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TENDENCIES OF DEVELOPMENT OF SPECIAL ELECTROMETALLURGY OF TITANIUM IN UKRAINE

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The analysis was carried out on the main tendencies of development of special electrometallurgy of titanium in Ukraine. It is one of five countries, having complete cycle of titanium production from extraction of titanium-containing ores, their enrichment and production of spongy titanium to melting of titanium alloy ingots and production of virtually complete spectrum of titanium semi-products. Metallurgical processing of spongy titanium into ingots in Ukraine is based on technology of electron beam melting with cold hearth, which finds wide application in the world for melting of ingot-slabs. This technology provides guaranteed removal of refractory inclusions and the possibility to get the ingots of various cross-section per one remelting from charge materials of low price that ensures high technical-economical indices of melting process. Production of semi-products of titanium alloys from the ingots was organized at the Ukrainian enterprises. There are castings, forgings, rods, hot- and cold-rolled pipes, mechanical properties of which correspond to requirements of the standards. Today Ukraine has got a competitive for the world's markets production of high-quality ingots and ingot-slabs from titanium and alloys on its basis, which has large perspectives for further development. 8 Ref., 1 Table, 10 Figures.

Keywords: *titanium, electron beam melting, ingot, quality, refractory inclusions*

Titanium and alloys on its basis are unique structural materials, which allow significantly increasing service characteristics of new equipment. Due to high specific strength and good corrosion resistance, they have found wide application in rocket- and aircraft construction, power and chemical machine building, shipbuilding and production of medical equipment, including endoprostheses and implants.

Ukraine is one of five countries in the world, having complete cycle of titanium production from extraction of titanium-containing ores, their enrichment and production of spongy titanium to melting of titanium ingots and production of virtually complete spectrum of titanium semi-products, namely castings, forgins, rods, pipes and wire.

The main deposits of titanium-containing ores are concentrated in Dnepropetrovsk and Zhytomyr regions. Their enrichment is carried out at Volnogorsk Mining and Smelting and Irshanskii Mining and Processing Combines, respectively. These Combines not only completely provide with raw materials the Ukrainian producers of spongy titanium and pigmentary titanium dioxide, but supply titanium concentrates for export.

Production of spongy titanium in Ukraine at Zaporozhye Titanium & Magnesium Combine (ZTMC) is based on technology of melting of ilmenite concentrates in ore-thermal furnaces with production of titanium slags containing TiO_2 as in rutile concentrates. Moreover, cost of such slags is approximately 1.5 times less than rutile cost. Spongy titanium is obtained after slag chlorination in salt chlorination units by magnesium reduction of titanium tetrachloride. Now ZTMC has mastered production of the blocks of spongy titanium of 0.7 and 3.8 t weight per cycle and melting of ingots in the electron beam unit developed at the E.O. Paton Electric Welding Institute.

Regardless the fact that technology of vacuum-arc remelting (VAR) of titanium is traditional and more widespread industrial method for production of ingots of titanium and alloys on its basis, in the recent years the technology of electron beam melting with cold hearth (EBM) has found more and more application in titanium metallurgy. The latter differs by a series of advantages in comparison with traditional method of ingot production, namely vacuum-arc remelting:

- complete elimination from a technological cycle of an operation of consumable electrode pressing, which requires special pressing equipment of large capacity or specialized welding equipment;
- possibility of production of ingots of round as well as ingot-slabs of rectangular cross-section used as billets for sheet products production;
- guaranteed removal of refractory nonmetallic inclusions in the cold hearth, increase due to this of quality of ingots' metal;

