



Removal of mechanical additives from the surface of cast niobium

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Abstract. A combined method of the utilization of deposits from the shaft furnace of niobium production consisting of the stages of thermomechanical treatment, hydrogenation, grinding, and separation was elaborated in industrial conditions. This method enables to clean the surface of metallic niobium from slag ($3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$) and from graphite additives. Altogether more than 20 tonnes of Nb–Al (5%) powder meeting the requirements presented to commercial technical niobium was produced. Application of the proposed utilization technology increases the profitability of pure niobium production by 0.2–0.3%. The results obtained can be used for cleaning other refractory metals from slag and other surface additives.

Key words: wastes utilization, metallurgy, alloys production, shaft furnace deposits, thermomechanical utilization.

INTRODUCTION

In the ‘out-of-furnace’ process (i.e. without external heat access) of niobium pentoxide reduction in a shaft furnace on the graphite facing, a layer of deposit is formed in the zone where reactions and precipitation of molten products occur [1]. This is a result of physico-chemical actions between the compounds of the raw mixture, reduced metal, and slag with graphite. The reduction reaction proceeds at a significant temperature gradient between the furnace (2900°C) and on the surface of the facing ($18\text{--}20^\circ\text{C}$) in a few minutes (60–120 s). The mass of the niobium–aluminium ingots comprises about 2000 kg.

Compounds of raw mixture and products of the melt actively react with the material of the facing; processes of adhesion occur due to chemical reactions and mutual diffusion in the surface layer of the metal and graphite. The interfacial area between the deposit and graphite facing varies in the range $1.5\text{--}2.5\text{ m}^2$. Under the conditions where the temperature of the graphite facing at time zero is significantly lower than the temperature of the molten metal and slag [2], fast crystallization reactions proceed on its surface. The thickness of the deposit is in the range 10–80 mm with the total mass

over 70 kg. Coefficients of thermal expansion of graphite, slag, and metal differ by several orders [3], and during the cooling process of the products of the melt mechanical tensions (stress) appear at the interface of graphite–metal–slag. At the breaking load the most fragile compound, graphite, fractures (Fig. 1). A 5–15 mm deposit of graphite, which is impossible to remove mechanically, covers the surface of the metal that is in contact with this product.

During the preparation of the furnace for the following melting the deposit must be removed. The content of aluminium in the metal is 4.5–5.5% (mass), different admixtures comprise $10^{-1}\text{--}10^{-2}\%$ (mass). The metal is non-homogeneous in its chemical and phase composition and has different density through its volume.

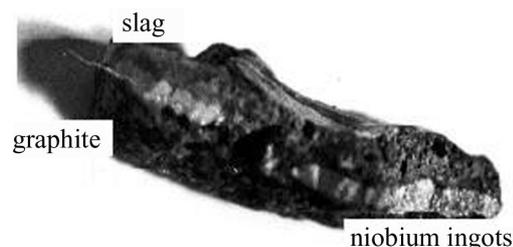


Fig. 1. Photo of a fragment of the deposit. Chemical composition of the slag: $3\text{CaO}\cdot 5\text{Al}_2\text{O}_3$.

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The deposit is an intermediate product and needs post-treatment for metal separation and utilization of graphite and slag. Statistical data obtained during a year of full-scale industrial meltings indicated that at the production of up to 2000 kg of ingots losses of niobium with the deposit comprise 1.25–2.84% and may even reach 3.33% [3]. At a capacity of 384 tonnes/year of niobium and average price of 40 \$/kg separation of niobium from the deposit would be justified [4].

For non-ferrous metals, technologies and apparatus for their separation and refining have been studied in detail and presented in the literature; however, for refractory metals (W, Mo, Ta, Nb), unsuitable for magnetic separation and grinding, only a few examples under concrete conditions have been described. For example, at Silmet Ltd. manual removal and refining of metal from slag and graphite has been applied. Lumps of metal are placed into the metal receiving hopper of the furnace, and during the next melting the molten metal precipitates on this material. However, temperature conditions in the shaft furnace do not allow total melting of the lumped product [2], and this has a negative impact on the quality of the following refining remelting the ingots in the electron-beam furnace.

