



## Reduction of tantalum pentoxide with aluminium and calcium: thermodynamic modelling and scale skilled tests

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Received 20 November 2009, revised 22 March 2010, accepted 25 March 2010

**Abstract.** High reactivity of powdered aluminium together with its relatively low price are the main reasons for the application of this metal as a reducing agent for the reduction of oxides and fluorides of rare and rare earth metals by the aluminothermal method. This technology is widely used in the production of master alloys for ferrous metallurgy. The “out-of-furnace” process (i.e. without external heat access) is the prevailing technology for metallic niobium production worldwide. However, aluminothermal reduction for industrial production of metallic tantalum has been limited because of the high required temperature, over 2800 °C.

In this paper the results of simultaneous reduction of tantalum(V) and iron(III) oxides by calcium–aluminothermal “out-of-furnace” process are presented. Powdered aluminium and metallic calcium were used as reductants. The pickup of tantalum at smeltings with the mass of raw materials over 1 kg reached 94%. The metal was obtained in the form of compact ingot; separation of metallic and slag phases was excellent. Crushed melt underwent refining remelting in an electron beam furnace.

For thermodynamic studies and optimization of the aluminothermal reduction processes of Ta<sub>2</sub>O<sub>5</sub> and Fe<sub>2</sub>O<sub>3</sub> in the temperature range of 1000–3000 °C a licensed computer simulation program “HSC Chemistry 6.1, 2007”, elaborated by the company Outotec Oy, was applied.

**Key words:** rare metals, tantalum pentoxide, ferric(III)oxide, aluminium, calcium, “out-of-furnace” reduction, thermodynamic functions, computational analysis.

### INTRODUCTION

Tantalum belongs to the group of high-performance metals that have gained acceptance due to their several unique properties since the beginning of the technical revolution at the end of the 20th century. The technology for tantalum production has developed in several directions. The main technologies used nowadays worldwide are able to produce this metal of required quality. The world’s largest companies producing tantalum and its alloys are HC Starck-Bayer in Germany and Cabot Corporation in the USA. These

companies are responsible for about 85% of the world tantalum production in the form of ingots, powder, wire, and oxides.

However, changes in basic raw materials, extension of equipment capacities, and market requirements are evoking further studies in this field. Sodio-thermal reduction of potassium tantalum fluoride, K<sub>2</sub>TaF<sub>7</sub>, where metallic sodium is used as the reductant, is one of the first, but still in use, full-scale technologies [1,2]. Reduction is carried out in steel crucibles at a temperature of about 900 °C. The duration of the process is at least 2 min. Finely dispersed powder of metallic tantalum washed from the salts with about 2% oxygen content is led to a vacuum electric arc remelter and further to an electron beam furnace for deep refining.

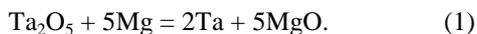
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Another, also widely used technology, applies chlorous treatment of the mineral raw material containing niobium and tantalum [1,2]. Pure tantalum chloride ( $\text{TaCl}_5$ ) is converted to  $\text{K}_2\text{TaF}_7$ , which is added to the melt of  $\text{NaCl}$  and  $\text{KCl}$  and after that electrochemically reduced from the melt  $\text{KCl-NaCl-K}_2\text{TaF}_7$  in the form of metallic tantalum powder (98–99% of Ta). Compact metal is produced by sintering the stocks pressed from powder at 2500–2700 °C or by heating them up to 2200–2500 °C under vacuum. The stocks are remelted by the electrovacuum process in an electric arc or electron beam furnace.

The processes described above allow manufacture of metallic tantalum of high quality, but are energy consuming and use complicated facilities. In Estonia (at the present Silmet JSC) the process of aluminothermal “out-of-furnace” reduction of oxides of rare and rare earth metals was introduced in full scale in the 1990s. The process took advantage of the exothermal effect of reactions. The quality of the tantalum produced corresponded to the requirements of the market and the process elaborated is outstanding having a high capacity. For example, according to [3], the maximum production capacity of Silmet JSC is 2000 kg per melt, which is unique in the world. According to [4,5], Silmet JSC produces 60–80 tonnes of metallic tantalum annually. Metals produced are in the form of ingots with a good separation of metallic and slag phases. Refining of melts is carried out in electron beam furnaces [6].

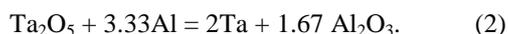
In principle, it is possible to reduce  $\text{Ta}_2\text{O}_5$  with three reductants: aluminium, magnesium, and calcium. The reduction reactions will proceed under the condition that the change in Gibbs free energy  $\Delta G < 0$  (or the equilibrium constant of reactions  $K_p > 1$ ).

In [7] the results of the reduction of  $\text{Ta}_2\text{O}_5$  with magnesium to produce tantalum powder with a large specific surface are presented:



The process is carried out in the regime of a self-progressing high-temperature synthesis. Another version of this reaction uses magnesium vapours as the reductant in the temperature range of 700–800 °C. The specific surface of the tantalum powders obtained is 2–8 m<sup>2</sup>/g, which corresponds to the grain diameter of 50–200 nm.