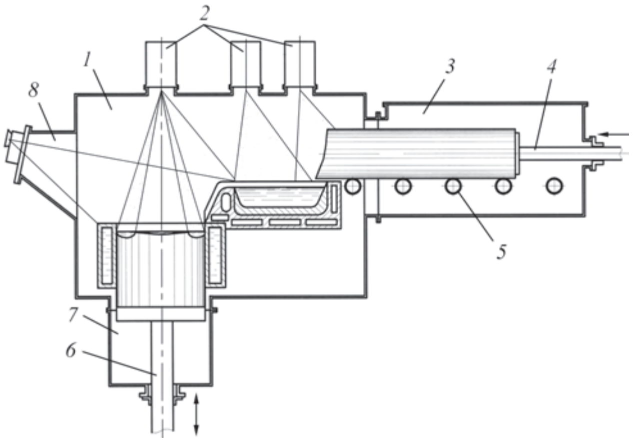

Figure 1. Scheme of unit: *1* — melting chamber; *2* — electron guns; *3* — billet chamber; *4* — billet feed mechanism; *5* — roll table; *6* — mechanism of ingot drawing; *7* — ingot chamber; *8* — view system

• obtaining the structurally and chemically homogeneous ingots with equiaxial structure;

• increase of metal yield due to reduction of amount of remelts (one instead of two-three).

EBM process is carried out in high-vacuum at the electron beam unit chamber (pressure of residual gases in the melting chamber is kept in 0.01–1.00 Pa range) and lies in successive melting of initial charge into the cold hearth under effect of heating with electron beams, melt refining in the cold hearth and its pouring down in a intermediate copper water-cooled mould, where ingot formation takes place (Figure 1).

Up to the moment there are 32 electron beam units of megawatt class in commercial operation in China, Japan and Ukraine and three more are in construction stage. Germany and Kazakhstan each have got one electron beam unit of megawatt class for melting of titanium ingots. Such a wide application of EBM technology is caused by good quality of obtained metal as well as high technical-economical indices of the process, in particular, in melting of ingot-slabs of rectangular section. Usage of the ingot-slabs allows eliminating from the technological chain of titanium rolled stock production a capital intensive and energy-consuming operation of reforging of cylinder ingots into slabs. The mechanical properties of hot-rolled sheet produced from titanium ingot-slabs completely correspond to the requirements of domestic and foreign standards.

An important problem in production of titanium ingots and semi-products is the problem of removal from metal of refractory inclusions with increased content of interstitial impurities, namely nitrogen, oxygen and carbon stabilizing α-phase. They consist of solid particles of α-titanium, saturated with these impurities as well as compounds of these elements with titanium, i.e. nitrides, oxides and carbides [1]. Besides, a serious problem is also inclusions formed

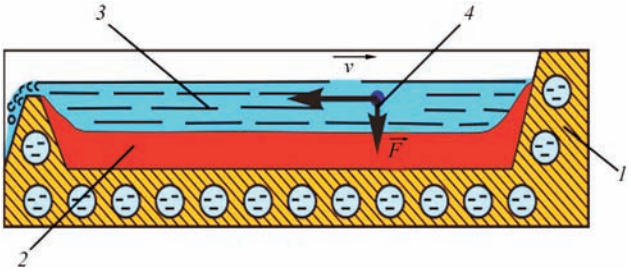

Figure 2. Scheme of process of refractory inclusion deposition: *1* — cold hearth; *2* — scull; *3* — melt; *4* — refractory inclusion

by compounds with large density and high melting temperature. A source of their formation is, as a rule, fractions of cutting tool based on carbides of refractory metals (WC, MoC, and others), which enter the metal together with charge components, most often, with chips [2]. Presence of such refractory defects in the products from titanium significantly reduces fatigue characteristics of metal.

One of the main mechanisms of removal of refractory inclusions from titanium is their gravitation settling: in process of melting the liquid metal in the cold hearth flows horizontally, whereas inclusions with higher density than density of liquid titanium go down under effect of gravity force (Figure 2), deposit on the surface of scull and freeze in it.

The investigations carried at the E.O. Paton Electric Welding Institute of the NAS of Ukraine showed that in process of EBM virtually all refractory inclusions, except for titanium dioxide, will be deposited on the bottom of cold hearth and removed from the melt. Found dependencies allow determining the dimensions of cold hearth, which will provide guaranteed removal of the refractory inclusions from titanium by means of their deposition (Figure 3).