In the 1990s a method of thermomechanical cleaning of metal from slag and graphite with the following grinding to powder and oxidative burning to niobium pentoxide was elaborated and tested at full scale at the Sillamäe Chemical Factory together with the Scientific Research Institute Mehanobr (St. Petersburg) and Scientific Research Institute of Chemical Technology (Moscow). Several tonnes of good quality commercial product were obtained. The elaborated technology enables to manage without manual work, to design a totally mechanized process, and to obtain niobium pentoxide with a stable composition. The results of the pilot and full-scale tests are of theoretical and practical interest, and, except a patent [5], have not been published earlier.

MATERIALS AND METHODS

A typical deposit from the shaft furnace containing metal and slag phases together with mechanical additives of graphite was studied. The following utilization procedures were carried out:

- thermomechanical treatment of the deposit at 900 °C for the removal of slag and graphite
- hydrogenation of metal
- grinding of the metal hydride to powder in a vibrating mill in the atmosphere of inert gas
- separation of the hydride powder in a gravitational apparatus (on a concentration table) from the non-metal product.

Thermomechanical treatment of the deposit was carried out in a rotary kiln VGTP-8 (length 8 m) in the presence of air. The efficiency of the process depends on the difference of the coefficients of thermal expansion of metal, slag, and graphite. Optimal regimes of temperature and residence time were established. The aim of the hydrogenation of metal was to make it more fragile and prepare it for grinding to powder in the atmosphere of argon.

For thermoanalytical examinations a derivatograph DuPont 1090 was used. The phase composition was studied with a diffractometer DRON-3M. The shape and particle size of the metal powder were established under an electron microscope JEOL JSM-840.

RESULTS AND DISCUSSION

Thermomechanical treatment of the deposit

Metal phase

The metal phase of the deposit is a niobium–aluminium (4–5%) alloy, a solid solution on the base of niobium with Brinell hardness of 750–780 MN/m² [3]. Melt from the shaft furnace in the form of ingots (180 × 180 × 700 mm) has similar physico-chemical parameters. For comparison, Brinell hardness of pure niobium is 450 MN/m². The strength of niobium does not change much with temperature: it is 342 MN/m² (34.2 kg/mm²) at 20 °C and 312 MN/m² (31.2 kg/mm²) at 800 °C. Differently from niobium–aluminium alloys, it is possible to compact pure niobium to a thin sheet.

Ingots from the shaft furnace with a small aluminium content are resistant at collisions and the refining process in the electron-beam furnace proceeds fast and without any eruptions of metal. The hardness of niobium–aluminium alloys (5.5–6.0% Al) is by 50–70 units greater than that of pure niobium or alloys with a small Al content. At the collisions of these ingots metal clasts (fragments) are liberated, breaking into 2–3 parts is also possible; difficulties in refining occur.

The grinding of the niobium–aluminium (4–5%) alloy to powder is possible only after preliminary hydrogenation. The hydrogenation reaction proceeds poorly when the surface of metal is covered with mechanical additives (slag, graphite). Heating the deposit up to 800–900 °C and applying the effect of thermal deformation simultaneously with mechanical forces makes it possible to obtain good results of separating the metal phase from slag and graphite.

Thermal deformation of materials is characterized by the coefficient of thermal expansion. The coefficient of linear expansion α is the relative extension of a coupon at the temperature increase by 1 °C. The coefficient of volumetric expansion (β) is equal to 3α . These coefficients are valid only below the melting temperature of the material [6].

Niobium and its alloys with aluminium belong to isotropic metals and for them a certain relation between the coefficient of linear expansion α and the melting temperature T_m exists:

$$\alpha = \varphi(T_m). \tag{1}$$

This function can be described by the following equation [7]:

$$\alpha = 0.13232 \cdot T_m^{-5/4}, \text{ K}^{-1}. \tag{2}$$

For the niobium–aluminium (5%) alloy $T_m = 2233 \text{ K}$ (1960°C).

