaporation of alloy VT14 demonstrated possibility of using EB evaporation by «flash» method for deposition of materials and coatings containing chemical elements, vapor pressure of which differs by several orders, whereby correspondence between calculation and experimental data was registered.

3. By evaporating small portion of alloy (in our case of 0.2 g mass of VT14 alloy) one may obtain chemically and structurally homogeneous coatings.

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# PECULIARITIES OF TECHNOLOGY FOR PRODUCING STRIPS WITH AMORPHOUS STRUCTURE BY SPINNING METHOD WITH APPLICATION OF PLASMA HEATING

V.A. SHAPOVALOV, G.F. TORKHOV, Yu.A. NIKITENKO and O.V. KARUSEVICH E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Influence of technological parameters on formation of rapidly hardenable strip is considered. Results of experimental studies are given, and peculiarities of the plasma-arc installation operation for producing strips with amorphous structure are described.

**Keywords:** amorphous structure, spinning, plasma heating, rigidity of structure

For producing alloys with amorphous structure by the spinning method a metal is molten in a crucible and then released from the melting space through a small hole under action of gravity and pressure of gas, which acts on surface of the liquid metal. Then a jet of molten metal contacts with surface of a rapidly rotating cooler-disc. After contact with the disk the melt is quickly cooled, solidified, forms a continuous strip, and then it is thrown off under action of centrifugal force. This technology ensures continuous production of a strip with amorphous structure at speed 10--50 m/s.

The main points in this process are contact of a jet with a rotating disk and formation of the strip, whereby on the disk a minimum stationary pool of molten metal is formed, in which metal may be considered as intermediate state between the melt and a solidified strip, viscosity of which being changed not stepwise, but gradually. Geometry, structure, and other characteristics of produced strips are determined by a combination of technological factors.

In the E.O. Paton Electric Welding Institute of the NAS of Ukraine an installation was designed and commissioned for producing amorphous and microcrystalline metals and alloys by application of plasmaarc heating and hardening from liquid state (the spinning method) [1].

Instead of a quartz crucible in the form of an ampoule (Figure 1) [2], a water-cooled metal crucible with changeable ceramic nozzle was used. In the process of plasma-arc melting skull is produced, which excludes interaction of molten metal with material of the crucible. Application of changeable ceramic nozzle did not solve the issue of a molten metal contact with ceramics, but allowed significant reducing the contact area and ceramics mass.

Application of optimum angles of inclination of internal sides of the nozzle and size of the shape-forming slot made it possible to ensure stable temperature of metal in the pouring area and speed of its efflux on the cooler-drum, and compensate thermal expansion of a ceramic nozzle-insert.

From design viewpoint the crucible is a melting unit, which is attached to the main chamber not rigidly, but through a resilient tight seal and a mechanism for adjustment of parallelism of clearance between the drain nozzle and surface of the cooler. In spinning method clearance between the nozzle edge and the cooler surface may vary within wide range ----from several millimeters in case of pouring through



Figure 1. Installation for spinning with quartz ampoule and UHF generator

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Figure 2. Feeding of melt on cooler-disk (diameter of outlet opening is 0.8 mm)

the dosing nozzle with cylindrical opening (Figure 2) [3] to shares of a millimeter in case of using a flat slot.

So, we may assume that when cylindrical outlet opening is used, relatively narrow strips are produced, and clearance between the drain nozzle and the coolerdisk does not matter much. For wider strips an opening of rectangular section with higher ratio of the sides is used. In the process of manufacturing wide, good quality strips of required size, an important factor is stability of maintaining assigned clearance between the drain nozzle and surface of the cooler-disk, i.e. it is necessary preserve stability of parameters of the intermediate pool.

Process of a strip formation on the installation with plasma-arc heating, using spinning method, is shown in Figure 3.

Study of the strip formation process showed that for producing a strip of homogeneous width and thickness formation of a stable pool that acts as a local reservoir, from which a strip is continuously pulled out, is necessary in the place, where jet gets on surface of the disk.

Determination of thickness of produced strips, depending upon technological parameters, is of interest. It is found that thickness of a strip is calculated by formula

$$d = k \frac{a_{\rm s}}{v_{\rm d}} \frac{\sqrt{2P_{\rm m}}}{\rho}$$

where *k* is the coefficient of proportionality;  $a_s$  is the width of the nozzle slot;  $v_d$  is the speed of the disk;  $P_{\rm m}$  is the pressure above the melt;  $\rho$  is the melt density.

Coefficient k depends first of all upon the clearance, temperature of the melt, its viscosity, coefficient of surface tension, and level of the melt overheating [4].

Local changes of width of the formed strip occur because of fluctuation of the coefficient of heat transfer from the melt to the cooler, the reason of which may be dust particles, which get on the melt and the disk from surrounding atmosphere, products of the melt reaction with environment, gas bubbles entrapped into the space between the melt and the disk, and imperfection of the disk surface. In addition, periodic changes of the strip thickness, connected with fluctuations of the pool as a result of pressure fluctuation in it and vibrations, are possible.

Important part in stabilization of the strip production process is played by choice of the parameters (sizes of the slot) and shape of the nozzle edge, which forms and maintains intermediate pool. In certain cases additional dependences are established between separate geometric parameters of the nozzle and clearance between the nozzle and the disk.

In [5] dependence of clearance between the nozzle and the disk upon width of the slot is shown. Size of the slot may constitute 0.1--1.0 of the slot width, whereby the slot should be located perpendicular to direction of the disk rotation, and its thickness should be  $\approx$  0.3--1.0 mm.

Taking into account the fact that stability of clearance between the drain nozzle and the cooler-disk should be guaranteed by rigidity of the structure, it is rather difficult to determine change of linear di-



Figure 3. Process of melt spinning on installation with plasma-arc heating



Figure 4. Scheme of clearance change under action of excessive pressure and temperature



mensions of the ceramic ampoule  $\Delta$  and clearance *h* (Figure 4) under action of temperature and excessive pressure, especially in the area of high temperatures.

Application of optical monitoring instruments does not guarantee accuracy of measurements because of heat-up of the ampoule in cold atmosphere resulting in formation of boundary layer with changed optical properties, which cause refraction of light and distortion of the values obtained.

The contact method causes error in the form of heat loss associated with reduction of the nozzle temperature. In addition, rather limited number of instrument types may operate at high temperatures with sufficient accuracy.

Application of a ceramic crucible causes its significant expansion during heating. As far as physical properties of ceramic items are not stable, correction factors may be applied to linear-thermal expansion coefficient of only one set of crucibles.

In presented equipment influence of linear-thermal expansion coefficient is significantly reduced due to reduction of the ceramics volumes. Application of a rigid metal structure allowed exact prediction of the vertical position change. In such form correction factor remains stable for a long time and instead of the constant check requires only for a single measurement after assembly of the equipment.

As far as hot trials are difficult and influence of linear expansion of ceramics in such form is negligibly small, it is sufficient to determine displacement of the crucible under action of excessive pressure in the chamber in order to check slump of the melting unit (Figure 5). Measurement was performed by micrometer of the clock type rigidly attached to the support,



**Figure 5.** Diagram of dependence of crucible slump under action of excessive pressure

error of which was 0.01  $\mu$ m, mounting seat of the drain nozzle being sealed and excessive gas pressure *P* similar to the working one being created in the chamber. Determination of the correction factor made it possible to maintain clearance more accurately and stabilize the process.

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## COMPUTER SYSTEM TO DESIGN TECHNOLOGIES FOR REPAIR AND HARDENING OF METALLURGICAL EQUIPMENT PARTS

**Purpose.** The system is intended to design technologies for repair and hardening of metallurgical equipment parts by the electric arc surfacing methods. The computer system is based on the experience accumulated by 16 metallurgical plants in the field of surfacing. It allows design of a surfacing technology for 350 different parts (selection of surfacing consumables, methods, conditions, equipment, etc.) at a level of a highly skilled specialist. The system operation result has the form of a process sheet.

**Application.** The system can be used at metallurgical enterprises. It is intended for welding technologists working at a plant engineering department.





Contacts: Prof. Makhnenko V.I. E-mail: d34@paton.kiev.ua

## **EXPERIMENTAL INVESTIGATION OF EROSION OF COPPER WATER-COOLED ANODES**

V.A. SHAPOVALOV, G.A. MELNIK, O.M. VISLOBOKOV, K.A. TSYKULENKO, M.S. PRIKHODKO and D.M. ZHIROV E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Experimental investigations of erosion of copper water-cooled anodes in argon at different values of arc current in direct-action plasmatron were carried out. Approximate service life of these electrodes was determined and recommendations were issued for further investigations to create a powerful long operational life arc heating sources.

**Keywords:** arc discharge, copper water-cooled anode, erosion, operational life

Scientific publications contain since 1960s rather much data on erosion of copper anodes used under peculiar operation conditions with arc heat sources of various designs, whereby level of specific erosion of copper anodes varies from  $4.50 \cdot 10^{-8}$  [1] to  $1.68 \cdot 10^{-3}$  g/C [2].

Minimum values of specific erosion were obtained in investigations of indirect action plasmatrons, in which anode is represented by a copper output nozzle with forced movement of the arc tie-up spot. Publications [3, 4] were devoted to study of erosion of the anodes of similar design. Generalized data, contained in [4], show that specific erosion of copper tubular anodes in air and hydrogen atmosphere at arc current values 30–1000 A is  $1 \cdot 10^{-7}$ – $1 \cdot 10^{-6}$  g/C. Due to this authors drew conclusion that mean specific erosion of copper electrodes of such design does not depend in first approximation upon arc current.

In opinion of some researchers [2], maximum values of specific erosion of copper rod anodes with constricted discharge (Figure 1) don't meet erosion stability requirements established for electrodes of arc heat sources. That's why of interest is such mode of anode operation with diffusion tie-up of arc (Figure 2), when constricted anode spot is not formed on the electrode surface.

For the purpose of developing powerful arc heat sources with long operational life the task was assigned to study erosion of copper electrodes (anodes) in diffusion mode of arc burning in argon.

Tests were carried out on the installation consisting of the air-tight chamber (Figure 3). In its upper part water-cooled electrode assembly with copper electrode-anode was installed on the insulator (Figure 4), which was connected to positive pole of power source. In the chamber bottom water-cooled bottom plate was placed, which was connected to negative pole of the power source. Tungsten rod with addition of yttrium, mounted on the bottom plate, was used as hot cathode. Argon was passed through the chamber within 3--5 l/min. Such flow of argon in combination with hot tungsten cathode ensured protection of electrodes against oxidation and diffu-



Figure 1. Electric arc in constricted discharge mode: 1 --- constricted anode spot; 2 --- arc column; 3 --- cathode spot

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Figure 2. Electric arc in diffusion burning mode: 1 --- diffusion anode spot (2 and 3 are the same as in Figure 1)

sion mode of the anode spot tie-up at the currents 150--400 A and arc length 15--30 mm. Arc voltage was 25--30 V.

Copper electrode erosion at any time interval was estimated by difference of the volumes of forced out by it liquid from a special vessel with its subsequent recalculation into the mass. Control weighing of copper electrode before and after tests showed that relative error of this method didn't exceed 6 % of total erosion. Tests of electrodes were performed at arc current 150, 300 and 400 A. For each current mode a new electrode was used. Total time of tests for each electrode at various values of arc current was: 150 A --- 250, 300 A --- 232, 400 A --- 75 h.

In Figure 5 copper electrode after tests at arc current 400 A is shown. Diagrams of dependence of total and current specific erosion of electrodes upon time of tests are given in Figures 6 and 7.

Approximation of diagrams of the anode wear dependence upon time of operation at various values of arc current represents in first approximation a collection of straight lines with different angles of slope to



Figure 3. Installation for investigating of erosion of copper electrodes



Figure 4. Appearance (a) and scheme (b) of tested copper anode





Figure 5. Appearance of copper anode after testing in argon at arc current 400 A



**Figure 6.** Erosion *m* of copper anode at various values of arc current: 1 - 400; 2 - 300; 3 - 150 A (here and in Figure 7 solid line represents experimental data, dash line represents assumed values)

abscissa axis (see Figure 6). Angle of slope depends upon the arc current value.

Diagrams of dependence of current specific erosion values of anodes upon time of operation (Figure 7) have clearly pronounced minimums, parameters of which coincide with calculated optimum thickness of a copper electrode in the zone of location of active spots (10--12 mm) for selected values of current in the arc. It is also confirmed by steepness of specific



**Figure 7.** Specific erosion G of copper anode at various values of arc current (1-3 are the same as in Figure 6)

erosion curves. The initial thickness of the anode wall being 20 mm, significant reduction of erosion was registered by means of its wear down to optimum thickness. After optimum thickness of the wall and, therefore, optimum conditions of its cooling is achieved, specific erosion increases insignificantly up to burn-through of the anode.

Data obtained allow determining optimum thickness of copper anode wall in the arc tie-up zone and modes of its cooling, and predict operational life of the anode.

#### CONCLUSIONS

1. It is shown that mean specific erosion of copper water-cooled anode during operation in diffusion mode of the arc tie-up in atmosphere of argon at arc current values 150--400 A does not exceed  $5 \cdot 10^{-7}$  g/C, which guarantees operational life of several hundred hours.

2. It is established that specific erosion of anode depends upon accuracy of maintaining of the mode parameters, which ensure diffusion mode of arc burning, and this has to be taken into account when developing heat sources for real conditions of operation.

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## INFLUENCE OF MANGANESE ON PROPERTIES OF LANTHANUM-ALLOYED CHROMIUM ALLOYS

A.P. RUDOJ, L.P. ZHUCHENKO, V.Kh. MELNIK and A.P. PORTNOV Institute of Material Sciences Problems, NASU, Kiev, Ukraine

Ingots of alloys of high-purity chromium with manganese and lanthanum are melted in a furnace with copper mould by induction method. Hardness and temperature of brittle transition of these alloys are studied. It is shown that influence of manganese in alloys depends to great degree on content of lanthanum and conditions of production of ingots.

**Keywords:** chromium, manganese, lanthanum, alloy, hardness, brittle transition temperature

In this work study of influence of small quantities of transition metals on mechanical properties (hardness HV and brittle transition temperature  $T_{\rm b}$ ) of high-purity chromium alloyed by lanthanum is continued.

Earlier influence on the Cr–La alloy of metals of the VIII group of periodic table (iron, cobalt, and nickel), which have close to chromium values of atomic numbers and dissolve in it within 0.6 wt.% was studied [1].

For further study of transition metals manganese was selected. In contrast to Fe, Co and Ni, Mn dissolves well in Cr. So, at 1310 °C its solubility makes up  $\approx$  70 wt.% [2]. On one hand, it is located in the periodic table between chromium and mentioned metals, and on the other hand it enters into the VII group like rhenium, which has similar chemical properties and influence of which on ductility of refined by lanthanum high-purity chromium is studied in [3].

Addition of manganese to chromium (several percent) causes drastic embrittlement of the latter [4, 5]. At the same time these alloys, especially provided they contain 40--60 wt.% Mn, are susceptible to formation of the surface layer subject to crack formation because of active absorption of nitrogen by them [6].

In [7] data are given on influence of alloying additions of manganese on elastic properties of chromium (modulus of shear G and Young's modulus E), and their influence on ductility is considered. It is noted that there is reverse relationship between change of the brittle transition temperature and change of the modules of elasticity and, respectively, strength of interatomic bond, which they represent.

So, increase of manganese content in chromium from 0 to 40 wt.% causes reduction of G from  $1.1 \cdot 10^5$ to 0.7  $\cdot 10^5$  Pa, and E ---- from 2.7  $\cdot 10^5$  to 1.7  $\cdot 10^5$ , while T<sub>b</sub> noticeably increases.

It is registered that parameter of crystalline lattice of chromium after its alloying by manganese starts to significantly increase from  $\approx 25$  wt.% of the latter, and if the share of manganese is less the said parameter remains practically unchangeable.

The authors assume that the reason of worsening of the temperature of cold brittleness of chromium in case of its alloying by metals of the VII group, in particular manganese, is a not completely clarified character of change of a number of physical characteristics like dislocation structure, energy of stacking fault, solubility of interstitial elements, degree of twinning deformation development, etc.