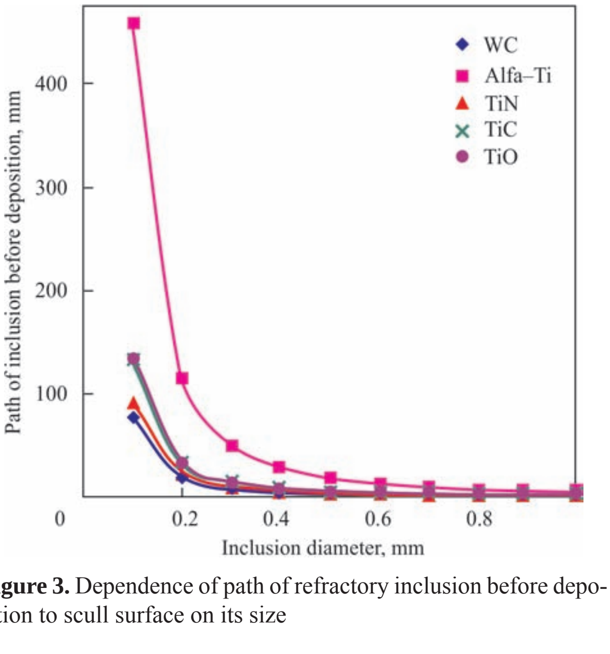

Figure 3. Dependence of path of refractory inclusion before deposition to scull surface on its size

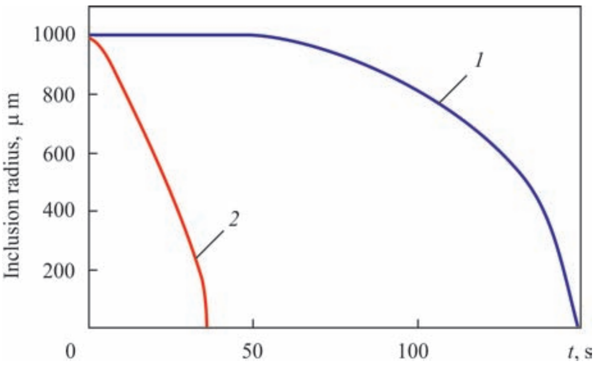

Figure 4. Dependence of radius of α-Ti inclusion on time of staying in the melt: *1* — T = 1950; *2* — 2000 K

Regardless the fact that temperature of melting of the low density refractory inclusions can significantly exceed the temperature of titanium melting, and, respectively, melt temperature, entering of such inclusions into the titanium melt provokes process of their dissolution. A mechanism of dissolution of LDI inclusions in the titanium melt was studied experimentally [3] as well as theoretically [4] and is caused by diffusion processes of interstitial impurities (nitrogen, oxygen and carbon) from inclusion volume to the melt.

Investigation of the process of dissolution of the refractory inclusions showed that the nature of dissolution of these inclusions significantly depends on melt temperature [5]. Thus, for example, α-titanium particle dissolves virtually at constant speed (displacement speed of interphase surface makes around 28 μm/s) at overheating of titanium melt by 59 °C over titanium melting temperature, whereas at overheating by 9 °C, dissolution speed of such particle is considerably nonlinear, i.e. at initial stage the dimensions of inclusions remain virtually the same, and then its dimensions start reducing with rising speed up to complete dissolution (Figure 4).

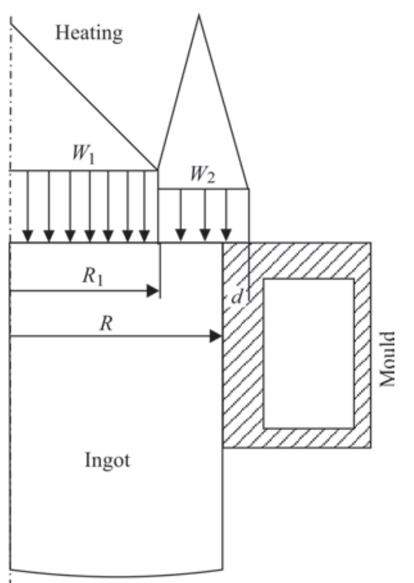

Figure 5. Scheme for modeling a process of formation of cylinder ingot in EBM

Also, the time of complete inclusion dissolution for solid particles of different chemical compositions and dimensions was determined. Thus, the investigation of processes of dissolution of refractory inclusions (particles of α-titanium, nitride, carbide or titanium oxide) in liquid titanium allowed calculating the speed of their dissolution and determining the time of complete dissolution of such inclusions depending on chemical composition and initial dimensions.