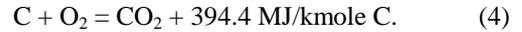
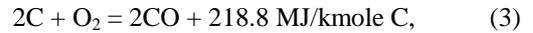
Equation (2) was used to determine the values of α for niobium–aluminium alloys and metals used in the reduction process (Fig. 2). The melting temperature was found on the basis of the phase diagram Nb–Al [8]. According to [9], pure niobium at $T_m = 2275 \text{ K}$ has the value of $\alpha = 6.8 \cdot 10^{-6} \text{ K}^{-1}$, and calculated from Eq. (2) the value is $\alpha = 8.38 \cdot 10^{-6} \text{ K}^{-1}$.

Graphite

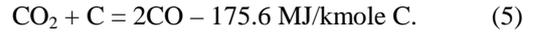
Physical properties of graphite depend on the orientation of the particles of coke from which it was formed by pressing. Graphite GMZ, applied for the facing of the shaft furnaces, is produced by the method of extrusion, and like other materials made by this method, has clearly exhibited anisotropic properties. Grains are oriented strictly perpendicularly to the direction of pressing and are able to resist big mechanical loads at high temperatures and also at steep temperature falls. Graphite GMZ is a great facing material for the high-temperature ‘out-of-furnace’ process, its coefficient of thermal expansion is $4.45 \cdot 10^{-6} \text{ K}^{-1}$ [10].

In the presence of excess air graphite starts to oxidize at 477°C [11]. Therefore, during the thermomechanical treatment of deposits from shaft furnace at

900°C the processes of gasification and burning take place:



Carbon dioxide in the zone of burning will be reduced by carbon to carbon monooxide CO:



Reactions (3–5) proceed in the intermediate regime, and their velocity depends on the kinetic as well as diffusion factors and on the degree of breaking and removal of graphite from the surface of the metal. During the thermomechanical treatment also some enrichment of the surface of the metal with carbon takes place, its content increases by 0.01–0.02%. Graphite is an excellent protector of metal from oxidation at 900°C.

Slag

Linear coefficients of thermal expansion α of slag (3CaO·5Al₂O₃) and graphite are close. When the temperature increases in the interval 200–900°C, coefficient α of slag does not change much – in the range $(60\text{--}79) \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ [12].

The large rugged area of the cast metal part of the deposit and the slag phase create very good conditions for mutual adhesion. The density of the slag phase (3CaO·5Al₂O₃) is at least 3.7 g/cm³. The bending strength of this constraint is 320 MPa (3200 kg/cm²). Only deformation changes can break it.

Thermomechanical treatment of deposits was carried out in a rotary kiln with a length of 8 m. The initial lumped material (max diameter 150 mm) of optional shape underwent treatment at different temperature and time regimes. After unloading the product was mechanically separated to metal and slag phases. The sample of metal was hydrogenated and ground. Data on the chemical composition of the metal obtained after thermomechanical treatment at 900°C are presented in Table 1.

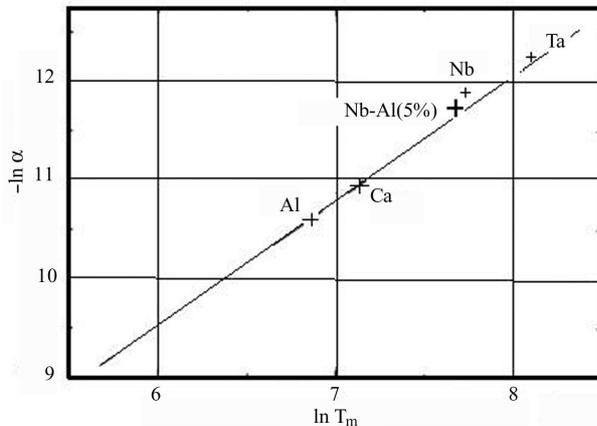


Fig. 2. Calculation of α in the logarithmic coordinates.

Table 1. Chemical composition of the metal obtained in the process of thermomechanical treatment of the deposit at 900°C

Duration of the process, min	Chemical composition of metal, % (mass)							Nb in the slag, %
	Nb	Al*	Ca*	Si	C*	N	Fe	
30	24.1	32.1	20.4	0.09	22.1	0.15	0.15	2.15
60	73.8	18.9	3.1	0.09	2.4	0.14	0.31	2.1
90	88.5	8.1	1.2	0.08	0.68	0.15	0.29	4.3
120	89.1	7.56	1.1	0.09	0.45	0.12	0.19	8.2

* – Result of analysis taking into consideration additives of the slag and graphite on the metal.