Manganese, having comparatively weak chemical affinity to interstitial elements, can not, in contrast to lanthanum and other rare-earth metals, refine chrome matrix of these impurities. Contained in chromium carbides are peculiar for extremely high propensity to segregation on grain boundaries, where they are located in the form of lamellar precipitates and cause drastic embrittlement of chromium, while alloying of the latter by lanthanum does not allow changing morphology, shape and location of carbides and, as a result, affect ductility. That's why microadditions of manganese were introduced as the third component into binary Cr--La alloy for checking possibility of positive action on distribution in chromium structure of, first of all, such inclusions as carbides.

Ingots for the study were molten from high-purity charge materials. The alloys were based on electrolytic, refined in hydrogen, commercial chromium of ERKh grade with total content of interstitial element impurities at the level  $\approx 0.017$  wt.%, comprising besides 0.005 % N, 0.005–0.006 % C, 0.005 % O, sulfur, silicon and iron. Melting was performed in an induction furnace with copper water-cooled mould. Produced ingots had diameter 34 mm and mass up to 1.5 kg.

As far as chromium has rather high thermodynamic affinity to interstitial elements (oxygen, nitrogen and carbon), for preventing their getting into the alloys before each melting deep vacuum scavenging of the working space of the furnace down to  $(1.33-2.66)\cdot10^{-3}$  Pa and vacuum-heat treatment of the charge at 200–250 °C and vacuum not less than  $6.65\cdot10^{-3}$  Pa were performed, whereby oxygen, nitrogen and carbon, adsorbed by walls of the degassing chamber and surface of the charge materials, were removed.

Argon, which corresponded to commercial purity (GOST 10157–79), was used as protection environment in first series of meltings; in second series of meltings the same argon was used, but after it was additionally cleaned of impurities of moisture and foreign gases by passing it at 600–750 °C through special reaction columns with active metals (Ca, Ti–Zr alloy).

From produced ingots specimens were made according to standard technology for measuring temperature of cold brittleness and hardness. Values  $T_b$  were determined during three-point bend tests of flat specimens, having size  $1 \times 4 \times 30$  mm, subjected to grinding and subsequent electrolytic polishing at speed of movement of the rod with bending blade 20 mm/min. Tempera-

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VACUUM-INDUCTION MELTING °ſ  $T_{\rm b}$ 60 0 0 0 40200.20.3 040.1 Mn. wt.%

Figure 1. Influence of manganese on  $T_{\rm b}$  of cast alloy Cr-La (commercial argon)



**Figure 2.** Influence of manganese on  $T_{\rm b}$  of cast alloy Cr--La (highpurity argon): 1, 2 --- 0.75 and 0.50 wt.% (in charge), respectively

ture of transition from brittle to ductile state was determined as mean value between minimum temperature, at which a specimen was bent at 90° without failure, and the maximum temperature, at which it failed. The number of specimens for these tests being selected in such way that maximally reduce this range.

On basis of the test results graphic dependences of *HV* and *T<sub>b</sub>* upon content of lanthanum and manganese in cast alloys of high-purity chromium were constructed. Content of manganese in the charge varied from 0 to 0.5 wt.%, and content of lanthanum in the charge of one group of alloys was 0.5 and in the charge of the other group 0.75 wt.%, which, taking into account its assimilation by chromium, in reality made up, approximately, 0.30 and 0.45 wt.% in molten ingots.

In Figure 1 the curve of dependence of T<sub>b</sub> on content of manganese in alloys Cr--La--Mn (0.5 wt.% La was introduced into charge of the alloy) molten in commercially pure argon and without using degassing operation before bleeding-in shielding gas, i.e. under so called «dirty conditions», is shown. The alloys are characterized by increased value  $T_b$ , which proves their insufficient ductility. So, at 0.12 wt.% Mn temperature of cold brittleness exceeds 60 °C, and further increase of its content within studied concentration range practically does not effect its value. Such properties are, evidently, stipulated by increased content of interstitial element impurities in molten ingots.

The curves, which represent influence of manganese on  $T_{\rm b}$  of the alloys of high-purity chromium, ingots of which were produced under «clean» conditions, i.e. using operations of the charge degassing before melting and argon, which passed additional cleaning in special installation, as shielding environment, look differently (Figure 2).

So, alloys doped by 0.75 wt.% La (curve 1) have higher values of cold brittleness temperature in compari-



Figure 3. Influence of manganese on hardness of cast alloy Cr-La (0.5 wt.% La in charge)

son with the ones, into which 0.5 wt.% La was introduced (curve 2). Most probably, it is explained by the fact that in the first group of alloys excessive lanthanum is present, i.e. not bound by nitrogen and oxygen, precipitated in the form of interlayers over grain boundaries, which is the reason of a certain loss of ductility.

When comparing curves presented in Figure 2, one can note that influence of micro-additions of manganese on ductility of Cr--La alloys is more pronounced in the alloys, which contain more lanthanum, whereby by means of increase of manganese content in both groups of alloys  $T_{\rm b}$  first increases, achieves maximum at  $\approx 0.25$  wt.%, and then reduces and takes on the same values at 0.5 wt.% Mn. Taking into account shape of produced curves, it is possible to assume with high degree of probability that when manganese content exceeds 0.5 wt.%, alloys of high-purity chromium with 0.75 wt.% in charge will be more ductile than with smaller amount of lanthanum. For a time being we don't have satisfactory explanation of this phenomenon.

In Figure 3 graphic dependence of hardness of cast low-alloy alloys of the system Cr--La--Mn on manganese content is shown. Over the whole range of concentrations monotonous reduction of hardness and, therefore, strength is registered, which corresponds to the results of  $T_{\rm b}$  measurement of the alloys produced under «clean» conditions, but does not explain why ductility of alloys of the system Cr--La--Mn increases by means of manganese content increase, instead of reducing like in alloys Cr--Mn. It is possible to assume that reduction of  $T_{\rm b}$ should be connected with possible change of the character of the cast alloy failure from inter- to trans-crystalline one, which, evidently, does not happen in alloys of the system Cr--Mn. However, for confirmation of this hypothesis it is necessary to carry out further studies. In addition, of interest may be data on  $T_b$  of the alloys, which contain more than 0.5 wt.% Mn.

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## STRENGTH AND PHYSICAL METALLURGY OF BRAZED JOINTS OF CAST NICKEL ALLOY ChS70 VI

I.S. MALASHENKO<sup>1</sup>, V.V. KURENKOVA<sup>1</sup>, A.F. BELYAVIN<sup>1</sup>, L.V. CHERVYAKOVA<sup>2</sup> and A.N. SHELKOVOJ<sup>1</sup>

<sup>1</sup>Research Center Pratt&Whitney Paton, Kiev, Ukraine <sup>2</sup>E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Efficiency of phase compositions of brazing alloys used in repair brazing of cast alloy ChS70 VI has been considered. Interrelation between the structure of brazed joints and technological parameters of the brazing process was studied. Satisfactory level of strength of brazed joints of alloy Ch70 VI at uniaxial tension under 20 °C conditions is obtained. Quality factor of the joints is 85-92 % of mean value of the base metal strength. High quality of joints has been attained by fine-grain structure of the seam metal, complete wetting and dissolution of filler particles by a brazing alloy, minimum depth of chemical interaction (erosion) of mated surfaces, and rational heat treatment of ready joints in vacuum in compliance with standard mode for the alloy ChS70 VI.

**Keywords:** nickel alloy ChS70, repair brazing, boron-containing brazing alloy, brazed joint, strength, microstructure, carbide phase

The process of argon arc welding is lately being replaced by repair brazing of nickel high-temperature alloys (HTA) in renovation of components of hot portion of aviation turbines and commercial (power generation) gas turbine installations [1--6]. It concerns, first of all, guide vanes of turbines and combustion chambers, which have a system of perforation openings that ensure film cooling of turbine blade surfaces and combustion chamber walls. Irreversible geometric changes of separate units and disturbance of mounting seats take place in welding because of high metal temperature. Welding causes many cases of «slamming» of perforation openings and the need of their restoration by their piercing with laser beam.

Hazardous residual thermal stresses and undesirable changes of geometrical shape of renovated components don't take place in brazing. Contact-reaction brazing of nickel HTA is equivalent by its technological possibilities to argon arc welding and ensures necessary physical-mechanical properties of the joints [2].

Expediency of using repair brazing of items, manufactured from nickel (cobalt) HTA, is determined by high cost of such items. Their replacement for new ones is connected with irrational additional expenses.

Application of repair brazing instead of argon arc welding with tungsten electrode of components of HTA is based on the effect of activated diffusion interaction between particles of a composite brazing alloy and surfaces to be joined in local areas of the parts, which is the result of contact melting of surfaces of particles and walls of the part by low-melting component of the brazing alloy and further heat treatment of a brazed joint at the temperature, which is by 100--120 °C lower than maximum temperature of isothermal brazing [7]. Duration of heat treatment is 1--2 h and more and temperature is 1050--1120 °C. Mentioned temperature values should be coordinated with conditions of standard technological operations (annealing) of specific items from respective alloys.

The main designation of the repair brazing process and subsequent heat treatment of a renovated component consists in bringing the seam metal structure nearer to microstructure of the treated item metal. That's why temperature of homogenization annealing of a renovated component should be elevated before repair brazing up to the temperature of the isothermal brazing process.

As new HTA are introduced into commercial use, new special repair materials have to be developed ----brazing alloys and respective fillers. Materials of a brazed seam should have high strength, be resistant to impact loads, and their microstructure should correspond to the greatest degree to the metal structure of a item to be renovated. The latter is ensured by application in repair of the components of close chemical composition [2, 4]. It is advisable to use brazing alloys with maximum possible similarity of their composition (at least of the filler) with chemical composition of the repaired component. It is achieved by introduction into commercial brazing alloys of powders of the alloys being brazed in the form of fillers.

Alloy ChS70 VI relates to the second generation of nickel HTA used in state-of-the-art power engineering and gas turbine building industry. It is peculiar for relatively low level of short-term strength at normal temperature and satisfactory high-temperature strength (creep resistance) at working temperatures 750--900 °C. The alloy preserves initial level of short-term strength within temperature range 20--800 °C. Hardening of the alloy is ensured by complex doping with tungsten, aluminium, titanium and carbon, which provides necessary combination of solid solution and dispersion matrix hardening. Increased content (up to 16 wt.%) of chromium provides the

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Grade of alloy,	Mass share of elements, %												
alloy	Со	Cr	В	С	Si	Fe	AL	Nb					
Alloy ChS70 VI	9.5-12.5	15.0-16.7		0.060.12	<0.30	<0.08	2.4-3.2	-					
No.1	8.89.5	13.0-14.0	2.4-2.6				3.2-3.8						
Rene-142	11.4512.05	6.67.0	0.010.02	0.100.14	0.06	0.2	5.946.30	0.1					
VPr-11		14.0	2.5	0.55	4.50	4.0	0.45						
VPr-24	9.0	7.0	0.3	0.15	3.0		4.50	10.0					

Table 1. Materials for repair brazing of turbine components from high-temperature alloy ChS70 VI

Table 1 (cont.)

Grade of alloy,			Mass share o	f elements, %			Conditions of isothermal brazing	
alloy	Ti	W	Мо	Hf	Hf Ta		Conditions of isothermal brazing	
Alloy ChS70 VI	4.25.0	4.5-6.5	1.5-2.5				-	
No.1		-	-				11751210 °C, 1015 min,	
Rene-142	0.02	4.7-5.1	1.3-1.7	1.31.7	6.26.5	2.32.6	pressure 1.3·10 <sup>-2</sup> Pa	
VPr-11	-						1120 °C, 5–6 min in argon atmosphere, 2–3 min, pressure 1.3·10 <sup>–2</sup> Pa	
VPr-24	1.0	9.0	1.8				1210 °C, 20 min, pressure 1.3·10 <sup>-2</sup> Pa	
Note. Base ni	ckel.							

alloy with high corrosion resistance in sulfur-containing gas flows, especially when turbines operate on liquid organic fuel.

That's why it is necessary to perform repair brazing of components made from the alloy ChS70 using composite brazing alloys, containing filler materials, which in addition to satisfactory strength and fracture toughness ensure sufficient level of corrosion resistance. This characteristic is determined by chemical and phase compositions of the brazed seam metal and limited zone of thermal diffusion interaction with the base metal [8].

Serviceability of repaired components of gas turbine engines subjected to brazing depends to a great degree upon mechanical properties of the metal of brazed seams and conditions of operation. That's why when developing technological process of repair brazing it is necessary to establish rational types of brazing alloys and mechanical properties of respective brazed joints under standard conditions and at operation temperature.

Mechanical properties of brazed joints of cast alloy ChS70 VI have been determined, for which purpose composite Ni--Co--Cr--Al--2.5 % B brazing alloys of foreign (brazing alloy No.1) and national production (VPr-11 and VPr-24) were used. Chemical composition of brazing alloys is given in Table 1.

Powders of alloys ChS70 and Rene-142 were used as filler materials in developed composite brazing alloys. Granulometric composition of powders corresponded to  $60-120 \ \mu m$  particle size.

Application of the alloy Rene-142 powder in composite brazing alloys exerts favorable effect because composition of the filler includes rhenium (which improves resistance to scaling), tantalum (which improves high-temperature strength of  $\gamma$ -solid solution and increases thermal stability of  $\gamma$ -phase), and hafnium (which refines morphology of precipitated carbide phases).

**Materials and technique of the experiment.** Cast plates of the alloy ChS70 VI of 2.8--3.0 mm thickness, produced by vacuum-induction melting, were used for investigating mechanical properties of brazed joints. Before brazing the plates were subjected to homogenization annealing at temperature 1170 °C for 1 h. Powders of brazing alloy No.1 and the filler were mixed in a cylindrical vessel within at least 4 h.

Composite brazing alloy (brazing alloy No.1 + filler) was mixed on acrylic binder up to the consistence of thick sour cream and applied on end surfaces of plates to be brazed. The plates were compressed in a special device with application of 50--100 N force. A certain portion of the plates to be brazed was assembled with 0.1 or 0.2 mm clearance, without or with minimum clearance determined by dispersity of used powders. An additional layer of brazing alloy of 1--2 mm height was applied on ends of the plates to be brazed for improving properties of joints.

For brazing ChS70 cast plates billets of  $15 \times 25$  mm size were cut out and ground for leveling their surfaces.

After application of the brazing alloy assembled billets were dried in oven at the temperature 120--



130 °C and then placed into vacuum furnace SNV-2 for brazing under conditions, which corresponded to each investigated brazing alloy (see Table 1). Brazing of specimens was performed in vacuum  $6.5 \cdot 10^{-3}$  Pa, whereby they were heated stepwise up to the maximum temperature. Isothermal brazing of specimens was performed within limited time (5--10 min) at liquidus temperature of the used brazing alloy.

After brazing billets were cooled down to room temperature, the quality was analyzed (visually), and they were subjected to further heat treatment in vacuum.

Heat treatment of joints. As far as process of repair brazing of components of HTA proceeds at the temperature values, which achieve complete solubility of hardening  $\gamma$ -phase in  $\gamma$ -solid solution (1180--1240 °C depending upon chemical composition of the alloy), brazed components have to be subjected to restoration heat treatment.

By means of increase of high-dispersion  $\gamma$ -phase content in alloys (which is characterized, first of all, by total amount of aluminium, titanium, and niobium) temperature of its complete dissolution in the matrix increases, although temperature of the beginning of dissolution changes insignificantly. The structures achieve the highest thermal stability in alloys in case of their complex doping with elements, which enter both into solid solution and into  $\gamma$ -phase (tantalum, hafnium) [9].

Tungsten is the element, which efficiently increases thermal stability of  $\gamma$ -phase and high-temperature strength of nickel alloys, that's why diffusion of tungsten from the alloy into the brazing alloy material or its presence in the composition of a filler has positive effect in technological process of brazing.

After brazing of items from cast alloy ChS70, standard heat treatment in vacuum (in purified argon) is performed, which is used, for example, in manufacturing of guide blades of commercial gas turbine units (GTE-115). Conditions of complete heat treatment of turbine blades made from alloy ChS70 VI consist of the following three stages:

• annealing at the temperature  $(1170 \pm 10)$  °C within 2 h (for thin-wall small size components ---for 1 h); furnace cooling. It is desirable to maintain cooling rate within 15--20 °C/min at the cooling interval down to 650 °C;

• annealing at the temperature 1040--1050 °C within 2--4 h; furnace cooling;

 ageing at 850 °C within 16 h. For simplification of the technological process duration of ageing at  $(900 \pm 10)$  °C is 3 h. Reduction of the ageing process duration is used in heat treatment of turbine stator components.