EBM technology provides not only high refining from detrimental impurities and nonmetallic inclusions, but significant improvement of ingot structure. This is caused by division of the processes of melting and refining of metal in the cold hearth and solidification of metal in the mould.

E.O. Paton Electric Welding Institute of the NAS of Ukraine has developed a mathematical model of heat processes in EBM [6] for determination of dependencies of solidification of ingots from titanium alloys. This mathematical model allows getting distribution of temperatures in the ingot at any moment of time, and, respectively, configuration of liquid pool and zone of solid-liquid state of metal depending on technological parameters of electron beam melting, i.e. efficiency of process, frequency of melt pouring into the mould and power of electron beam heating.

The model considers the process of ingot formation in a copper water-cooled mould (Figure 5).

The ingot surface is heated with two electron beams, moreover power of one of them is uniformly distributed in the central zone ($0 < r < R_1$) and another in the periphery zone ($R_1 < r < R$). The controlled technological parameters in the mathematical model are the power of central and periphery beams W_1 and W_2, value of portion, frequency of pouring, melting efficiency. A heat transfer process is described by a heat conductivity equation in the cylinder system of coordinates (r, o, z) for a case of axial symmetry, where axis OZ matches with the ingot axis (symmetry axis), and axis OR with radial direction. Start of the coordinates is set at lower end face of the ingot. The heat conductivity equation in this case has the next form:

$$\tilde{n}\rho \frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda(T)\frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z}\left(\lambda(T)\frac{\partial T}{\partial z} \right), \quad (1)$$
$$0 < r < R; \quad 0 < z < s(t); \quad t > 0.$$

where T is the temperature; C is the specific heat capacity; ρ is the material density; λ is the heat conductivity; $s(t)$ is the current position of ingot upper end face.

Heat application due to heating with electron beams and radiation of heat on Stefan-Boltzmann law takes place in the upper end face of the ingot. A

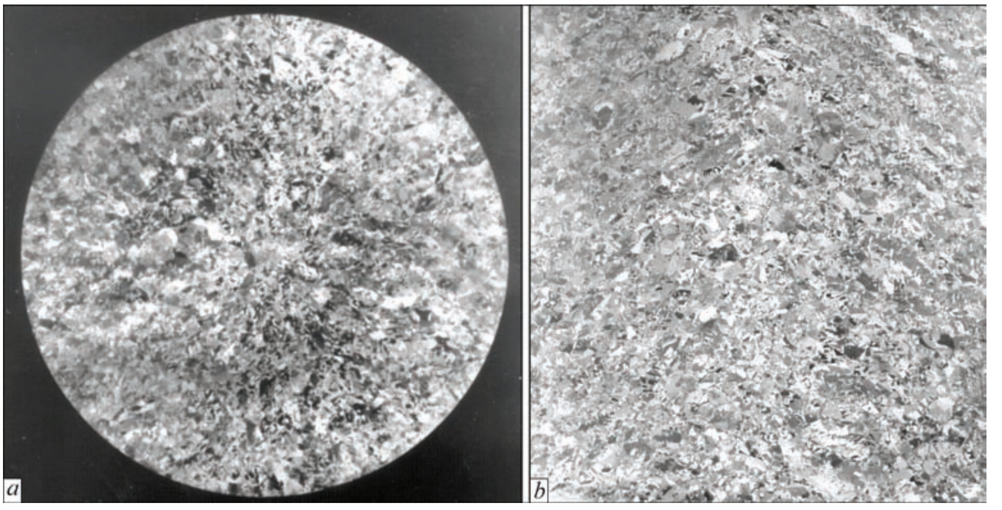

Figure 6. Macrostructure of VT6 titanium alloy ingot in cross (*a*) and longitudinal (*b*) sections