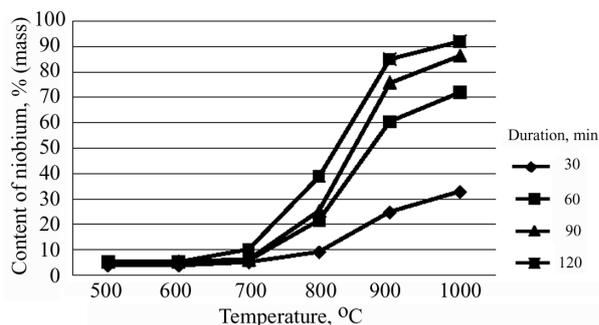


Fig. 3. Content of niobium in the alloy after thermal treatment depending on temperature at different durations of the process.

During a 120 min process the slag part of the deposit was enriched with niobium due to the oxidation of the open surface of the metal and transfer of niobium pentoxide into the slag. Phase analysis of the metal indicated presence (in decreasing order) of Nb, Al_2O_3 , and Nb_3Al . Figure 3 illustrates the dependence of the niobium content in the metal phase on the temperature of treatment at different durations of the process.

Hydrogenation

One of the most advanced methods for the preparation of powder from niobium ingots is the hydrogenation reaction. As a result a solid solution with the hydrogen content of up to 10 atom% containing $\text{NbH}_{0.7}$ to NbH is formed. Niobium hydride losses its strength very easily and undergoes grinding to any size. The hydrogenation technology elaborated for pure niobium [13] was used with minor changes. The retort with alloy was degassed up to the residual pressure of 10^{-1} to 10^{-2} mm Hg. Saturation of the alloy with hydrogen started at 750°C with step-wise reduction of temperature (Fig. 4). The total duration of the process was about 20 h. Differently from the hydrogenation of alloys extrapure hydrogen and dehydrogenation are not required. The parameters

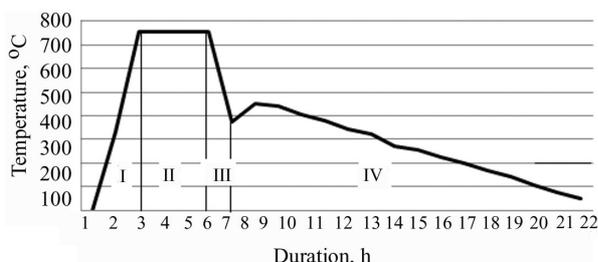


Fig. 4. Zones of the hydrogenation of Nb–Al alloy: I – heating up, degassing; II – hydrogenation; III – hydrogenation with temperature reduction, forced air cooling of the retort with product; IV – cooling down without air blow.

established coincide with the recommendations given in [14] for the technology of hydrogenation of refractory metals.

Grinding

Grinding of the hydrogenated Nb–Al alloy was performed in a vibrating mill MV, KPRU-700 [15]. Steel balls of different size filled 80% of the grinding chamber, the volume of hydrogenated alloy comprised the residual 20%. The duration of the process did not exceed 40 min. To prevent oxidation and autoignition of the powder grinding was carried out in the atmosphere of argon (at a pressure of 100 mm Hg). Table 2 presents data on the granulometric composition of the metal hydride after grinding, and in Table 3 chemical analysis of the powder obtained is given. It can be seen (Table 3) that the finest fraction ($-0.1+0.063$) mm has a reduced Nb content and an increased content of Al and Ca, which can be explained by the ‘break-through’ of the ground slag phase. At a very small size of the particles the van der Waals forces of molecular attraction prevail and formation of flocs (aggregates) takes place. Due to the abrasion of the steel balls in the mill some addition of iron (0.01–0.03% (mass)) was discovered.