High-temperature heat treatment of brazed joints of nickel HTA allows, in addition to restoring base metal microstructure, minimizing negative influence of metallurgical defects on properties of joints (removal of small gas pores, cavities and microvoids, shrinking porosity, and crystallization cracks). It is possible to limit porosity caused by uncompensated diffusion of the base metal components and brazing alloy through boundary of brazed joints. Diffusion porosity is resolved due to solid-phase dissolution of chemical (boride and silicide) compounds near junction line, and general and local chemical erosion is leveled.

Mechanical tests of specimens. After brazing and heat treatment brazed plates were ground and specimens for mechanical tests were cut out from them by electrospark method. Then surface of specimens was ground till roughness  $R_a$  was not more than 0.6  $\mu$ m.

From the remained part of brazed plates fragments of joints were cut out for microstructural investigations of the seam metal, thermal diffusion zone, and characteristics of the base material.

Mechanical tests of the base material and brazed joints at room temperature were performed on flat specimens having working part length 10--11 mm and cross section  $2 \times 3$  mm.

Parameters, upon which depends serviceability of a brazed joint in operation, are tensile strength, yield strength, and relative elongation. For their determining the specimens were tested for uniaxial extension on a rigid tensile testing machine R-05 with the speed of the holding device movement 1 mm/min. Deformation curve was registered on the electron potentiometer dial according to readings of dynamometer.

Interrelation of structure and mechanical properties of brazed joints of the alloy ChS70 at 20 °C. All brazed joints were produced under constant thermal physical conditions of stepwise mode of isothermal brazing.

Strength of brazed joints of the alloy ChS70 VI equaled 78--92 % of standard strength of the base metal. Base value of the alloy ChS70 VI strength was assumed 853 MPa. Four values obtained on one cast plate of  $3 \times 32 \times 110$  mm size in longitudinal direction after annealing and ageing corresponded to 790--850 MPa.

Assuming standard brazing alloy No.1 (Ni--Co--Cr--Al--2.5 % B) as the base and introducing into it increasing amount of fillers of various chemical composition, it became possible to get stable level of strength of brazed plates of the alloy ChS70 VI. Statistical processing of strength values of produced joints has somewhat vague character, which is connected with diversity of brazing options (Figure 1). Criterion of quality factor Q of a brazed joint was accepted ratio of a brazed joint tensile strength  $\sigma_t^{BJ}$ to tensile strength of the base metal  $\sigma_t^{BM}$ : D =

 $=\frac{\sigma_t^{BJ}}{\sigma_t^{BM}}$ . Share of specimens with high level of quality

factor (70--90 %) made up 60--70 %. This gives us basis to consider results obtained in brazing of ChS70 plates with brazing Ni--Co--Cr--Al--2.5 % B alloy + filler (powders of alloys Rene-142 and ChS70, or mixture thereof) quite satisfactory.

Results of tensile tests of brazed joints of alloy ChS70 plates at 20 °C are generalized in Figure 2.



Figure 1. Strength of brazed joints of alloy ChS70 VI produced using different composite brazing alloys

Into the first group specimens of brazed joints from alloy ChS70 were included, which were formed at 1200 °C within 10 min by simple brazing alloy No.1 of Ni--Co--Cr--Al--B system, which due to good spreading and sufficient wettability allowed ensuring reliable filling of clearances and forming defectless joints (seams) (Figure 3, a, b).

Brazing of billets using only brazing alloy No.1 allowed forming joints with quality factor 56.5--66.5 %, which may be considered satisfactory, but having relatively low strength characteristics. In considered case brazing was performed without clearance and with 0.1 mm clearance.

Compositions of the brazing alloy material and a brazed metal differ in content of alloying components. Titanium, tungsten and molybdenum were completely absent in low-melting brazing alloy and content of chromium was reduced (13.5 %). Boron (2.5 wt.%) was used as a depressant in the brazing alloy.

In the process of isothermal heating between the base and molten metals of the seam mutual diffusion of the components takes place. After crystallization brazed seam was produced, which contained, wt.%: 4.6W, 1.9Mo, 3.64Ti, i.e. dissolution of base being brazed and occurrence of the front of intensive transfer of the base components into the seam metal were registered (Figure 3, *a*; Table 2).

Crystallized metal of the seam represents matrix solution with minor amount of secondary phases: disperse (titanium- and hafnium-base) carbides MeC, carbides of eutectic type  $Cr_{21}(Mo, W)_2C_6$ , and rare boride phases located on edges of eutectics (Figures 3, *b*; 4, *a*; 5, *a*; Table 3). Carbide eutectics (compounds of Chinese font type) in seam metal, which are rich in refractory components, contain, %: 24--33.6W, 33.7--41.8Cr, 17--18Mo, 4.7--5.5Ni.

Fusion line between a brazed metal and the seam metal proper is rather vague. It is stipulated by intensive penetration into the base metal of a brazing alloy, containing 2.5 wt.% B. «Tongues» of penetration of brazing alloy No.1 into the base metal were detected at the depth up to 300–350  $\mu$ m (Figure 3, *a*, *b*). Carbon and boron, which have small radii, easily diffuse over grain boundaries and precipitate in the form of plates of carbide phases Me<sub>23</sub>C<sub>6</sub> (Table 3; Figure 5, *a*). Such precipitates enable embrittlement of the junction metal, due to which value *Q* of the brazed joint does not exceed 66.5 % (in case



Figure 2. Strength of brazed joints of alloy ChS70 VI produced using composite and commercial brazing alloys (dash line designates  $\sigma_t$  of alloy ChS70 VI equal to 830--835 MPa according to specifications)

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**Figure 3.** Microstructure of brazed joints formed at T = 1190-1200 °C (5–10 min) using composite brazing alloys: *a*, *b* — No.1 (*a* — ×26; *b* — ×180); *c*, *d* — 40 % No.1 + 60 % Rene-142 (*c* — ×26; *d* — ×85); *e*, *f* — 40 % No.1 + 30 % Rene-142 + 30 % ChS70 (*e* — ×26; *f* — ×100); *g*, *h* — 40 % No.1 + 60 % ChS70 (*g* — ×23; *h* — ×100)

of brazing without clearance) and 56.5 % (in case of brazing with 0.1 mm clearance). Presence of boron was detected in spectrum of carbide phases. (In case of presence of molybdenum certain difficulties occurred in quantitative separation of boron and molybdenum.)

Introduction of the filler (60 wt.% of powder Rene-142) into composition of mentioned brazing alloy increases level of strength of the joints produced at the temperature of isothermal brazing 1200 °C for 10 min, up to the quality factor 86.0--91.5 %. Reduction of brazing temperature to 1190 °C for 10 min, with simultaneous reduction of the filler amount down to 40 wt.%, allows preserving stable level of strength of the joints: *Q* values are 79.0, 79.1, 85.4 %.

Composite brazing alloy No.1 + Rene-142 both in brazing with clearance and without it ensures formation of a quality seam with minimum amount of micropores (Figure 3, c, d). Introduction of the filler-powder increases ductility of the brazing alloy and



System of	Investigated zones				Mass	share of elem	ents, %				
brazing alloy	of brazed joint	Ni	Al	Со	Ti	Cr	W	Мо	Si	Ñ	Fe
	Alloy ChS70 VI	Base	2.4-3.2	9.512.5	4.25.0	15.016.7	4.56.5	1.5-2.5		0.060.12	
100 %	Base metal	57.96	2.50	11.05	4.54	15.86	5.94	2.15			
No.1 (NiCoCr Al2.5 % B)	Diffusion zone	59.23	2.77	11.10	3.80	15.76	5.61	1.75			
	Seam metal	60.76	2.80	10.32	3.64	15.89	4.66	1.91			
40 % No.1 +	Base metal	58.20	2.47	11.49	4.07	15.83	5.72	2.22			
60 % Rene-	Diffusion zone	60.62	2.68	11.08	3.39	15.24	5.32	1.68			
142	Seam metal	62.09	3.33	11.22	3.24	14.62	4.12	1.36			
40 % No.1 +	Base metal	60.50	3.00	11.38	3.53	15.07	5.22	1.30			
30 % Rene-	Diffusion zone	59.43	2.81	11.01	3.57	15.28	5.84	2.07			
JS-6U	Seam metal	57.97	2.56	10.92	4.22	16.06	6.28	1.99			
100 % VPr-11	Base metal	59.06	2.34	10.35	4.60	15.90	5.78	1.97			
	Diffusion zone	60.09	2.16	9.95	4.14	15.66	6.19	1.80			
	Seam metal	62.04	1.78	7.80	4.89	15.08	0.96	0.96	0.91		0.96

Table 2. Chemical composition of metal of main structural zones in alloy ChS70 brazed joints produced using different composite brazing alloys

reduces its reaction interaction with metal being brazed.

Composition of composite brazing alloy differs from that of the base metal (see Table 2). Refractory components (Ti, W, Mo, Hf and Ta) contained in the powder Rene-142 act as modifying agents and refine grain in the seam metal. They enable formation of thermally stable phases ---- disperse carbides of the MeC type (24--30 % Ti, 2--7 % Hf, 4--5 % Nb, 28--29 % Ta) with high microhardness (26 10<sup>3</sup> MPa). Density of distribution of separate carbides of cubic form and primary carbides of eutectic kind is not high (Fi-gures 3, *d*; 5, *b*; Table 4). In the process of crystallization of molten metal in the seam, precipitation from the solution of carbides  $MeC_6$  (28--34 % W, 4.0--4.5 % Re, 17--28 % Cr) and polyhedral carbides  $Me_{23}C_6$  (32--60 % Cr, 12--17 % W, 8--12 % Mo) was registered.

In the process of brazing, penetration of molten brazing alloy metal into the base metal takes place. As a result of such interaction, over grain boundaries



Figure 4. Peculiarities of microstructure ( $\times$ 500) of solidified metal of brazed seam depending upon used type of composite brazing alloys: a - No.1; b - 40 % No.1 + 30 % Rene-142 + 30 % ChS70; c - 40 % No.1 + 60 % ChS70; d - VPr-11



Analysis	Mass share of elements, %												
spectrum	С	Al	Ti	Cr	Со	Ni	Nb	Мо	W				
1	3.29		2.20	34.77	2.19	4.84		18.12	34.59				
2		2.93	4.39	13.71	10.44	64.19		1.09	3.25				
3	2.84	2.50	3.35	15.14	10.45	59.01		1.60	5.11				
4	15.44		42.01	2.18	0.68	5.64	5.58	3.63	24.83				
5	14.06		38.66	3.78	2.11	13.59	5.74	3.23	18.82				

Table 3. Chemical composition of different phases in seam metal of brazed joint ChS70/No.1/ChS70 formed without clearance

Cr-, W- and Mo-base carbides of the  $Me_{23}C_6$  type and within the grain volume disperse particles MeC precipitate (Table 4; Figure 5, *b*). These phases are discrete and exert minor influence on occurrence of stresses on grain boundaries in the process of tensile tests.

For reducing chemical micro-inhomogeneity between brazed base metal and formed seam, as well as production cost of brazing process, 30 wt.% of the filler were replaced in composite brazing alloy No.1 + Rene-142 for powder of the alloy ChS70, whereby temperature of isothermal brazing was reduced without exerting negative influence on the brazed joint strength. At maximum brazing temperature 1190 °C within 5 min quality factor of the joints was 87.0, 92.0, 104.4 %, i.e. on heat treated (annealing + age-



**Figure 5.** Areas of X-ray spectral analysis of separate phases in seam metal of brazed joints produced under following conditions: a - 1200 °C, 10 min, ×600 (Table 3); b - 1200 °C, 10 min, ×500 (Table 4); c - 1190 °C, 5 min, ×1000 (Table 5); d - 1190 °C, 5 min, ×500 (Table 6); e - 1200 °C, 10 min, ×180 (Table 7)



Analysis	Mass share of elements, %													
spectrum	С	Al	Ti	Cr	Co	Ni	Nb	Мо	Hf	Та	W	Re		
1	3.08		0.36	60.13	2.81	3.23		8.20			17.76	4.43		
2	3.44		0.72	59.23	2.63	3.33		8.55			17.58	4.52		
3	3.95	2.07	3.42	12.69	13.26	61.56		0.78			2.28			
4	12.92		28.91	0.98	0.56	3.43	4.95	3.92	1.81	28.82	13.69			
5	11.42		24.91	1.24	1.32	6.79	4.04	2.50	6.88	28.75	12.14			
6	4.09	0.67	2.72	22.6	3.76	22.44		12.31			28.57	2.84		
7	4.62		1.88	32.55	2.83	6.03		16.34			32.65	3.09		
8		3.04	3.97	11.11	11.42	67.15		0.59		0.65	2.08			
9	2.31	3.46	2.12	13.2	10.38	60.91		0.92		1.08	4.31	1.33		

**Table 4.** Chemical composition of different phases in seam metal of brazed joint ChS70/40 % No. 1 + 60 % Rene-142/ChS70formed with 0.1 mm clearance

ing) brazed specimens maximum level of strength was achieved. So, in brazed joints of specimens, produced using composite brazing alloy 40 % No.1 + 30 % Rene-142 + 30 % ChS70, the highest parameters of strength characteristics were achieved.

In tests of a specimen of brazed joint ChS70/No.1 + 30 % Rene-142 + 30 % ChS70 record breaking result was achieved: its strength turned out to be somewhat higher than that of the base metal (see Figure 2). Formation of neck in the specimen with maximum level of quality factor (104.4 %) was registered in the area adjacent directly to the seam.

Brazed joints were produced without clearances and with 0.1 and 0.2 mm clearances. Increase of clearance enables increasing the volume of crystallized melt and width of the formed brazed seam and occurrence of shrinkage microporosity in the seam metal. Despite performance of homogenization treatment, shrinkage pores in such specimens were preserved over seam line, thus weakening free cross-sectional area, which, however, did not cause noticeable reduction of tensile strength of brazed joints. Brazed joints of alloy ChS70 VI with 0.2 mm clearance were also characterized in various experiments by high values of parameter *Q*.

For example, one specimen of a joint (produced using brazing alloy 60 % No.1 + 40 % Rene-142), having 0.2 mm clearance, had Q = 85.4 %, while specimens without clearance and with 0.1 mm clearance had quality factor 79 %.

According to the data of X-ray spectral analysis of joints ChS70/40 % No.1 + 30 % Rene-142 + 30 %

ChS70/ChS70, chemical compositions of the seam and the base metal are similar and differ only by presence of a small amount of refractory components, which enter into composition of precipitated in the metal phases (Figures 3, *e*, *f*; 5, *c*; Table 5).

In the seam metal colonies of disperse W- and Ti-base carbide particles were detected. In inter-axial spaces precipitated primary carbides (W, Cr)C with particle size up to 8  $\mu$ m across. Thin acicular particles (Ti, Hf)C were detected over solid solution boundaries (Figure 4, *b*). Matrix of the seam metal represents as a result of interaction with the filler and brazed metal austenite system of the following chemical composition, wt.%: 61Ni--11Co--13Cr--3W--1Mo--1Ta--3.3Al--2.75Ti (Table 5, Figure 5, *c*).

Fusion line in brazed joints is vague, depth of brazing alloy penetration into the brazed metal achieves  $150-200 \,\mu\text{m}$ . Diffusion zone consisted mainly of disperse precipitates of thermally stable carbides MeC and discrete thin precipitates of Cr-base carbides of Me<sub>23</sub>C<sub>6</sub> type over grain boundaries (Figure 3, f).

The highest heat temperature (1210 °C, 10 min) of components from HTA in formation of brazed joints was used in work with brazing alloys of the system No.1 + 60 wt.% of powder of alloy Rene-142. At the same brazing parameters brazing alloy, containing 60 % of Ch70 powder as the filler, had reduced strength of joints. It's Q parameter didn't exceed 77.8-87.0 %.