boundary condition on upper end face of the ingot is presented in form of

$$\lambda(T)\frac{\partial T}{\partial z}\bigg|_{z=s(t)} = -\varepsilon\sigma(T^4 - T_{\text{med}}{}^4) + w(r,t), \quad (2)$$

at that specific power of electron beam heating $w\,(r,\,t)$ is distributed in the following way:

$$w(r,t) = w_1(t) \text{ at } r < R_1;$$

$$w(r,t) = W_2(t)\sin^2\pi\left(\frac{r - R_1}{R + d - R_1}\right) \quad (3)$$

$$\text{at } R_1 < r < R.$$

On side surface of the ingot, contacting with the walls of mould and bottom plate, the heat exchange takes place on Newton–Richmann law

$$-\lambda(t)\frac{\partial T}{\partial r}\bigg|_{r=R} = \alpha(T - T_{\text{med}}), \quad (4)$$

where α is the coefficient of heat transfer between the ingot and copper water-cooled wall; T_{med} is the temperature of medium having heat exchange with the ingot.

On the free side surface of the ingot, the heat exchange is described by Stefan–Boltzmann law:

$$-\lambda(t)\frac{\partial T}{\partial r}\bigg|_{r=R} = \varepsilon\sigma(T^4 - T_{\text{med}}^4). \quad (5)$$

The results of calculation on the mathematical model of heat processes in titanium ingot at EBM showed that varying a power of electron beam heating of the melt free surface in the mould and melting rate, it is possible to change the volume of liquid pool metal and shape of solidification front, thus, controlling formation of ingot structure [6]. Carried full-scale experiments on melting of titanium ingots at different technological modes showed high level of adequacy of the designed models and proved the possibility of production of ingots from titanium and its alloys with fine equiaxial structure in performance of melts with the optimum technological parameters (Figure 6).

In melting of titanium alloy ingots by EBM method there is a problem of providing a set chemical composition of metal. It is caused by the fact that in EBM the alloying elements with vapor pressure exceeding titanium vapor pressure evaporate more intensively than in VAR. Aluminum, chromium, manganese and others refer to such elements. But, first of all, it refers to aluminum, since it is an alloying element of virtually all titanium alloys.

Carried at the PWI fundamental investigations of the processes of alloy components evaporation from the melt in vacuum under conditions of heating of surface with electron beam allowed designing the mathematical models of processes of evaporation of alloy components in EBM [6, 7]. They set the dependence of concentration of alloying elements in titanium ingot from the technological parameters of melting and concentration of these elements in consumed billet:

$$\frac{\partial}{\partial t}\int_{V_j}\rho[X_i]_j\,dV = m_{j-1}[X_i]_{j-1} - S_j\pi_j^i - m_j[X_i]_j;$$

$$\frac{\partial}{\partial t}\int_{V_j}\rho[\text{Ti}]_j\,dV = m_{j-1}[\text{Ti}]_{j-1} - S_j\pi_j^{\text{Ti}} - m_j[\text{Ti}]_j, \quad (6)$$

where $i = 1, 2 \ldots n$ indicate alloying elements; $j = 1, 2, 3$ are the melting zones (film of liquid metal on the end face of consumable billet, pools of liquid metal in the cold hearth and in the mould); V_j is the volume of liquid metal in jth zone of melting, m^3; ρ is the melt density, kg/m^3; $[X_i]_j$ is the concentration of ith alloying element in jth zone of melting, mass fraction; $[\text{Ti}]_j$ is the concentration of titanium in jth zone of melting, mass fraction; S_j is the area of liquid metal free surface in jth zone of melting, m^2; π_j^i and π_j^{Ti} are the specific flows of alloying elements and titanium through interphase surface into vapor phase in jth zone of melting, kg/(s·m^2); m_{j-1} is the mass velocity of melt coming in