Separation of the metal and slag phases on the concentration table

To separate the metal hydride from the non-metal phase gravitational enrichment on the concentration table SKO-2 was applied. This table can take the feed of sludge ($0.2+0.04$) mm and the feed of sands ($-3.0+0.2$) mm. Depending on the density the batch of

Table 2. Granulometric composition of metal hydride after grinding

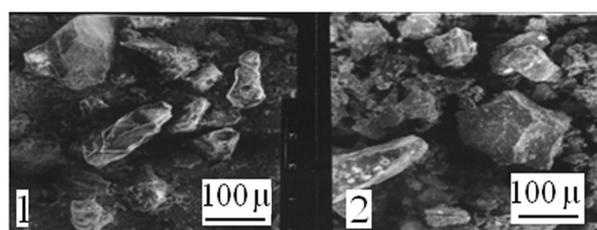
Particle size, mm	Content, %
–1.6+1.0	0.05
–1.0+0.63	0.05
–0.63+0.4	0.51
–0.4+0.32	3.04
–0.2+0.16	12.85
–0.16+0.1	31.78
–0.1+0.063	51.72

Table 3. Chemical composition of the powder, % (mass)

Fraction, mm	Nb	Al	Ca	Si	C	N	Fe
–0.63+0.4	92.5	6.32	0.72	0.11	0.8	0.13	0.24
–0.4+0.315	92.8	6.3	0.62	0.1	0.5	0.15	0.23
–0.2+0.16	91.4	7.3	0.92	0.1	0.35	0.14	0.23
–0.1+0.063	88.53	8.57	1.2	0.093	0.38	0.14	0.22

Table 4. Chemical composition of the products of gravitational enrichment

Product	Content, % (mass)			
	Nb	Al	Ca	C
Concentrate 1	94.5	4.1	0.38	0.12
Intermediate 1	19.0	26.29	13.63	0.8
Intermediate 2	18.0	23.96	10.37	9.0
Tailings 1	40.3	13.99	4.83	22.0
Concentrate 2	93.3	4.3	0.12	0.1
Intermediate 3	83.3	8.59	1.14	0.3
Intermediate 4	76.2	10.55	1.92	0.3
Tailings 2	70.6	12.51	2.56	1.0

**Fig. 5.** Results of the gravitational enrichment under electron microscope: 1 – concentrate; 2 – metal hydride powder before enrichment.

hydride powder can be divided into two parts: one is enriched with heavier fractions and has the minimum density of $\sim 8.0 \text{ g/cm}^3$, and the other has the density of $4.0\text{--}4.5 \text{ g/cm}^3$. However, on the table also the medium and intermediate products can be separated.

In Table 4 the chemical composition of the products of gravitational enrichment is given. The content of niobium in concentrate 1 is 94.5% and in concentrate 2 93.3%. In the intermediate products the content of niobium is lower and those of Al and Ca are significantly higher. Figure 5 illustrates the results of enrichment. The initial metal hydride powder with slag is in the form of volumetric splinters together with fine fractions (Fig. 5.2). After enrichment the fine fractions including residues of slag are removed (Fig. 5.1). The quality of concentrate 1 corresponds to the requirements presented to commercial technical niobium.

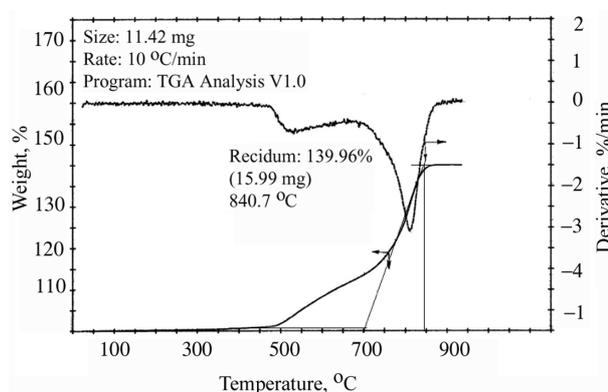
Safety problems

To prevent self-ignition (or autoignition) of the powder, the relevant tests were carried out (Table 5). At the ignition of the fraction $(-0.1+0.063) \text{ mm}$ the front of fire spread along the surface at a velocity of $0.1\text{--}0.2 \text{ mm/s}$, and after that descended into the lower layers. Burning proceeded quietly, with a small flame, which at the initial stage was soot-forming. Derivatographic analysis (Fig. 6) showed that the metal hydride of the fraction $(-0.1+0.063) \text{ mm}$ started to oxidize in the

Table 5. Temperature of self-ignition of Nb–Al (5%) hydride powder depending on the size of the particles

Fraction, mm	Temperature of self-ignition of the layer in the air, °C	Temperature of self-ignition of aerosol in the air, °C
0–0.04	330 ± 10	530 ± 10
0.01–0.04	370 ± 10	560 ± 10
0.04–0.063	450 ± 10	630 ± 10
$-0.1+0.063$	480 ± 5	–

– No self-ignition.