In contrast to Rene-142, alloy ChS70 does not contain tantalum, rhenium and hafnium, it is less thermally

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**Table 5.** Chemical composition of different phases in seam metal of brazed joint ChS70/40 % No.1 + 30 % Rene-142 + 30 %ChS70/ChS70 formed with 0.2 mm clearance

Analysis		Mass share of elements, %												
spectrum	С	Al	Ti	Cr	Fe	Co	Ni	Zr	Nb	Мо	Hf	Та	W	Re
1	11.0		5.13	2.42		2.19	8.62	4.66	6.81	2.10	46.07	9.94	1.07	
2	5.53		0.69	56.17		2.52	3.08			9.29			17.98	4.74
3	4.99		1.98	23.36		2.02	4.62			16.85			44.07	2.10
4	4.64	1.95	2.94	19.23	0.53	7.24	41.42			6.92			15.14	
5	3.61	3.29	2.76	13.08	0.57	10.92	60.68			1.03		0.90	3.16	

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Analysis	Mass share of elements, %												
spectrum	С	Al	Ti	Cr	Fe	Со	Ni	Мо	W				
1	2.97	1.77	12.84	4.48		7.98	69.19	0.47					
2	14.06		38.66	3.78		2.11	19.33	3.23	18.82				
3	3.29	2.49	4.15	14.59	0.67	11.12	58.77	0.96	1.76				
4	1.99	2.48	6.18	12.63	0.64	11.49	62.45	0.39					

**Table 6.** Chemical composition (main components) of different phases in seam metal of brazed joint ChS70/40 % No.1 Ni-377-2 +60 % ChS70/ChS70 formed without clearance

stable in heating, and because of this reason powder of the filler enters more freely into diffusion contact with a brazed metal. Depth of chemical interaction of a brazing alloy with solid phase achieved 500  $\mu$ m on both sides. Penetration of melt over grain boundaries of the base metal was noted (Figure 3, *g*, *h*).

In case of using only one filler (alloy ChS70), in the seam metal skeleton-like form of precipitation of carbides was detected in the volume of adjacent grains. Isolated carbide phase represents Ti-base carbides MeC (Figure 4; 5, d; Table 6). In the volume of solidified phase, which penetrated into the base metal, acicular carbide particles were registered. Microporosity in the seam metal was practically absent. Composition of carbide eutectics (Chinese font) corresponded to the type Cr21(Mo, W)2C6 with 3--40 % Cr, 5--18 % Mo, 20--32 % W. In case of 0.2 mm clearance, volume of molten brazing alloy increased, and because of this reason morphology of precipitated phase changed. The greater amount of metal (and respectively of the filler) was subjected to melting, the more developed (coarsened) carbide phase Cr23C6 (33--40 % Cr) was detected in metallographic analysis of a brazed seam.

It may be noted that under constant thermal physical conditions of brazing (1190 °C, 5 min) a filler from 30 % Rene-142 + 30 % ChS70 in composition of the brazing alloy has lower interactive capacity in brazing than a composite brazing alloy with 60 % of the alloy ChS70 powder as the filler.

When home brazing alloy VPr-24 was used (see Table 1, Figure 2) in the process of brazing at temperature 1200 °C for 10 min, low Q values were obtained ---- 46.5 and 45.7 %. Si-containing brazing alloy VPr-24 has significant amount of refractory components (Ti, W, Ni, Mo), the temperature of its complete melting is 1210 °C within 20 min. Parameters of this mode of brazing turned out to be insufficient for complete melting of the brazing alloy and its interaction in liquid state with the filler in the composition 40 % VPr-24 + 60 % ChS70. Limited wettability by brazing alloy of the alloy ChS70 powder and increased ductility of the system stipulated formation of inhomogeneous seams with high number of shrinkage pores, voids, and unmelted components.

In case of application of brazing alloy VPr-11 (see Table 1), brazing temperature was reduced to 1120 °C for 10 min. Brazing alloy, containing high amount of depressing agents (4.5 % Si and 2.5 % B), has good

fluidity and freely flows into the natural clearance between contacting surfaces (see Figure 4, d). However, cast shrinkage cavities, namely big pores, formed in the seams, which are clearly seen in structures and fractures of specimens after tensile stresses (Figure 6, g, h). Strength of brazed joints, produced using brazing alloy VPr-11, is higher than that of the joints produced using brazing alloy VPr-24, but lower than that of the joints, produced using composite brazing alloys (see Figure 2).

Due to high total share of depressing agents (Si + B), active diffusion interaction between the base metal and the solidifying brazing alloy VPr-11 takes place. Depth of penetration of low-melting brazing alloy components over grain boundaries of the base metal made up more than 300  $\mu$ m (in some places up to 1 mm). Strong cross diffusion of the brazing alloy and base metal components took place because of difference in their chemical composition. It was demonstrated by transfer of the base metal refractory components into the seam metal (see Table 2). Concentration of alloying additives in the latter made up, wt.%: 4.34W, 1.8Mo, 4.6Ti, while in initial brazing alloy these elements were absent. Especially significant was increase of cobalt concentration (along fusion line 9.8 %, in seam metal more than 7 %, while its content in brazed base metal was 12--13 wt.%). Transfer of cobalt into the seam metal enabled, in its turn, higher dissolution of carbon in matrix solution.

Appearance of a significant volumetric share of carbides in the seam metal and mainly near the fusion line is a result of increased concentration of carbon in alloy VPr-11 used for brazing (see Figure 4, d). Probably it is more advisable to use brazing alloy VPr-11 for brazing components from low-carbon alloys subjected to thermomechanical treatment.

In the process of the seam metal solidification and subsequent heat treatment of joints (ageing) hardening  $\gamma$ -Ni<sub>3</sub>Al-phase precipitated from matrix solution of brazed specimens (Figure 7). Satisfactory strength characteristics of the specimens were ensured due to precipitation in all zones of brazed joints (in the base alloy, diffusion zone, and seam metal) of hardening phase with density about 30 vol.%. Size of the hardening  $\gamma$ -phase in the seam metal, in the fusion line zone and in the base metal during heating for brazing, isothermal soaking (1190 °C, 5 min), quick cooling, and two-stage heat treatment in vacuum (1050 °C, 2 h + 900 °C, 3 h) is approximately the same ----



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**Figure 6.** Failure pattern of specimens of brazed joints produced using composite brazing alloys in case of uniaxial tension:  $a (\times 20)$ ,  $b (\times 200) - 40 \% \text{ No.1} + 30 \% \text{ Rene-142} + 30 \% \text{ ChS70}$  (Q = 92 %);  $c (\times 20)$ ,  $d (\times 465) - 40 \% \text{ No.1} + 30 \% \text{ Rene-142} + 30 \% \text{ ChS70}$  (Q = 104.4 %);  $e (\times 20)$ ,  $f (\times 200) - 40 \% \text{ No.1} + 60 \% \text{ ChS70}$  (Q = 77.8 %);  $g (\times 130)$ ,  $h (\times 465) - \text{VPr-11}$  (Q = 82.3 %)

0.1--0.4 µm, whereby in the junction and seam zone particles  $\gamma$ -Ni<sub>3</sub>Al had spherical shape, which proved lower discrepancy of parameters of matrix lattices and precipitates (up to 0.2 %) than in the base alloy with cubic form of particles (having size 0.5--0.7 µm). Optimum size (dispersion) and high volumetric density has hardening  $\gamma$ -phase in the seam metal produced

using composite brazing alloy 40 % No.1 + 30 % Rene-142 + 30 % ChS70 (Figure 7, d), which is a determining factor for achievement of high strength parameters of brazed joints (see Figure 1).

Microstructural peculiarities of tensile failure of brazed joints. Analysis of fractures of brazed joints after tensile tests of specimens allowed obtaining data



**Figure 7.** Microstructure  $(\gamma - \gamma)$  of base alloy ChS70 (a) and metal of seams formed using different types of composite brazing alloys: b --- No.1/ChS70 after heat treatment; c --- No.1 + 60 % Rene-142; d --- No.1 + 30 % Rene-142 + 30 % ChS70 (×5000)

on homogeneity of the seam metal phase composition, character of plastic deformation, and sources of stress concentration, which may cause premature failure of a brazed composition.

The main mechanism of a brazed joint tensile failure is a transcrystalline one with elements of intergrain fracture. Comparison of fracture of joints produced with different amount of introduced into the brazing alloy filler showed that the finest grain structure of a seam metal was produced when equal parts of powders of alloys ChS70 VI and Rene-142 were used as fillers (see Figure 6, d).

Strength of brazed joints produced in the process of isothermal brazing of billets at 1190--1200 °C for 5--10 min was, approximately, the same. The best results were achieved in the process of 5-minute brazing at maximum temperature. Ductile component in combination with transcryslattine failure prevailed in fracture of the specimens (see Figure 6, *b*, *d*).

Fracture of brazed joint of alloy ChS70, produced using as a filler 60 % of powder of the same alloy, corresponds to the pattern of brittle failure (see Figure 6, e, f). The fractogram corresponds to the case, when achieved level of strength (quality factor) is 77.8 % of the base metal strength.

As showed X-ray spectral analysis (Table 7, Figure 5, e), locus of origination of a crack in the seam metal during loading of a specimen are coarse particles of refractory carbides (W, Cr, Mo)<sub>6</sub>C.

In the seam metal fracture, in addition to mainly shear failure of the matrix solution elements, voids and cast microporosity were detected over boundaries of separate crystallites. Evidently increase of isothermal brazing duration under selected heating conditions would be rational, as well as insignificant increase of the brazing temperature (by 8--10 °C). Judging from the pattern of fracture, in the seam metal insignificant portion of the filler has preserved, which did not interact with the brazing alloy in the process of isothermal brazing (see Figure 6, f). That's why in this case amount of the filler introduced into brazing alloy had to be reduced to 50 %.

Structure of a seam metal of the joint studied may be considered satisfactory. The seam grain is rather

**Table 7.** Chemical composition (main components) of different phases in fracture of seam metal of brazed joint ChS70/VPr-11/ChS70 formed without clearance

Analysis spectrum					Mass s	hare of elem	ents, %				
	С	Si	Ti	v	Cr	Fe	Co	Ni	Zr	Mo	W
1	3.26	0.36	24.68		4.95		4.55	45.03		16.25	0.92
2	12.23	1.94	29.23		1.99		1.98	19.61	3.53	26.99	2.50
3	8.18	3.19	25.97		2.61		3.34	30.27	3.61	22.84	
4			0.84	0.48	78.81	0.62	2.19	6.60		5.41	5.05



small with diameter about 80--100 µm. Brittle boride phases practically were not detected. This ensured high level of strength of brazed joints of alloy ChS70 in tensile tests.

Chemical compositions of the brazing alloy and the filler exert significant influence on character of fracture and seam strength of HTA brazed joints (see Figure 6). When brazing alloy VPr-11 was used (which contained boron and carbon), in the specimen fractures spherical shrinkage porosity and big carbide plates were registered, formation of which was connected with increased amount of carbon in initial powder of the brazing alloy (Table 7, Figure 5, e). Strength of brazed joints in this case was at satisfactory level. Quality factor Q equaled 69.5--82.3 %.

#### CONCLUSIONS

1. Pilot-commercial technology for repair brazing and producing brazed joints of cast high-temperature nickel alloy ChS70 VI using composite boron-containing brazing alloys was developed.

2. Process of heating joints for brazing was performed stepwise at the rate 10--15 °C/min with intermediate soaking at 650 (20 min) and 1050 °C (15 min). Maximum temperature of isothermal brazing (5--10 min) achieved 1210 °C. Brazed billets were subjected to heat treatment at 1050 °C (2 h), cooling down to room temperature + ageing at 900 °C (3 h).

3. Satisfactory strength level of specimens was obtained at 20 °C. Quality factor of the joints makes up 85--92 % of mean value of the base metal strength. High level of quality factor is achieved due to obtaining in the seam metal of fine-grain structure, complete wetting and dissolution by the brazing alloy of the filler particles, minimum erosion of mated surfaces, and rational heat treatment of ready joints in vacuum.

4. In case of brazing without clearance using base brazing alloy Ni--Co--Cr--Al--2.5 % B, quality factor of the alloy ChS70 joints does not exceed 66.5 %.

5. It is determined that optimum physical-mechanical properties of brazed joints were achieved when in repair brazing composite brazing alloy was used, which consisted of 40 wt.% of low-melting component of the system Ni--Co--Cr--Al--2.5 % B and 60 wt.% of the filler consisting of equal portions of powders of alloys Rene-142 and ChS70 of 40--60 µm dispersity.

6. It is established that presence of the filler reduces volumetric share of boron in the seam material and weakens possibility of its penetration over boundaries of crystallites into depth of a brazed base metal. Boron contained in the brazing alloy is, on one hand, its depressor and, at the same time, refractory components of the filler compensate its fluxing action at the boundary of the contact of brazing alloy with base brazed material.

7. It is shown that introduction of the Ti-, Hf-, Ta-, Nb-containing alloy Rene-142 powder, enables mainly formation of stable discrete carbide phases of MeC type, while W, Mo, Re and Cr enable formation of Me<sub>6</sub>C type carbides. Refractory components of the filler act as modifiers and cause refining of a solidified seam grain structure. Two-stage heat treatment in vacuum enables dissolution of coarse carbide phases and ensures homogeneous precipitation of hardening  $\gamma$ -phase particles in matrix solution of the seam metal and the brazed joint as a whole.

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# INNOVATION TECHNOLOGICAL PROCESSES OF ELECTRIC FURNACE FERRONICKEL REFINING BY PROGRESSIVE INDUSTRIAL METHODS Part 1. Thermodynamic properties of nickel-base systems and binary compounds

N.V. NOVIKOV, I.I. KAPRAN, K.D. SOKOLOV, M.I. GASIK and A.N. OVCHARUK Pobuzhsky Ferronickel Integrated Works Ltd., Dnepropetrovsk, Ukraine

Thermodynamic premises of electric furnace (crude) ferronickel refining are analyzed on the basis of data on diagrams of phase equilibriums in metal systems and thermodynamic properties of nickel-base alloy systems and compounds.

**Keywords:** ferronickel, phase equilibriums, nickel-element systems, properties of compounds

General information and assignment of the task. Production of ferronickel in Ukraine started in 1972, when Pobuzhsky Nickel Plant was put into operation [1]. This mining-electrometallurgical complex includes quarry for extraction of oxide nickel-containing ore (about 0.1 % Ni) of Pobuzhsky deposit; electrometallurgical plant proper with rotary drum furnaces for roasting of the ore, two powerful ore-smelting arc electric furnaces of RPZ-40TsI type, installations for extra-furnace (ladle) desulphurization of (electric furnace) ferronickel, four 50-ton converters with acid and basic lining for consecutive refining of ferronickel from silicon, chromium, carbon, phosphorus and sulfur, casting machines for mechanized casting of merchantable ferronickel, and a bay for processing of dump slag for production of crushed rock for road-transport construction. Ferronickel, which was produced in pre-perestroika period, contained 5--6 % Ni. Production of «lean» ferronickel turned out to be low-efficient and since 1990s non-profitable, because of high specific consumption of electric energy (up to 70,000 kW·h per ton of nickel in ferronickel) and constantly growing price for electric energy.

As far as «lean» ferronickel was mainly used in the past at the internal market, it became uncompetitive under conditions of market economy both as to the content of nickel and accompanying impurities and as to the cost. Under conditions of transition economy production of ferronickel was completely stopped, and it was restored after coming of Russian financial capital.

Carried out technological and economic audits showed that high efficiency of production and putting of the ferronickel on international markets may be achieved in work on relatively «rich» oxide nickel ore of foreign deposits, use of which at the plants of foreign companies in many countries allows producing «rich» ferronickel (20--25 %).

Unfortunately, amount of scientific-technical information on the essence of ferronickel melting processes in electric furnaces and its refining from regulated impurities is rather limited in foreign literature.

In this connection specialists of Pobuzhsky Ferronickel Integrated Works jointly with Chair of Electrometallurgy of National Metallurgical Academy of Ukraine, scientific-manufacturing company «Tekhnosplavy», and other organizations carried out systemic study for selection of rational parameters of ferronickel production using imported (New Caledonia<sup>\*</sup>) [2] and partially «lean» Pobuzhsky ore.

Preliminary scientific-technical audit of technological processes confirmed that further improvement of the processes at each stage of the ore (charge) processing and ferronickel refining is possible only on the basis of substantial physical-chemical investigations of metal (Ni-base alloys) and oxide (slag) systems.

Analysis of phase equilibriums and thermodynamic properties of Ni-base alloys and compounds. Nickel with iron in liquid state form continuous solutions [3]. In solid state nickel, as austenite-forming element, expands temperature-concentration area of austenite structure existence and forms  $\gamma$ -structure. Liquidus curve of the Fe–Ni system alloys has concave form (Figure 1) with minimum temperature 1439 °C at  $\approx$  69 wt.% Ni. When nickel content in Fe–Ni alloys exceeds 20 %, solidification interval makes up 5--10 °C, at 1425 °C liquidus and solidus curves coincide. By means of temperature reduction below 910 °C, area of  $\alpha$ -solid solution, which is solution of the same composition as  $\gamma$ phase and bi-phase area  $\alpha + \gamma$ , expands.