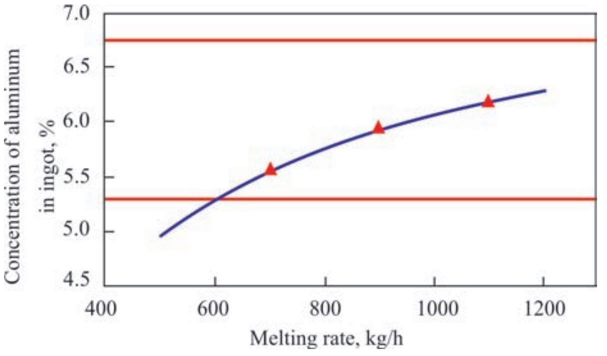

Figure 7. Dependence of aluminum content in EBM ingot of VT6 alloy on melting rate (solid line — calculation; dots — experiment)

jth zone of melting, kg/s; m_3 is the mass velocity of melt solidification in the mould, kg/s.

The dependencies of content of aluminum in the ingot on melting rate were plotted by the example of evaporation of aluminum from the melt of titanium alloy Ti–6Al–4V (wt.%) in vacuum using mathematical model (4). Comparison of data of experimental melts of Ti–6Al–4V titanium alloy ingots with obtained dependencies showed high accuracy of description of developed model of real process of aluminum evaporation in EBM (Figure 7).

Application of these models allows predicting compositions of melted titanium alloy ingots and providing production of the ingots with guaranteed composition. Compensation of component loss of alloys with high vapor pressure in EBM is carried out by additional alloying with these elements of initial charge. Homogeneity of distribution of alloying elements on ingot volume has great importance in melting of titanium alloy ingots. Under EBM conditions this is provided by homogeneity of burdening of consumed billet, stability of technological parameters in melting and special technological means.

Carried complex of theoretical and experimental investigations of the EBM process allowed developing a technology for production of high-quality ingots of high-strength and heat-resistant titanium alloys of up to 840 mm diameter and design equipment for their commercial realizing (Figures 8, 9).

Figure 9. Appearance of commercial electron beam unit UE5812

For evaluation of metal quality in produced ingots there were carried out an examination of composition of the samples taken on length of the ingot from upper, middle and lower parts. The results of analysis of metal composition of the produced ingots (Table) showed that distribution of alloying elements on ingots' length is uniform and correspond to grade composition. EBM titanium alloy ingots have no inhomogeneities, nonmetallic inclusions of more than 1 mm size as well as dense accumulations of finer inclusions. Metal structure is dense, crystalline inhomogeneity and zonal liquation are absent in the ingot.

In process of ingots production due to a series of reasons, caused by metallurgical and technological peculiarities, their surface layer turns out to be defective. In order to eliminate such defects the surface of produced ingots and cast billets are subjected to mechanical treatment, as a result of which amount of wastes can reach up to 15 % of weight of treated ingot.

In order to reduce metal loss instead of mechanical treatment the PWI has developed a technology of electron beam melting of side surface of ingots of round as well as rectangular section by electron

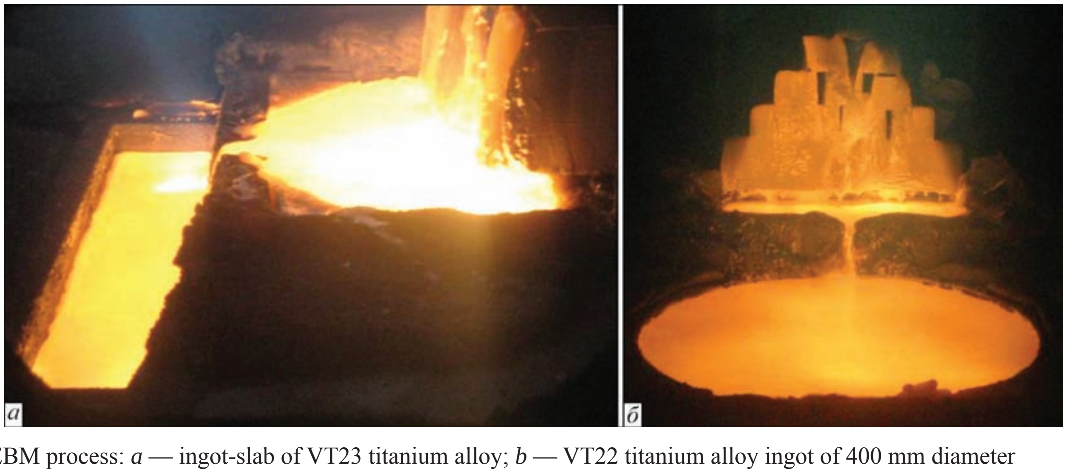

Figure 8. EBM process: *a* — ingot-slab of VT23 titanium alloy; *b* — VT22 titanium alloy ingot of 400 mm diameter