**Fig. 6.** Derivatogram of $(-0.1+0.063) \text{ mm}$ powder.

atmosphere of air at 350°C , activation of the reaction started at 480°C . An exothermic effect and maximum gain in mass occurred at the temperature of 840°C ; an endothermic effect, connected with the removal of hydrogen, can be followed in the temperature range $550\text{--}700^\circ\text{C}$. In the case of powders of larger grain size no spread of the flame across the layer was established.

According to [16] the fine-grained powder of pure niobium hydride ($<0.05 \text{ mm}$) is inflammable and explosive, and its concentration in the layer must be less than 3% (mass). Application of the inert gas argon keeps the process of oxidation under control; however, formation of the aerosol may cause safety problems.

CONCLUSIONS

A combined method of the utilization of the deposit from the shaft furnace consisting of the stages of thermomechanical treatment, hydrogenation, grinding, and separation was elaborated in industrial conditions. Thermomechanical treatment of the deposit was carried out in a rotary kiln at 900°C in the presence of air. The efficiency of the process depends on the difference in the coefficients of thermal expansion of the metal, slag, and graphite. Optimal regimes of temperature and

residence time were established. The aim of the hydrogenation of the metal was to make it more fragile in order to prepare it for grinding into powder in the atmosphere of argon. The retort with the alloy was degassed up to a residual pressure of 10^{-1} to 10^{-2} mm Hg. Saturation of the alloy with hydrogen started at 750°C with stepwise reduction of temperature. The total duration of the process was about 20 h. Grinding of the hydrogenated Nb–Al alloy proceeded in a vibrating mill. The duration of the process did not exceed 40 min. Gravitational enrichment gave two concentrates (1 – 94.5% of Nb, 2 – 93.3% of Nb), four intermediate products, and two tailings. Aluminium and calcium were concentrated into intermediate products and tailings. The quality of concentrate 1 corresponds to the requirements set to commercial technical niobium. Altogether more than 20 tonnes of Nb–Al (5%) powder was produced. Inflammability of the powder of different grain size in the air was studied.

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Mehaaniliste lisandite kõrvaldamine alumotermiliselt toodetud niobiumi jääkide pinnalt

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Töötati välja meetod niobiumi alumotermilise tootmise šahtahju seintele ladestunud jääkniobiumi puhastamiseks šlaki ja grafiidi lisanditest tööstuslikes tingimustes, kasutades termomehaanilist töötlust, hüdreerimist, jahvatamist ning separatsiooni. Tekkinud jäägi termomehaaniline töötlus viidi läbi pöördahjus temperatuuril 900°C õhu juuresolekul. Määrati töötlemise optimaalne temperatuuri režiim ja materjali viibimisaeg ahjus. Järgneva hüdreerimise eesmärgiks oli muuta saadud metalli sulam hapramaks ja valmistada ette järgneva pulbriks jahvatamiseks argooni atmosfääris. Hüdreeritud sulam Nb–Al jahvatati vibroveskis. Järgneva separatsiooni käigus eraldati Nb kontsentraat (93–95% Nb) alumiiniumi ja kaltsiumi rikastusjääkidest. Kokku toodeti üle 20 tonni Nb–Al (5%) pulbrit, mis kvaliteedilt vastas kaubanduslikule tehnilisele niobiumile. Väljatöötatud niobiumi jääkide utiliseerimise tehnoloogia võimaldab suurendada alumotermilise niobiumi tootmise protsessi rentaablust 0,2–0,3% võrra. Määrati toodetud niobiumipulbri süttimispiir.