Enthalpy of mixing and thermodynamic properties of the Fe--Ni system liquid alloys [4], obtained as a result of investigation at 1600 °C, are as follows:

<sup>\*</sup>Old name of Scotland.

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$ ilde{o}_{ m Ni}$	0.1	0.2	0.3	0.4	0.5
$a_{ m Ni}$	0.073	0.147	0.222	0.294	0.387
$a_{ m Fe}$	0.899	0.799	0.695	0.593	0.479
∆H <sub>Ni</sub> , J∕ mol		10124	10172	8865	6891
∆H <sub>Fe</sub> , J∕mol		+589	+592	160	1844

As one can see, liquid solutions of Fe--Ni system have negative deviation from ideal solutions (Raoult's law). By means of increase of nickel concentration in the alloy its activity increases, while enthalpy of mixing  $\Delta H_{Ni}$  reduces.

In Ni--O system compounds NiO,  $Ni_2O_3$  and  $Ni_2O$  are present (Figure 2). The most stable at high tem-



peratures is NiO (21 wt.% O). At temperature 18 °C oxide NiO has rhombohedral lattice (a = 0.2952 nm,  $\alpha = 60.7^{\circ}$ ), and above 200 °C ---- the cubic one (a = 0.4186 nm). On the diagram of phase equilibriums in the Ni--O system NiO of stoichiometrical composition is shown, although, according to the literature data, this oxide has area of homogeneity from NiO<sub>1.002</sub> to NiO<sub>1.32</sub>. Two isobars on Figure 2 mean that at low partial pressure of oxygen in gas phase and increased temperatures thermal dissociation of NiO takes place.

Temperature dependence of standard Gibbs energy change of NiO formation reaction has the form

$$Ni + 1/2O_2 = NiO;$$

 $\Delta G_{298}^{0} = -261870 + 108.6T \, [\text{J/mol}].$ 

Condition  $\Delta G_T^0 = 0$  at  $\mathcal{D}_{O_2} = 101.3$  kPa is fulfilled at the temperature 2410 K.

Oxide NiO melts at 1957 °C. In liquid nickel solubility of oxygen increases by means of temperature increase, which is confirmed by the following data:

Ò, °Ñ	1465	1494	1504	1554	1590	1613	1652
[O] <sub>Ni</sub> , at.%	1.35	1.45	1.51	2.49	3.68	5.40	5.80
[O] <sub>Ni</sub> , wt.%	0.35	0.40	0.42	0.68	0.93	0.98	1.58

As a result of mathematical processing of experimental data given in [4], we obtained the following analytical dependence of oxygen solubility in liquid nickel upon temperature (Figure 3):

lg [O]<sub>Ni</sub> [wt.%] = 
$$-\frac{12380}{T} + 6.5962.$$

Solubility of oxygen in pure iron within temperature range 1508--1850 °C is described by the expression

lg [O]<sub>Fe</sub> [wt.%] = 
$$-\frac{6629}{T} + 2.939$$
,

and within 1850--2046  $^{\circ}$ C ---- by the equation (Figure 4)

$$lg [O]_{Fe} [wt.\%] = -\frac{9380}{T} + 4.496.$$

Calculations showed that at 1652 °C (1925 K) solubility of oxygen in pure nickel  $[O]_{Ni}$  is 1.58, and in pure iron  $[O]_{Fe}$  ---- 1.31 wt.%. One can see from the presented data that solubility of oxygen in liquid nickel





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is higher than in liquid iron. This peculiarity positively affects processes of oxygen refining of the crude commercial ferronickel melts (15–25 % Ni) from impurities.

Crude nickel produced in ore-smelting electric furnaces according to carbon-thermal technology has high content of carbon (1.8-2.5 %). In the process of oxidizing refining of ferronickel from carbon in oxygen converters its amount reduces, whereby partial oxidation of iron takes place accompanied by nickel content increase in ferronickel up to 20--22 % in comparison with initial one (15-17%). In this connection for technological process of ferronickel decarburization of practical interest is thermodynamic analysis of the system Ni--C. This system has carbide Ni<sub>3</sub>C (17 wt.%), which melts, according to Figure 4, at 1057 °C (nickel melting temperature is 1455 °C). As follows from [5], dependence of standard Gibbs energy change upon temperature of carbide Ni<sub>3</sub>C formation reaction has the following form:

$$3Ni_{sol} + C_{sol} = Ni_3C_{sol};$$
  
 $\Delta G_T^0 = -33899 + 7.11T [J/mol].$ 

System Ni--C relates to simple eutectic type. Eutectic reaction

$$L \leftrightarrow [Ni] + L_{graphite}$$

has the following coordinates: temperature 1319 °C and carbon content about 2.2 wt.%. Solubility of carbon in solid nickel at temperature 1392 °C equals 2.7 at.%. At temperature values 1400--1700 °C, when oxidation process of nickel decarburization takes place, solubility of carbon  $x_{\rm C}$  in atomic percent is described by the expression

$$\lg x_{\rm C} = 1.55 - 896 / T_{\rm c}$$

where T is the temperature, K.

Transformation of atomic percent into mass ones may be performed according to the formula

$$\frac{[C] \text{ wt.\%}}{100 - [C] \text{ wt.\%}} = \frac{M_{\rm C}}{M_{\rm Ni}} \left(\frac{[C] \text{ at.\%}}{100 - [C] \text{ at.\%}}\right)$$

where  $M_{\rm C}$  and  $M_{\rm Ni}$  are the atomic masses of carbon and nickel, respectively. For the purpose of obtaining data on carbon content in nickel the upper scale in Figure 4 has to be used, where carbon is indicated in mass shares of percent.

Calculations according to the formula of transformation of carbon content in liquid nickel from atomic shares of percent into mass percent are as follows:

Temperature, °C	1450	1500	1550	2490
Solubility of carbon:				
[C], at.%	10.9	11.9	12.5	25.0
[C], wt.%	1.96	2.91	2.92	6.54

One of the complex tasks in electric furnace nickel refining is selection of rational technological parameters of sulfur removal, content of which makes up from 0.2 to 0.4 wt.%. This stipulates need for analysis of thermodynamic properties of nickel sulfides, because there is no sufficient data in literature on system Ni--S in melting and refining of ferronickel. Among



Figure 4. Diagram of phase equilibriums in system Ni--C

a number of nickel sulfides (Figure 5) of special interest is NiS (35 wt.% S) with homogeneity interval 4 at.% S. Melting point of NiS is 992 °C. In nickel corner of the diagram there is eutectic with temperature 637 °C and 33.4 at.% S.

Standard Gibbs energy of reaction of sulfide NiS formation depending upon temperature has the form

Ni<sub>sol</sub> + 
$$1/2S_{2gas} = NiS_{sol};$$
  
 $\Delta G_T^0 = -146216 + 71.92T [J/mol]$ 

Thermodynamic stability of compounds (sulfides, oxides) may by estimated by the level of tension of their thermal dissociation, if in the process gaseous molecules of the substance are formed (sulfur, oxygen). According to the data of J. Chipman, values of thermal dissociation tension of oxides is several orders lower than those of sulfides (Table).

In the process of ferronickel refining, participation of not the pure sulfide NiS, but iron-nickel sulfide  $(Ni_{1-x}Fe_x)S$  is possible.

For the sulfide formation reaction Fe +  $1/2S_2 =$ = FeS dependence  $\Delta G_T^0(T)$  has the form  $\Delta G_T^0 =$ = -150770 + 53.25 $\dot{O}$  [J/mol]. At 1600 °C (1873 K)  $\Delta G_T^0$ (FeS) = -51033 [J/mol] and  $\Delta G_T^0$ (NiS) = = -11510 [J/mol].

Data obtained allow assuming that in the process of oxidation refining of ferronickel and increase of nickel content in it thermodynamic characteristics of sulfide phases (solutions of sulfur) may change.

Content of phosphorus in electric furnace ferronickel, produced using New Caledonian oxide nickel ore, as a rule does not exceed 0.03 %, and in melting of Pobuzhsky nickel ore it achieves 0.15 %. As far as in production of Cr–Ni corrosion-resistant steels merchant-





Figure 6. Diagram of phase equilibriums in system Ni--P

able ferronickel is used, and in the process of steel melting phosphorus is practically completely assimilated by steel pool, content of phosphorus in merchantable ferronickel should not exceed 0.015– 0.020 %. At the same time refining of ferronickel from phosphorus, as well as from other impurity elements, represents certain thermodynamic and technological difficulties.

Nickel forms with phosphorus a number of phosphides [3, 6], the most refractory among which is Ni<sub>5</sub>P<sub>2</sub> ( $T_{\rm m} = 1175$  °C) (Figure 6). To nickel corner of the diagrams phosphide Ni<sub>3</sub>P (35 wt.% P) is adjacent. Standard enthalpy of  $\Delta I _{298}^{0}$ (Ni<sub>3</sub>P) formation is 199.93 kJ/mol, and entropy  $S_{298}^{0}$ (Ni<sub>3</sub>P) is 107.84 J/(K·mol) [5].

For comparison we shall note that similar thermodynamic properties of iron phosphide Fe<sub>3</sub>P are

Thermal dissociation tension of some sulfides and oxides relating to slag systems of ferronickel production

Dissociation real $2\tilde{1} eS \rightarrow$	ction of sulfide 2Me + S <sub>2</sub>	$\begin{array}{l} Dissociation \ reaction \ of \ oxide \\ 2MeO \rightarrow 2Me \ + \ O_2 \end{array}$							
Sulfide	$D_{S_2}$ , Pa	Oxide	$\mathcal{D}_{\tilde{1}_2}$ , Pa						
CaS	$5 \cdot 10^{-42}$	CaO	$2 \cdot 10^{-51}$						
MgS	$3 \cdot 10^{-29}$	MgO	$3.10^{-46}$						
$\mathbf{Cr}_{2}\mathbf{S}^{*}$	$6 \cdot 10^{-17}$	$Cr_2O_3$	$3 \cdot 10^{-26}$						
FeS	$5 \cdot 10^{-6}$	FeO	$1 \cdot 10^{-16}$						
$NiS^*$	$3 \cdot 10^{-2}$	NiO	$2 \cdot 10^{-11}$						
CuS	$1 \cdot 10^{3}$	CuO	1.10						
<i>Note.</i> By the star sulfides are marked, which are calculated by the method of single-type compounds.									

characterized by the following data:  $\Delta I 2_{98}(\text{Fe}_3\text{P}) =$ = --163.86 J/mol;  $S_{298}^{0}(\text{Fe}_3\text{P}) =$  107.84 J/ (K·mol). So, heat of nickel phosphide formation is higher than that of iron phosphide, which is one of the reasons of complex thermodynamic conditions of ferronickel

dephosphorization. Oxide ores, used for melting of ferronickel, contain in composition of certain minerals chrome oxides [2]. In carbon-thermal melting of ferronickel from these ores in electric furnaces conditions are created for reduction of chromium from slag melt by carbon with its dissolution in ferronickel. Chromium reduction process may be represented by the following reaction [1]:

$$Cr_2O_3 + 81/23C = 2/23Cr_{23}C_6 + 3CO,$$
  
 $\Delta G_T^0 = 749452 - 526.5T [J/mol].$ 

Theoretical temperature of beginning of the reaction is 1423 K (1150 °C). Amount of chromium in ferronickel tapped from electric furnace may achieve 2 % and more, which significantly exceeds allowable limit of its content in ferronickel of the grade FN-5M (maximum 0.03 % according to TU 43-3500-9--94).

For reducing amount of chromium, sulfur, phosphorus and carbon, as well as improving quality characteristics of merchantable ferronickel, crude nickel, produced both in electrical and in shaft and blast furnaces, is subjected to refining.

Analysis of state-of-the-art commercial methods of ferronickel refining in different countries and physical-chemical peculiarities of multistage technological scheme of sulfur, chromium, phosphorus and carbon content reduction in electric furnace ferronickel, developed and introduced in Pobuzhsky Ferronickel Integrated Works, will be given in information 2.

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## ON TEMPERATURE DEPENDENCE OF THERMOANTHRACITE ELECTRIC RESISTANCE

V.I. LAKOMSKY<sup>1</sup> and S.V. KUTUZOV<sup>2</sup>
 <sup>1</sup>E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine
 <sup>2</sup>Ukrainian Graphite, Ltd., Zaporozhie, Ukraine

Results of measurement of a differentiated temperature coefficient of electric resistance of thermoanthracite at different temperatures are presented. It is shown that both mean and differential values of temperature coefficient of specific electric resistance of thermoanthracite decrease by means of temperature increase.

**Keywords:** thermoanthracite, temperature coefficient of electric resistance, differentiated temperature coefficient of electric resistance

Several years ago for the first time specific electric resistance (SER) of thermoanthracite in monolith state was determined [1], the monolith being produced at Dneprovsky Electrode Plant of Ukrainian Graphite, Ltd. from the coal supplied by Obukhovskaya Central Concentrating Mill of the Gukovanthracite Association. Anthracite of mentioned supplier is well processed in calcination furnaces of the plant. SER value of produced thermoanthracite as the main parameter of the calcinated coal quality turned out to be rather low, which proves achievement of the coal thermal treatment goal. Mean arithmetic SER value of eight studied specimens made up (107.7  $\pm$  15.6)  $\mu$ Ohm·m.

In addition to low SER value, essential fluctuations of the measurement results of parallel specimens are observed ( $\pm$  15 %). This is explained by both inhomogeneity of the anthracite itself, as a result of anisotropy of its structure, and of the coal within one face, which is peculiar for this mineral [2].

In [1] for the first time temperature coefficient  $\beta$  of thermoanthracite SER within temperature range from the room one to about 600 °C was determined. As it turned out, mean value of coefficient  $\beta$  within mentioned temperature range is  $3 \cdot 10^{-3} \text{ K}^{-1}$  with sign minus. (In [1] instead of  $-3 \cdot 10^{-4} \text{ K}^{-1}$  for thermoanthracite one has to read  $-3 \cdot 10^{-3} \text{ K}^{-1}$ , and instead of  $4 \cdot 10^{-4} \text{ K}^{-1}$  for pure metals  $-4 \cdot 10^{-4} \text{ K}^{-1}$ .)

In this article not mean values of temperature coefficient of thermoanthracite SER within 15--700 °C range are presented, but its differential value determined within each 50-degree interval of thermoanthracite heating within the same temperature range.

Among carbon materials, which are widely used in electrometallurgy, the class of coal graphite and the class of graphitized materials may be singled out. Let us consider them in the aspect of temperature dependence of specific electric resistance.

Electric resistance of coal graphite materials in the process of heating first reduces and then, after

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passing a certain minimum extremum, increases [2--5]. The more ordered is crystalline structure of the coal graphite material, the earlier starts inversion of the temperature coefficient sign of electric resistance in the process of heating, i.e. the higher is content of graphite component in the structure, the lower is the temperature at which mentioned extremum is detected. So, for example, inversion of the temperature coefficient sign of electrical resistance of bottom block material of aluminium electrolytic furnaces, produced at the same plant, starts at the temperature about 730 °C [6]. Carbon charge of mentioned blocks consisted at that time of 60 % of gas calcinated thermoanthracite, 20 % of graphite dust, and 20 % of coal-tar pitch.

But if we consider carbon materials with purely graphite structure, we'll see that in their heating inversion of the sign of SER temperature dependence is not registered at all. In graphitized carbon materials, like in pure metals and majority of their alloys [7], electric resistance always only increases irrespective of the heating temperature.

In [4] general scheme of SER temperature dependence of carbon materials within temperature range from 273 K to the temperature zone of their complete graphitizing is proposed (Figure 1).

As one can see from the Figure, in the process of heating of carbon materials, characterized by amor-







phous structure, value of their SER reduces at a certain rate  $d\rho/dt$  (solid line). If heating of amorphous carbon materials is continued up to the level, which exceeds temperature of its preliminary annealing  $T_{p.a}$ , intensity of SER reduction as a result of significant development of the crystalline structure ordering processes in coal heating will sharply increase (dash line). It is explained by development at mentioned temperature values of amorphous carbon graphitizing processes, because electric conductivity of graphite in comparison with amorphous carbon is much higher, and SER of considered material intensively reduces. Point *a* corresponds to the moment of termination of graphitizing processes, in which dash line coincides with the dash-dot line. The latter represents SER temperature dependence of pure graphite.