Distribution of alloying elements and impurities on length of titanium alloy ingots, produced by EBM,wt.%

Alloy grade	Ingot part	Al	Mo	V	Fe	Zr	Cr	O	N
VT23	Upper	4.5	2.0	4.7	0.5	0.01	0.9	0.11	0.012
	Middle	4.6	2.1	5.0	0.6	0.01	0.9	–	–
	Lower	4.3	1.9	4.7	0.5	0.01	0.9	–	–
OST 190013–81		4.0–6.3	1.5–2.5	4.0–5.0	0.4–1.0	<0.3	0.8–1.4	<0.15	<0.05
VT22	Upper	5.1	4.2	4.9	0.90	0.01	1.3	0.11	0.012
	Middle	5.2	4.5	4.7	1.0	0.01	1.4	–	–
	Lower	5.0	4.1	5.0	1.0	0.01	1.4	–	–
GOST 19807–91		4.4–5.7	4.0–5.5	4.0–5.5	0.5–1.5	<0.3	0.5–1.5	<0.15	<0.05
VT20	Upper	6.85	1.60	2.05	0.10	1.60	<0.1	0.08	0.019
	Middle	6.90	1.63	2.05	0.11	1.63	<0.1	–	–
	Lower	6.70	1.63	2.08	0.11	1.60	<0.1	–	–
GOST 19807–91		5.5–7.0	0.5–2.0	0.8–2.5	<0.25	1.5–1.5	<0.1	<0.15	<0.05

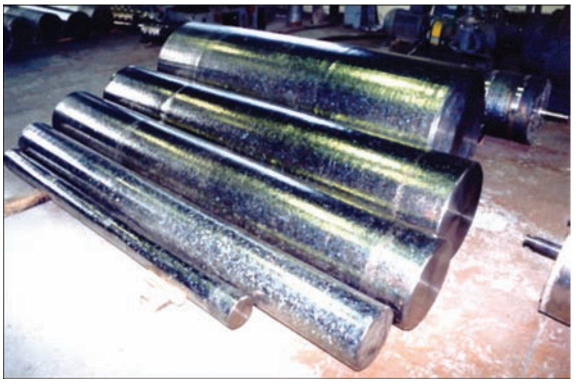

Figure 10. Appearance of titanium alloy ingots of 100–600 mm diameter with melted side surface

beams and corresponding equipment for its realizing (Figure 10). Developed technology provides effective removal of surface defects at up to 10 mm depth ensuring at that the quality of side surface and correspondence of composition of the melted layer at the level of requirements of standards, rising at that metal yield by 7–15 % depending on section and dimensions of the ingot [8].

Check of quality of the semi-products in form of rods and forgings, produced from EBM ingots, showed that their mechanical properties correspond to all the requirements, which the industry makes to titanium alloy quality. At that the semi-products are isotropic on mechanical properties.

In cooperation with the enterprise-partners, in Ukraine there was organized a production of hot- and cold-rolled pipes from the titanium alloy ingots, made by EBM method. Their quality completely corresponds to the standard requirements.

Developed at the E.O. Paton Electric Welding Institute of the NAS of Ukraine technological processes of electron beam melting provide the possibility to obtain high-quality ingots of titanium and its alloys with uniform defect-free structure. The developed technologies allow reducing prime cost of the titanium semi-products due to application of cheaper raw materials and increase of through metal yield and, thus, rising competitiveness and expanding fields of application of titanium in different branches of industry.

Realizing the EBM technology under conditions of commercial enterprises permitted to organize in Ukraine competitive on the world markets production of high-quality ingots and ingot-slabs of titanium, which have large perspectives for further development.

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