As it seems to us, scheme of dependence  $\rho = f(T)$ , shown in Figure 1, may be considered universal one. In relation to thermoanthracite,  $T_{p.a}$  may be treated as temperature of the «crude» anthracite calcination, which does not exceed in gas furnaces 1500 °C, and dash line has to be considered as temperature dependence of thermoanthracite SER in case of calcination temperature increase up to 2000 °C and higher. In this case in high-temperature calcination of anthracite graphitizing processes of amorphous part of the material structure intensively develop, and dependence  $\rho = f(T)$  will correspond to the dash line.

It should be noted that it is rather easy to study experimentally presented dependence for thermoanthracite within the range from 273 K to  $T_{p.a}$ . Both in heating and in cooling of the specimens (it is shown by arrows in Figure 1) results of experimental data, allowing for the experience error, coincide well, phenomenon of hysteresis being absent. The same may be said about graphitized material, behavior of dependence  $\rho = f(T)$  for which is represented by the dash-dot line. In contrast to these two states of carbon materials, determination of SER values of carbon material in the process of its graphitizing is possible only in heating of a specimen (arrow on the dash line). Difference in behavior of specimens of carbon materials with different structures is connected with the



**Figure 2.** Dependence of SER temperature coefficient of thermoanthracite upon temperature, °C: 1 --- 20-200; 2 --- 20-250; 3 ---20-300; 4 --- 20-400; 5 --- 20-500

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fact that in case of thermoanthracite and graphite, heating of the specimens does not cause any noticeable change of the carbon material structure, in contrast to the process of amorphous material graphitizing. In this case by means of temperature increase the share of graphite component in the carbon material structure increases, and, as a result, reduces electric resistance of experimental specimens.

Curve  $\rho = f(T)$  (see Figure 1) within temperature range from 273 K to  $T_{p.a}$  is presented not by a straight line, but by a low-curvature line, which proves variability of the coefficient  $\beta$ .

So, SER temperature coefficient, which is determined by the formula  $\rho_t = \rho_0(1 + \beta \Delta t)$ , where  $\rho_t$  and  $\rho_0$  are the SER of thermoanthracite at temperatures  $t_1$  and  $t_2$ , respectively, and  $\Delta t$  is the difference  $t_2 - t_1$ , which represents mean value  $\beta$  in mentioned temperature range, which is applicable only for engineering calculations. Determination of value  $\beta$  for different temperature ranges (from the room temperature to selected in advance  $T_i$ ) showed that in case of thermoanthracite, SER temperature coefficient reduces by means of  $T_i$  increase (Figure 2). Within temperature range 20–200 °C value  $\beta$  is  $-4.8 \cdot 10^{-3} \text{ K}^{-1}$ , while at 20– 500 °C it is  $-1.9 \cdot 10^{-3} \text{ K}^{-1}$ , and mean arithmetic value of five separate determinations equals  $-3.2 \cdot 10^{-3} \text{ K}^{-1}$ .

Having differentiated presented above dependence with respect to temperature, we will obtain  $d \frac{\rho_i}{dt} = \frac{1}{\rho_0} \beta$ . In this case  $\beta$  is ideal value of the coefficient at any assigned temperature. Its experimental

ficient at any assigned temperature. Its experimental determination is rather cumbersome procedure, that's why it would be rational to determine mentioned  $\beta$  within narrow range (15--50 degrees) on the temperature scale.

For the experiments thermoanthracite of the same plant, produced in rotary drum furnaces, was used. Methodology of determining numerical values of  $\rho$  and  $\beta$ , described in [1], was added, in particular, by the process of heating of thermoanthracite specimens before measurement cycle up to about 800 °C for the purpose of removing from the coal adsorbed moisture, absorbed by porous thermoanthracite under uncontrollable conditions of storage of the coal specimens. For measuring values p thermoanthracite specimens were used produced from «crude» anthracite of different suppliers, whereby applicability of «crude» anthracite for calcination was determined. Thermoanthracite produced from the coal supplied by the Obukhovskaya Concentrating Mill of Gukovanthracite Association has rather low SER value, while that of thermoanthracite, produced from the coal of Nagalchanskaya Central Concentrating Mill (c. Anthracite), is one order higher and requires for repeated calcination.

In this work specimens of thermoanthracite were used, which was produced from coal of both suppliers. SER of specimen No.1 at 15 °C was,  $\mu$ Ohm·m: 334.5 ± 12.5; No.2 at 20 °C ---- 336.4 ± 0.9; No.3 ---- 4001 ± 68; No.4 ---- 3971 ± 9; No.5 ---- 3230 ± 21; No.6 ---- 3392 ± 32; No.7 at 50 °C ---- 5156 ± 42.



Specimen							$-\beta \cdot 10^3 \text{ K}^-$	<sup>1</sup> at <i>T</i> , °C						
No.	80	110	135	175	225	275	325	375	425	475	525	575	625	675
3		N/D		1.64	1.43	1.32	1.21	1.20	1.27	2.37	2.13	NZ	′ D	1.62
4	1.93	1.79	2.18	1.64	1.29	1.08	1.10	0.94	1.06	1.04	0.92	0.77	0.76	0.96

**Table 1.** Differential values  $\beta$  at various  $T_i$ 

**Table 2.** Mean values  $\beta$  within temperature ranges  $T_{i}$ - $T_{0}$ 

Specimen No		$-eta\cdot 10^3~{ m K}^{-1}$ at $~T_{j}$ , $ m ^{\circ}  m { m \tilde{N}}$											
Speemen ivo.	100	150	200	250	300	350	400	450	500	550	600	700	
5	N/D	3.0	2.5	2.1	1.9	1.7	1.5	1.4	1.4	1.2	1.1	1.0	
6	2.5	2.3	1.7	1.6	1.6	1.4	1.3	1.2	1.2	1.1	1.0	1.0	
7	2.3	1.9	1.8	1.7	1.5	1.5	1.4	1.3		N/	´D		
Note. Value $T_0$ for	<i>Note</i> . Value T <sub>0</sub> for specimen No.5 is 35, No.6 40, No.7 50 °C.												

In investigation of SER temperature coefficient of thermoanthracite the latter specimen is more applicable for experiments than the first one, because changes of its SER depending upon temperature are greater and because of this reason are measured with lower error.

Multiple measurements showed that differential value of SER temperature coefficient  $\beta$  at temperatures 15--700 °C is not constant. By means of temperature increase value of the coefficient reduces, in some specimens to such degree, that is exceeds limits of the third order. Clear reproduction of value  $\beta$  in all specimens was not detected. At the same temperatures values  $\beta$  differ in parallel specimens by 11--28 %, although ideal coincidences also happen (Table 1).

Analysis of results of the experiments showed violations of general regularity, which are difficult to explain; for example, in specimen No.3 at temperature 475 °C and in specimen No.4 at 135 °C. While it was possible to consider result of the measurement at 135 °C in specimen No.4 occasional, it's impossible to state the same in regard to specimen No.3 at 475 and 525 °C. In all probability, special investigation of mentioned effect will be needed, whereby it is necessary to accompany SER measurements by study of microstructure of thermoanthracite specimens. Such method will make it possible to determine influence of graphite component on value of coefficient  $\beta$ , and fluctuations of graphite content in thermoanthracite are quite possible because of inhomogeneity of the calcination furnace temperature field.

In determination of averaged value  $\beta$  another pattern was discovered. By means of the temperature range extension, within which measurements are performed, and, consequently, temperature  $T_i$  increase, value  $\beta$ steadily reduces. Here no deviations from natural series of measurements were registered (Table 2).

In this work value of temperature coefficient of electric resistance of graphitized material of grade EG-0 was determined, from which electrodes of electric arc steel-melting furnaces are produced (TU 4812-41--91). SER value of this material at 20 °C was (11.0  $\pm$  0.2)  $\mu Ohm \cdot m.$ 

Measurements of values of SER temperature coefficient of graphitized material EG-0 within the range from room temperature to 350 °C showed that  $\beta$  naturally increases with temperature increase. In contrast to thermoanthracite, no fall-outs of the measurement results were registered here.

Value  $\beta$  at the temperature 60 °C was 6.8 ·10<sup>-4</sup> K<sup>-1</sup>, and at 325 °C it increased up to 2.89 ·10<sup>-3</sup> K<sup>-1</sup>. In connection with this dash-dot straight line in Figure 1 should be presented in this case by slightly curved line.

Comparison of the results of measurements of SER temperature coefficient of thermoanthracite and graphitized material allows noting that at low temperatures value  $\beta$  of graphitized material is almost one order lower than in thermoanthracite, and in contrast to the latter increases depending upon temperature increase. At the same time rate of value  $\beta$  change both in thermoanthracite and in graphitized material is practically the same. Per each 100 degrees of temperature change value  $\beta$  in thermoanthracite changes by  $8.3 \cdot 10^{-4}$  K<sup>-1</sup>, while in graphitized material it changes by  $7.3 \cdot 10^{-4}$  K<sup>-1</sup>.

Radical difference of the compared materials consists in behavior of SER temperature coefficient. In thermoanthracite  $\beta$  changes sign from minus to plus be means of temperature increase, while in graphitized material it always remains positive.

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# PRESENT STATE AND WAYS OF IMPROVING TECHNOLOGY OF TITANIUM ALLOY GRANULE METALLURGY FOR THE PURPOSE OF INCREASING PROPERTIES AND RELIABILITY OF GAS-TURBINE ENGINE COMPONENTS

I.S. POLKIN, G.G. DEMCHENKOV and L.A. SNEGIRYOVA OJSC VILS, Moscow, RF

Technology of manufacturing special-purpose parts with high mechanical properties and material utilization factor has been developed on the basis of combination of two processes — production of spherical powders (granules) solidified at high cooling rates, and hot isostatic pressing. Mechanism of formation of spherical granules and influence of possible impurities on quality of future products is considered. Mechanism of formation of compact materials within the volume of a capsule of titanium alloy granules and in case of producing heterogeneous materials was studied with indication of appropriate characteristics, properties and structures. Examples of manufacturing complex billets of special-purpose parts, which are impossible to be produced using traditional methods, are given.

**Keywords:** spherical granules, hot isostatic pressing, capsules, material utilization factor, melt dispersion, impellers, centrifugal wheels

Successful combination of two processes ---- manufacturing of spherical granules of titanium alloys, solidified at high cooling rates, and hot isostatic pressing (HIP) ---- made it possible to develop rather promising technology for production of special-purpose parts, mainly for items of aerospace engineering. Originality of the technology was repeatedly confirmed by developments of VILS Company.

Granule technology has following advantages:

• possibility of manufacturing within one operation of HIP of capsules, containing titanium alloy granules, a billet with geometric parameters close to a ready part, which will need only minimum machining. According to traditional technology of manufacturing a disk of aviation engine, not less than 5--6 operations are needed, not taking into account intermediate heatings. So, production cost of items, manufactured using granule technology, is 2--4 times lower;

• material utilization factor (MUF), as a rule, deficient and strategic ones, is 6--8 times higher compared to traditional technology;

• cross-section of the parts, produced from granules, has fine-grain structure and properties that are unachievable for deformed semi-finished products, especially large-size ones, manufactured according to traditional technologies;

• granule technology makes it possible to manufacture complex parts with internal cavities and channels and high mechanical properties, which are rather difficult or practically impossible to be manufactured using traditional technology. Mentioned advantages may be implemented provided high culture of production and fulfillment of technological operations according to optimum conditions are in place. Granule technology is rather specific, and each its stage may exert decisive influence on quality of the final product. Let us dwell upon the most important aspects.

Taking into account higt chemical activity of titanium, hazard of its contamination exists even at the stage of production of granules using PREP method, i.e. dispersion of metal from the molten by plasma end of a rotating in inert atmosphere billet. Formation of a gas-saturated layer is possible during dispersion as a result of interaction of surface of granules with impurities of active gases (oxygen, nitrogen, etc.) in shielding atmosphere.

So, at pressure  $1 \cdot 10^{-4}$  Pa flow of molecules from gas atmosphere forms on a titanium granule a TiO layer of 0.3 nm thickness [1]. To control this phenomenon recirculation of cleaned inert gas is used in air-tight dispersers.

During passage through the technological chain there is possibility of contamination of mass of granules by particles of dust, sand, ceramics, oxides (because of contact with internal surfaces of the equipment and a capsule), steel (wear of drums of the disperser), copper and tungsten (erosion of the plasmatron nozzle), and sublimation (evaporation of alloying elements of the alloy during dispersion).

Studies showed that copper, tungsten and iron, which are present in the form of metallic inclusions, practically don't affect general level of properties. In particular, in study of the influence of copper on properties of a billet from alloy Ti--5Al--2.5Sn negative phenomena at temperatures +20 and --253 °C were not detected although size of particles achieved 1 mm in amount of 1 pc/2 cm<sup>2</sup>.

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Defects, detected in cracks or in places of their origination, are, as a rule, represented by non-metallic inclusions. They mainly consist of mixed oxides of iron, silicon, aluminium, calcium and potassium and are enriched with sulfur and chlorine, they are often surrounded by brittle zones and are a reason of low longterm strength and fatigue at increased and cryogenic temperatures. The most negative influence of inclusions is within  $1 \cdot 10^4 - 1 \cdot 10^6$  interval of cycles. So, for example, defects in the form of particles of  $Al_2O_3$  significantly reduce ductility and multi-cycle fatigue of the material when their size increases from 50 to 350 µm. For different titanium alloys a certain size of a defect exists, below which it may not be a reason of failure.

Studies of crack resistance of alloys with high values of strength VT22 and heat-resistance VT25U, carried out in VILS at static tension, long-tern static and low-cycle loading at 20, 300 and 500 °C, allowed establishing an allowable maximum size of a defect (for the alloy VT22 ---- 300  $\mu$ m, and for the alloy VT25U ---- 240  $\mu$ m).

So, for this technology size of possible defects in metal is commensurable with size of used granules, reduction of which unequivocally caused improvement of properties, in particular multi-cycle fatigue and long-term heat-resistance. However, existing centrifugal dispersers allow manufacturing granules with size of working fractions of only 100–250  $\mu m.$ 

To prevent getting of mentioned foreign inclusions into granules the following steps are taken: clean premises with toughened dust regime; regulated cleaning of the units; efficient methods of magnetic, aerodynamic, and electrostatic separation.

At present production cost of manufactured granules is high. It is connected with rather long process of manufacturing billets for dispersion, low productivity of units for dispersion of granules (about 50 kg per shift), and low yield of efficient granules from a billet.

To remove mentioned shortcomings and significantly reduce production cost of granules it is necessary to design units for producing granules from a melt. One of the versions of such unit developed in VILS is given in Figure 1, and comparative schemes of technologies for production of granules on existing and future units are given in Figure 2.

In the designed unit liquid metal is prepared according to the principle of skull melting in a crucible from scrap, charge and sponge, and then it is poured at constant rate on the disperser. Depending upon speed of rotation and design of the disperser it is possible to get granules having size of dozens microns, which will positively affect properties of future items.

Presented schemes don't need comments. In particular, existing scheme allows producing granules from a billet at 30 % yield, while in new version this parameter may reach 80--90 % and size of the granules may be reduced 4--6 times. New scheme is also attractive by the possibility to disperse any alloys, including complex-alloyed ones like intermetallic compounds, nitinol, and  $\beta$ -alloys.

Process of manufacturing billets of parts consists in hot volume deformation of capsules with titanium alloy granules in gas-static unit. A capsule is a tool, which forms future items. It has necessary strength, manufacturability, air-tightness, increased internal cleanliness, etc.

As a rule capsules are manufactured from lowcarbon steel. The issues of designing, calculation, manufacturing of capsules, laws of their form change in the process of HIP, and selection of materials for



Figure 1. Unit for producing granules of titanium alloys from melt



Figure 2. Technological schemes of dispersion of titanium alloy granules: I --- existing one; II --- new one

manufacturing are well studied and controlled. However, a capsule, being a disposable item, has sometimes rather complex design, production of which is connected with high manpower and production cost.

For reducing production cost of the capsules several solution were proposed, in particular, certain parts of the capsules are manufactured by stamping and rotational extrusion, and treatment on PNC machines. Experience is accumulated of repeated using certain elements in capsules of directed deformation. Serviceability of a capsule was tested, in which one of the elements is part of a future component from titanium alloy, etc.

An important operation, which affects properties of a produced from granules item, is HIP, conditions of which are selected depending upon a titanium alloy type, designation of a part, and design of the capsule



**Figure 3.** Dependence of density  $\rho$  of components produced from granules of alloy VT5-1 upon HIP pressure and soaking for 8 (*I*) and 0.5 (*II*) h in holes of following diameters at *T* = 960 °C: 1 — outside a die; 2 — 20; 3 — 10; 4 — 5 mm

and the part. Consolidation of granules in HIP process is performed as a result of simultaneous action on them of three parameters (temperature, pressure, and time). As a result a pore-free dense material is produced subjected for formation of the required structure and mechanical properties to heat treatment, except simple  $\alpha$ -alloys, for which technological annealing will suffice.

Gas-static process temperature is established taking into account temperature of polymorphous transformation of an alloy (depending upon working conditions of a part it is established higher or lower than temperature of phase transition). Pressure and time of soaking are assigned proceeding from a capsule design and possibilities of the equipment.

As a rule cross-section of the parts manufactured from granules vary significantly in thickness (from 1--2 to 100--200 mm), whereby because of specificity of a capsule design thin profile of a part is frequently formed in the center of a massive steel element which causes different properties in different areas of a part.

For determining mechanism of formation of properties and configuration of parts in HIP process, a capsule was manufactured with an insert having cavities of various section. HIP process of capsules with granules of VT5-1kt alloy was performed at various values of pressure, time of soaking, and constant temperature. Influence of these parameters on density of compact material is shown in Figure 3.

As one can see from Figure 3, formation of dense material in cavities of capsules with small cross-section is hampered and proceeds slower than in free volumes, that's why one has to pay attention at this when assigning HIP conditions.

Sometimes need occurs to manufacture combined parts. Granule metallurgy allows performing solidphase joining of dissimilar materials with properties of metal in the joint zone not worse, and in some cases even better than in initial materials. Kinetics of formation of diffusion joint of a stamped element and granules of alloy VT5-1kt may be seen from the Table, in which changes of mechanical properties of the joint zone depending upon pressure *P* and time



Cycle	HIP conditions			$T_{\rm evap}$ = 20 °Ñ				$T_{\rm evap} = -253 \ { m \circ} { m \tilde{N}}$			
No.	Ð, MPa	T, °Ñ	τ, h	σ <sub>t</sub> , MPa	σ <sub>0.2</sub> , MPa	δ, %	ψ, %	σ <sub>t</sub> , MPa	σ <sub>0.2</sub> , MPa	δ, %	ψ, %
1	35	970	0.5	711	651	5.2	5.9	1251	1189	1.6	2.1
2	35	970	8.0	800	753	11.2	28.4	1479	1297	4.3	15.8
3	90	970	0.5	806	750	10.2	30.5	1477	1342	4.0	16.0
4	90	970	8.0	802	741	12.6	29.7	1464	1327	8.3	17.6
5	170	970	0.5	803	747	12.1	30.2	1473	1328	8.3	16.4
6	170	970	8.0	803	744	13.7	30.8	1502	1313	8.6	19.2
А	.cc. to TU 1-	809-73784	l≥	736	687	12.0	20.0	1324	1226	8.0	15.0

Mechanical properties of joint zone of granules with insert of alloy VT5-1kt

of soaking in HIP are given. Joint zone of the materials was in the middle of the working part of a tensile test specimen.

In Figure 4 metal microstructure of the joint zone of a stamped element with granules of alloy VT25U is shown.

In the course of study of tensile test specimens, failure of materials in joints was not registered. Microstructure (see Figure 4), on which boundary may be detected only by transition from one grain point to another, also proves high reliability of diffusion bond of materials.

From all manufactured in VILS Company parts, which were approbated by the customers, granule technology of titanium alloys turned out to be, because of a number of reasons, irreplaceable for manufacturing super-complex parts with various types of ducts and concealed blades for items of aerospace engineering, i.e. parts, which it is practically impossible to manufacture with required level of mechanical properties using traditional methods (Figures 5 and 6) [2].

In Figure 5 billet of a centrifugal wheel of close type from alloy VT25U of 380 mm diameter and 210 mm height with concealed thin-wall complexprofile blades of two types developed with participation of specialists from the Federal State Unitary Enterprise «V.Ya. Klimov Plant» is shown. The wheel is designed for high-pressure compressors of civil aviation engines. Its mechanical properties and geometric size meet requirements of the customer. The part needs just surface machining and has MUF of 0.5. Successfully performed bench tests showed improvement of a number of characteristics of the engine (reduction of a load on shaft, improved aerodynamics of the gas flow duct, improved efficiency, and assumed reduction of fuel consumption).

Two more parts of this class were manufactured: impeller of 310 mm diameter from alloy VT5-1kt, which successfully operates in the unit for feeding cryogenic fuel in liquid-propellant rocket engine, and centrifugal wheel of 240 mm diameter for a helicopter engine from combination of alloys VT3-1 and VT8, which passed bench tests.



Figure 5. Billet of centrifugal wheel with covering disk of heat-resistant alloy VT25U



**Figure 4.** Microstructure of metal of joint zone of insert (upper part) to compacted granules (lower part) of alloy VT25U centrifugal wheel (×100)



Figure 6. Billet of shaft bearing of GTE compressor produced from granules of alloy VT25U  $\,$ 



Figure 7. Mechanical properties of alloy VT22 produced according to different technologies:  $1 - \sigma_t$ ;  $2 - \psi$ 

In Figure 6 a billet of a shaft bearing of aviation engine compressor disks, manufactured from granules of titanium alloy VT25U, with the bearing diameter 490 mm and height 105 mm, is shown. The bearing is manufactured according to traditional technology; it has channels, concealed cavities, shaped struts, etc. and represents a welded structure consisting from more than twenty parts. Technology of its manufacturing includes casting, stamping, metal treatment, welding and brazing operations, not taking into account manufacturing of special tools. Application of the granule technology made it possible to exclude these operations, whereby properties and reliability of the part improved and possibility appeared to reduce its mass due to reduction of thickness of the structure elements. The part is designed with direct participation of specialists from Moscow Aviation Institute and V.V. Chernyshov PE. At present it is in the stage of bench tests.

So, mechanical properties of various parts, produced from granules of titanium alloys in VILS, always corresponded or exceeded those of the parts from the metal produced according to traditional technology (Figure 7).

However, till now one more designation of the granule metallurgy is not implemented ---- new titanium alloys with higher level of characteristics were not designed, although real prerequisites for this exist.

One of possible directions of works, in which highrate solidification is used, is development of alloys by introducing into them increased amounts of carbon and boron, complex-alloyed  $\beta$ -alloys, and certain Tibase eutectic alloys.

High-rate solidification allows avoiding during dispergation of a melt difficulties, connected with unfavorable form of precipitation of various phases, development of a significant chemical inhomogeneity, and other defects occurring during solidification, which is confirmed by produced according to the granule technology alloy VT22 with introduced into it 0.15 % TiC (see Figure 7).

Another not less important work with application of the granule metallurgy is development of crack-resistant materials. In Figure 8 microstructure of de-



**Figure 8.** Microstructure of propagation of crack in specimen of alloy VT22 produced according to granule technology with introduced TiC inclusions (×500)

velopment of crack in a specimen of alloy VT22 with introduced into it TiC particles is shown. One can see that when a developing crack reaches a particle of titanium carbide, it brakes and changes direction.

So, presented materials show that possibilities of metallurgy of the titanium alloy granules are not exhausted at all, and development of this technology undoubtedly has good prospects.

### CONCLUSIONS

1. It is shown that metallurgy of granules allows manufacturing special-purpose parts of any degree of complexity and significant improving service characteristics of GTU.

2. It is established that parts manufactured from the granules are isotropic in their cross-section and have high level of mechanical properties and MUF.

3. It is determined that super-rapid solidification of granules allows producing titanium alloys, which contain difficult-to-introduce hardening phases, subsequent HIP of which allows manufacturing items, properties of which significantly exceed those of the existing ones.

4. For reducing production cost and increasing quality of parts from granules of titanium alloys it is necessary to produce granules directly from the melt, ensure absence of foreign inclusions in the granules, and improve technology of manufacturing capsules.

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## MATHEMATICAL MODELING OF HEAT PROCESSES IN CASTING OF CAST IRON BY MAGNETODYNAMIC METER-MIXER

M.S. GORYUK, N.I. TARASEVICH, V.I. DUBODELOV, V.K. POGORSKY and A.I. RYBITSKY Physical-Technological Institute of Metals and Alloys, NASU, Kiev, Ukraine

Results of mathematical modeling of heat processes in casting of cast iron by magnetodynamic meter-mixer are presented. Peculiarities of casting conditions are studied, in particular reduction of the melt mass in the mixer in the course of casting and its periodical replenishment with new batches of molten metal. Conditions of cast iron casting by doses from 10 to 500 kg are developed. The results obtained will be the basis for developing a new computerized system for controlling cast iron casting processes with application of the magnetodynamic meter-mixer.

**Keywords:** cast iron, casting, temperature, magnetodynamic meter-mixer, batch mass, inductor, electromagnet, power

Process of cast iron casting in foundries is characterized by periodicity and wide range of technological parameters (mass of produced castings, speed of feeding material into the moulds, duration of a cycle, etc.). Under such conditions it is important to ensure stable temperature of the metal casting, which is impossible without using state-of-the-art specialized independent multifunctional electro-technological units, such as magnetodynamic meter-mixers for overheating and casting of cast iron, developed by specialists of Physical-Technological Institute of Metals and Alloys (PTIMA) of the NAS of Ukraine [1].

For promoting efficiency of work of such equipment and improving systems of control of technological processes of casting production scientists of PTIMA developed mathematical model, which describes with high degree of adequacy thermal operation of the magnetodynamic meter-mixer [2]. Thermal conditions of the mixer operation during its commissioning, sintering of the refractory lining, and soaking and heating of cast iron were investigated using this model [2-5].

Later the developed model was used for investigating peculiarities of heat process, which proceed in batchwise casting of cast iron using a magnetodynamic meter-mixer. In this article results of the investigations are presented.

Comparison of the conditions of the cast iron overheating and casting was carried out according to the following technological schemes:

• traditional one used in majority of foundries, which consists in overheating up to the required casting temperature of the whole melt mass located in the technological casting unit. Such process, despite seeming simplicity of its implementation, is inefficient, especially under conditions of mass production, and first of all because of the power consumption increase, increased melting loss of the alloy components, and accelerated wear of refractory lining;

• new, energy conservation scheme, based on the principle of differentiated heating of the metal [3, 5,

6]. Mentioned process consists in soaking of the melt at reduced temperature and overheating up to the assigned casting temperature of the metal batch only during its release from the casting device. Practical implementation of new technology will allow significant reducing material and power consumption in the casting production process, increasing its safety and controllability, and reducing production cost. The most completely and efficiently mentioned principle and developed on its basis technological process may be implemented in magnetodynamic meter-mixers, design of which ensures release of the melt for casting directly from the liquid metal heating zone ---- induction channel.

Standard technological parameters of grey cast iron casting conditions in iron foundry of the enterprise (Table) and main technical characteristics of the most distributed among magnetodynamic casting devices ---- a meter-mixer MD-4000 for overheating and casting cast iron, which successfully operates in a number of foundries, were used as initial data for performance of the comprehensive calculation experiment [1].

#### Main technical characteristics of magnetodynamic meter-mixer of model MD-4000 for soaking, overheating and casting of cast iron

Maximum mass of cast iron in mixer M, kg	
Minimum allowable mass of cast iron in mixer	
(mass of «marsh») M <sub>marsh</sub> , kg	1500
Maximum total power of inductors P <sub>ind</sub> , kW	600
Maximum power of electromagnet Pem, kW	60
Range of mass flows of cast iron	
casting Q <sub>cast</sub> , kg/s	120

It allowed comparatively easy estimating correspondence of the developed mathematical model to the real process and making necessary corrections.

In the course of the comprehensive calculation experiment the metal temperature at each stage of the casting process was estimated and rational character of the inductor power of magnetodynamic metermixer was determined for ensuring required and stable temperature of cast iron casting.

In Figure 1 character of the metal mass change in magnetodynamic meter-mixer in case of rhythmic op-

Mass of cast batch	Durat	ion, s	Mass motal flow in casting	Maan cast iron casting	Allowable temperature range of casting $\Delta T_{\text{cast}} = (T_{\text{cast}} \pm 10) \ ^{\circ}\text{C}$		
m <sub>batch</sub> , kg	Casting	Time-out	$Q_{\text{cast}}$ , kg/s	temperature $T_{cast}$ , °Ñ			
0	$\tau_{\text{cast}}$	$\tau_{time-out}$					
10	3	10	3.33				
25	8	25	3.13				
50	6 30		8.33	1400	1000 1110		
100	10	60	10.0	1400	13901410		
500	50	180	10.0				

Initial data on technological process of cast iron casting used in performance of comprehensive calculation experiment

eration of the conveyer is shown. In this case average flow of metal in casting varies from 3.13 to 10 kg/s. If we assume that volume of melt in the mixer is 4000 kg, then, according to data of the Table, general duration of the metal casting from the mixer up to the «marsh» level (1500 kg) will be in case of casting by 10 and 25 kg batches ---- 54 min, and in case of casting by 500 kg batches ---- only 16 min. Change of the metal mass in the mixer and different duration of the casting process stipulate the need of determining the law of regulation of the inductor electrical parameters for ensuring stable temperature of casting.

At constant power of the inductor temperature of the melt increases by means of the cast iron mass reduction in the meter-mixer. The temperature growth rate directly depends upon the mass of a cast batch and duration of the casting cycle of one batch, i.e. it increases together with increase of mass flow of the metal casting.

It is especially manifested in casting of big (500 kg) batches of the metal (Figure 2). So, if the metal casting is performed at the power 190 kW, temperature in the meter-mixer after release of only one batch during the time-out between casting of two batches increases by 15 °C and exceeds established by the casting technology temperature change allowance, i.e. it is impossible to observe assigned by the casting technology temperature range at a fixed power. According to the results of the calculation experiment, after casting of the first batch power of the inductor has to be reduced down to 87 kW for maintaining melt temperature within assigned range. In this case power is spent more for compensation of the heat loss than for the metal heating. After drain of the next in turn batch of cast iron, it is necessary to reduce power of the meter-mixer inductor again.

One has to take into account that relatively low power of the mixer inductor (150 kW) does not allow achieving high mass flow of the metal casting (more



**Figure 1.** Change of cast iron mass *M* in magnetodynamic metermixer in casting of metal by batches of different mass  $m_{\text{batch}}$  (see the Table): 1 - 10-25; 2 - 50-100; 3 - 500 kg

than 5 kg/s) even at maximum power of electromagnet. It is explained by the fact that in creation of electromagnetic force participate both mentioned systems (both the inductor and the electromagnet), but range of the inductor power control is much wider (0--600 kW) than of the electromagnet (0--60 kW). Such ratio of the ranges of power control reflects as a whole influence of the inductor and the electromagnet on hydrodynamic parameters of casting. On the other hand, despite relatively low power, the electromagnet makes its contribution into heating of the metal, which does not exceed 5 %, though.

So, for saving energy resources it is frequently (especially in casting of big ---- more than 200 kg ---- batches of metal) expedient to significantly reduce power of the inductor and just immediately before release of the batch from the mixer to bring electric power of the inductor and the electromagnet up to the values, which ensure required hydrodynamic parameters of casting. Naturally, such conditions of operation of electromagnetic systems of the magnetodynamic meter-mixer set more stringent requirements to control and measuring equipment and control system, but achieved saving of energy resources justifies such approach.

So, in the course of the calculation experiment performance conditions of casting of cast iron batches of 100 kg mass (Figure 3) were developed, taking into account ensuring of stable casting temperature and change of the melt mass in the mixer and the inductor power. Characteristic peculiarity of the developed conditions is the following: by means of the



**Figure 2.** Change of cast iron temperature in process of its casting by 500 kg batches at different power of inductor  $P_{\rm ind}$  of magnetodynamic meter-mixer: 1 --- 280; 2 --- 190; 3 --- 150; 4 --- 87; 5 --- 40; 6 --- 0 kW;  $M_{\rm rem}$  --- mass of melt, which remains in mixer after release of next in turn batch



Figure 3. Change of technological parameters of cast iron casting process by 100 kg batches (see the Table) using magnetodynamic meter-mixer

metal mass reduction in the meter-mixer, power of the inductor has to be reduced as time passes more frequently, but at a smaller step.

Similar dependences were obtained for batches of other masses. By means of the mathematical model, dependences of the inductor power change in casting of cast iron according to the traditional technology (Figure 4) for assumed initial data (see the Table) were calculated.

Peculiarity of the processes of metal casting by magnetodynamic meter-mixers is passage of the melt during casting through cavity of the duct, in which significant thermal power is emitted and heating of the metal takes place. That's why such conditions are of special interest. New technology of casting is developed on their basis, in which soaking of the metal takes place at low temperature, and overheating of the melt up to the casting temperature is performed directly at the time of its feeding into the metal receivers.

Carried out calculation experiment allowed determining parameters of this technological process. Temperature of cast iron casting in this case equals

$$T_{\rm cast} = T_{\rm soak} + \Delta T,$$

where  $T_{\text{soak}}$  is the metal soaking temperature, °C;  $\Delta T$  is the level of a cast iron batch overheating in the process of its release from the magnetodynamic meter-mixer, °C. It is determined as follows:

#### $\Delta T' = \tau' \Theta$ ,

where  $\tau'$  is the duration of the metal stay in the induction heating zone during casting, s;  $\Theta$  is the metal heating intensity in zone of the highest heat emission (duct of the magnetodynamic meter-mixer), °C/s.

Results of the comprehensive calculation experiment allow obtaining dependence of the metal heating intensity for the assigned geometry of the induction duct and scheme of the melt movement in it. In the considered meter-mixer there is a E-like induction duct having the following sizes: length of central branch is 1.25 m, its section is  $100 \times 110$  mm, total length of two side branches is 2.96 m, their section



**Figure 4.** Change of power of inductor of magnetodynamic metermixer in process of cast iron casting, which ensures stability of metal casting temperature at  $m_{\text{batch}}$  (see the Table): 1 --- 10-25; 2 --- 50-100; 3 --- 500 kg

being  $60 \times 100$  mm. Casting of the metal is performed through central branch, overheating of metal during movement in it from the mixer crucible to the pouring nozzle makes up

$$\Theta = 8.21 \cdot 10^{-3} P_{\text{ind}}.$$

Duration of the metal stay in the induction heating zone during casting is determined by the time proper of a cast iron batch casting and the lead time in switching of the inductor necessary for heating up to the casting temperature of the cast iron, which was the first to be fed for casting (i.e. the melt, which is already in the duct). Mass of cast iron in the duct of mentioned geometry is about 220 kg, the mass in central branch of the duct being 95 kg. For a batch of a significantly smaller mass the lead time is comparable to the time of casting. For big (more than 100 kg) batches of cast iron the lead time is, on the opposite, much shorter than the time of casting, because in this case metal from the meter-mixer crucible is caught, and the melt in the processes of its release into the metal receiver passes practically over the whole length of central branch of the duct and has the time to acquire necessary temperature.

So, presented by the authors results along with previously obtained and published data make it possible to completely formalize process of producing cast iron casting, create new system of this process control, and implement to full degree in practice new energy conservation technology of cast iron casting by means of a magnetodynamic meter-mixer.

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# NEW FUNCTIONAL MATERIAL: OXIDE CATHODE OF WELDING ELECTRIC ARC Part 1

#### V.I. LAKOMSKY

E.O. Paton Electric Welding Institute, NASU, Kiev, Ukraine

Evolution of the oxide cathode idea (from electron tubes to electric arc) has been considered. Oxide cathodes allowed sharp increasing capacity of electron converters in electron tubes. In welding arc they significantly widen technological capabilities of the latter. Arc generator of controllable heat flow has been designed for operation in oxygen-containing gases.

**Keywords:** electric welding arc, oxide cathodes, liquid emission film, cathode erosion, new technological capabilities of the arc, types of oxide cathode design

More than 100 years have passed after invention by Wenelt of oxide cathodes of electron tubes, which are widely used in electron technology [1].

Oxide cathodes of that time represented a mixture of oxides of such alkaline-earth metals as calcium, strontium and barium. As far as they are notable for high hygroscopicity, it was difficult to manufacture cathodes from them, and because of this reason pallets of oxide cathodes were produced not from oxides, but from carbonates of mentioned metals. In such case operations, connected with production of oxide cathodes, could be carried out in open air without being afraid of humidification of the powders, and then the pallets were subjected in tubes to annealing for the purpose of removing from them carbon dioxide and activation of the oxide cathode material.

From the viewpoint of state-of-the-art chemistry of solid body [2], process of the cathode activation is a process of destoichiometrization of oxides. For this purpose a cathode was heated in vacuum up to 1000 K and direct current was passed through the oxide pallet, the value of which was gradually increased, whereby electrolysis of oxides took place. Oxygen ions, moving in electric field of the pallet, reached its interface with vacuum cavity of the tube and released their electrons into general current of the cathode emission. Oxygen ions themselves passed after electric neutralization in the form of oxygen molecules into cavity of the tube and were absorbed by the getter. In this way material of the cathode was enriched with alkaline-earth metals ---- elements with low electron work function. As a result of development of the works devoted to the oxide cathodes record low values of electron work function were achieved at that time ---- 1.00-- 1.25 eV (nickel cores of tubes impregnated with barium and strontium).

Classical cathode material ---- tungsten, despite rather high electron work function (4.52 eV) [3] in heating up to 2500 K is able to emit electron current up to 500 mA from each square centimeter of open cathode area, while some oxide cathodes showed at lower temperatures emission current density  $1 \cdot 10^4$  mA/cm<sup>2</sup>.

It turned out that it was impossible to use ingenious development of Wenelt in cathodes of welding electric arc, because for stable work of the welding arc it is necessary that mean density of current on the surface of a non-consumable cathode of welding arc, in addition to the current density in the cathode spot, exceeded mentioned density in the tubes at least by three orders [4]. In this connection it was necessary to carry out investigation for the purpose of developing a new cathode material for work of the arc in open air and oxygen-containing gases.

Three parts of information were written on the basis of materials of these investigations. In the first one principal ideas on chemical composition of oxide cathode of electric arc and its design are presented; the second one is devoted to structure of the cathode and form of existence of separate components of the cathode in solid active insert, liquid emission film, and arc atmosphere; in the third one original properties of produced arc discharge are considered.

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The E.O. Paton Electric Welding Institute of NASU started development of oxide cathodes of electric arc early in 1980s. By that time in welding equipment existed arc torches with so called zirconium cathode [5]. They originated in the USA and started to be used first of all for plasma arc cutting of metals [6]. Both argon and compressed air were used as a plasma gas.

Those were the first oxide cathodes of electric arc, in which zirconium oxide was used as cathode. American inventors themselves called these cathodes zirconium ones [6], and then all those, who borrowed from them this kind of cathodes, followed their example without going into the heart of the processes, which proceeded in the emission film [5].

However, in reality it was not zirconium that was used in cathodes of these torches, but a thin film of destoichiometrized zirconium dioxide in liquid state [7]. In these torches prior to the work a thin (2.0--2.5 mm diameter) zirconium or hafnium wire of maximum 4 mm length is pressed into copper water-cooled holder of the active insert. They try not to use wire of bigger diameter, because in this case erosion of the cathode sharply increases. The wire is used as active insert of the cathode. Its open end remains metallic only till the first ignition of the electric arc in air. Within extremely short time after ignition of the arc the metal is oxidized and zirconium dioxide, not having reached complete stoichiometry, remains in this form during the whole process of the arc operation. This phenomenon may be explained by rather high electric conductivity of destoichiometrized dioxide, sufficient for maintaining stable operation of arc discharge and low, in comparison with  $ZrO_2$ , electron work function. If oxidation of zirconium in the film were complete, burning of the arc discharge hardly would be possible even despite liquid state of the film, because of high electrical resistance of  $ZrO_2$  [8].

As proved long-term experience of operation of these torches, liquid oxide film of destoichiometrized zirconium dioxide is a good emitter for maintaining operation of the arc discharge.

Processes, which proceed in this film, were studied by authors of [9] and later they were added in [7, 10, 11] by study of chemical composition of the emission film.

The work function of electron emitted from destoichiometrized zirconium dioxide is rather high and makes up (depending upon degree of destoichiometrization of the oxide emission film) from 3.1 to 5.8 eV [3, 9], whereby high voltaic equivalent was also registered. Nevertheless, the burning of the arc is stable; form of the arc flame has a bell-like shape; the arc has a falling volt-ampere characteristic [5, 9].

Both shape of the arc flame and volt-ampere characteristic differ little from similar parameters of tungsten arc in argon. In this connection longitudinal gradient of voltage in the arc column is almost the same as in other freely burning arcs. The range of operation currents of the considered arc is usually maintained within 100--250, seldom 300 A. At higher current values the cathode active insert quickly burns out. Even in operation at mentioned currents service life of considered electrodes is rather short because of high heat input into the cathode. The cathode is especially intensively destroyed at the instant when the arc is ignited: solid emission film, which remained from previous operation of the arc, peels off from open surface of the cathode insert, not having time to melt.

Numerous attempts to improve operation of the considered cathodes by alloying zirconium or hafnium with elements of IIA sub-group of the periodic table were not crowned with success [12], because compact zirconium, as other reactive metals, is produced in vacuum-arc furnaces, and during melting of zirconium, barium, strontium and calcium, which have high vapor pressure, never preserve in it in any noticeable amounts.

When designing oxide cathode for welding electric arc we proceeded from the fact that the best base is destoichiometrized  $ZrO_2$ , and the best emission additives are oxides of alkaline-earth metals. As far as the technology itself of producing mixtures of these two components is concerned, we used for this purpose powder metallurgy. It allowed introducing into the alloy with zirconium dioxide any amounts of barium or strontium oxides.

Design of the developed oxide cathodes was similar to the one of their predecessors (Figure 1, *a*). The difference consisted in increase of the active insert diameter in copper water-cooled holder, depending upon allowable currents of the arc burning in air: up to 3 mm ( $\leq$  400 A), 4 mm ( $\leq$  650 A), and 5 mm ( $\leq$  800 A). Surface of internal cavity of the holder was produced without a stagnation point. It allowed intensifying heat transfer from copper wall to the water flow and bring heat transfer coefficient without water boiling up to 60 W/ (cm<sup>2</sup>·K).

Oxide cathodes were produced by pressing into copper water-cooled holder of active insert of the cathode, which represented a mixture of metal zirconium in the form of powder (more cheap than compact metal) and refractory Ba-containing salt in the form of a finely dispersed powder. The most appropriate for being used as the latter turned out to be cheap components of heat-resistant cements; other technological additives were also used, application of which improved certain properties of the designed cathode. In particular, powdered copper was added for increasing electric conductivity of the active insert. When oxide film was formed in the process of the arc operation, it completely evaporated and copper was never detected in composition of the emission film.

In addition to mentioned design of cap-type cathodes for operation on currents 15--100 A, pencil cathodes were manufactured (Figure 1, b).

Oxides of alkaline-earth metals are characterized by excellent thermal emission properties [13]. The



Figure 1. Cap-type and pencil oxide cathodes: a — appearance; b — section; 1 — copper holder; 2 — active insert; 3 — emission film

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electron work function, for example from BaO, makes up only 0.97--1.10 eV. In regard to this parameter barium oxide outstrips even cesium,  $\phi$  of which is significantly higher ---- 1.38--1.80 [3].

Despite so high level of emission properties, barium oxide is not, unfortunately, preserved at the temperatures of the non-consumable cathode of electric arc. Melting point of BaO is almost by 800 degrees lower than that of  $ZrO_2$ . So,  $T_{melt}$  of zirconium dioxide is 3003 K [14], BaO ---- 2196 K [13], normal boiling point, i.e. temperature, at which oxide vapor pressure above its melt achieves 0.1 MPa, equals for  $ZrO_2$ 4573 K, and for BaO ---- 3000 K [13].

According to the data of [15], temperature of electric arc cathode spot on zirconium dioxide achieves 4000 K. At this temperature barium oxide uncontrollably quickly transits in free state into gaseous phase without exerting any influence on operation of the electric arc. At the same time it is necessary that barium oxide be continuously fed into atmosphere of the arc while it operates. In connection with this the



**Figure 2.** Fusibility curve for system ZrO--Bao:  $A - \gamma ZrO_2$ ;  $B - \gamma ZrO_2 + liq$ ;  $C - \beta ZrO_2$ ;  $D - \beta ZrO_2 + liq$ ;  $E - \beta ZrO_2$ ;  $G - BaZrO_3 + liq$ ;  $H - BaZrO_3$ 

need occurred to learn how to maintain barium oxide in the emission film in such way that rate of its evaporation be controllable. The decision consisted in creating conditions for formation of thermodynamically strong chemical compound between zirconium dioxide and barium oxide. These requirements are met by barium metazirconate  $BaZrO_3$ , exactly monozirconate, but not other compounds in the  $ZrO_2$ -BaO system.

When analyzing constitution diagram of the  $ZrO_2$ --BaO system (Figure 2), one can see that this compound has acute maximum on liquidus line, which proves high thermodynamic strength of this compound in molten state [16]. Really, melting process of BaZrO<sub>3</sub> is congruent ---- in transition into liquid state barium metazirconate does not disintegrate into constituting it oxides.

Comparison of properties of barium metazirconate and its analogues shows that barium metazirconate has the highest thermodynamic strength (Table). It should be also noted that the melt temperature increase insignificantly affects strength of bond between constituting this compound oxides, i.e. the melt temperature increase does not cause intensive dissociation of the considered zirconate.

Attention has to be also paid to crystalline structure of all mentioned in the Table metazirconates, which represent the lattice of cubic perovskite (Figure 3).

Perovskites (generalized formula  $ABO_3$ ) are widely distributed in nature. In technology some of them are successfully used as ferroelectrics, for example BaTiO<sub>3</sub>, and superconductors. In our case big cation *A* is presented by barium, while small cations *B* are presented by zirconium. Oxygen ions O are

Metazirco-	T <sub>melt</sub> ,	ΔÍ <sub>Ò</sub> ,	$\Delta S_{\dot{O}}$ ,	$\Delta G_T$ , mol, at $\hat{O}$ , K				
nate	K	kJ∕ mol	J∕ mol	2800	3000	3200		
BaZrO <sub>3</sub>	2860	134.3	2.1	140.2	140.6	141.0		
SrZrO <sub>3</sub>	2910	81.6	3.6	91.7	92.4	93.1		
CaZrO <sub>3</sub>	2780	24.4	11.5	56.6	58.9	61.2		



Figure 3. Elementary lattice of perovskite

located in the middle of each edge of cubic lattice. The perovskite lattice structure itself shows that for destruction of the lattice and disruption of the bonds of a surrounded on all sides barium ion significant energy is needed.

Perovskites of ideal structure are dielectrics, while non-stoichiometric perovskites are rather good electrical conductors. They are usually characterized by deficit of oxygen, index of which A + B/O varies from 1.083 to 1.167. For perfect crystal this index equals 1.5.

Only due to mentioned chemical compound it became possible to design oxide cathodes of electric arc for operation on currents up to 1000 A in argon and up to 750 A in air at specific erosion  $2 \cdot 10^{-8}$  g/C. So low rate of erosion is registered only in tungsten electrodes in argon, because in the process of the electric arc discharge burning the bulk of barium oxide in liquid emission film is bound with zirconium dioxide in the form of destoichiometric barium zirconate, and because of this reason is strongly retained in the melt. A portion of barium in the form of  $BaO_{1-\gamma}$  is dissolved in liquid destoichiometric  $\mathrm{ZrO}_{2\text{--}x}$  and is constantly in equilibrium with barium oxide in zirconate. Barium oxide transits into atmosphere of the arc from the solution, into which new its portions are fed from zirconate. So, barium zirconate is a «reservoir» of volatile barium oxide and creates conditions for its gradual evaporation from the emission film.

As far as thickness of the emission film makes up just tenth shares of a millimeter, transition of  $BaO_{1-\gamma}$  from zirconate to the interface between the film and the arc atmosphere occurs in the diffusion way (Figure 3). Barium concentration on open surface of the



Figure 4. Scheme of barium distribution over emission film thickness:  $\delta$  — final film thickness

film increases because of its surface activity in the molten dioxide (Figure 4).

So, developed for welding and related technologies oxide cathode of electric arc with non-consumable electrode-cathode is out of competition with other non-consumable electrodes, in particular with a tungsten cathode. The latter may operate only in the atmosphere of shielding gases, most frequently in argon, while oxide cathode may operate in any O-containing atmosphere, up to pure oxygen.

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