The aluminothermal reduction process enables to smelt metal in the form of granules or ingots:

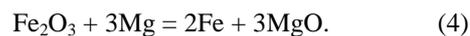
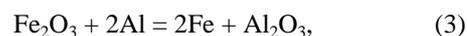


The duration of the process according to reaction (2) is about 90 s if the load of the feedstock is 100 kg. The intermetallic compound with the lowest melting point  $\text{AlTa}_2$  is formed at temperatures close to 2000 °C. The melting temperature of metallic tantalum is 3014 °C [8].

The melting temperature of the slag phase containing  $\text{Al}_2\text{O}_3$  is 2050 °C [9]. The slag of this type is classified as “short” as its crystallization occurs in a short time interval. For metal smelting and a good separation of phases it is required that the temperature of the process be kept over 3000 °C.

There is another option to carry out the reduction process of  $\text{Ta}_2\text{O}_5$  – to reduce the melting temperatures of the reaction products. In this case alloy-forming admixtures are added to the feedstock: 120% excess of aluminium according to reaction (2) and iron trioxide [10]. Iron and aluminium form alloys with tantalum [8]. By changing the composition of the alloy (i.e. iron and aluminium content), it is possible to reduce the melting temperature of the ingot by 350–500 °C from the melting temperature of tantalum (3014 °C).

Reduction of  $\text{Fe}_2\text{O}_3$  with aluminium (3) and magnesium (4) creates an additional exothermal effect of the process:

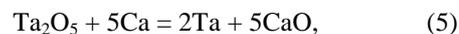


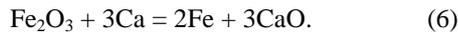
A remarkable reduction of the melting temperature of tantalum occurs when  $\text{SiO}_2$  takes part in the reaction together with  $\text{Fe}_2\text{O}_3$ . At the content of Ta–Si in the alloy up to 3 mass%,  $\text{Ta}_{4.5}\text{Si}$  with the melting temperature of ~2300 °C is formed [2]. Aluminium and silica form the eutectoid point (577 °C) at the silica content of 12.2% [8]. To improve the heat balance, the multiple-compound feedstock in the furnace is additionally heated up to 925 °C. The reduced metal is separated from the slag phase in the form of chips.

To reduce the melting temperature of the slag phase in the  $\text{Ta}_2\text{O}_5$  reduction process, calcium oxide is added to the feedstock [2]. At the 20 mass% concentration of  $\text{CaO}$  in the system  $\text{Al}_2\text{O}_3\text{–CaO}$  the melting temperature of the slag is reduced from 2050 to 1800 °C [9]. Addition of  $\text{CaO}$  also reduces the viscosity and surface tension of the slag promoting the separation of phases.

In [11] the laboratory scale process of  $\text{Ta}_2\text{O}_5$  aluminothermal reduction with  $\text{KClO}_3$  as a heat-releasing compound was studied. To reduce the melting temperature of the slag,  $\text{CaO}$  was added to the feedstock. Metal was separated in the form of ingots with 5 mass% content of aluminium. The pickup of tantalum in the melt comprised 90 mass%.

It is reasonable to replace  $\text{CaO}$  by metallic calcium. In this case there is no need to heat the furnace with the feedstock up [2,10]. The reaction of Ca with tantalum oxide (5) and ferric oxide (6) liberates an additional exothermal effect. It is possible to reduce the melting temperature of the alloy  $\text{Al}_2\text{O}_3\text{–CaO}$  to 1400 °C at the content of  $\text{CaO}$  up to 50 mass%:





In [12: 255–265, 13,14] the thermodynamic approach for the description of the fast reactions of the atomization of a specimen in plasma of graphite atomizers is discussed using atomic-absorption analysis. It is shown that at the vaporization and atomization rate <2000 K/s, the process is in the state of equilibrium. A similar criterion can be used for the description of the aluminothermal processes of niobium and tantalum production. In the “out-of-furnace” process of the reduction of niobium and tantalum pentoxides the rate of the temperature growth is in the range of 10–30 K/s [15]. This means that the assumption of the state of local thermodynamic equilibrium is totally justified. Achievement of equilibrium is also promoted by the high temperature and geometrical configuration of the reactor [16,17]. Of course, the assumption about the achievement of equilibrium in aluminothermal processes in using the method of thermodynamic modelling has to be verified by experimental data [15].

The main objectives of this study were thermodynamic analysis of the reduction process of tantalum pentoxide with combined reductants and in the presence of a heat-releasing compound, using a computer simulation program “HSC Chemistry 6.1, 2007”, elaborated by the company Outotec Oy; determination and description of the thermal regimes of the reduction process; carrying out a series of pilot test meltings to check and verify the results of computer simulation; and improvement of the aluminothermal process of tantalum pentoxide reduction.

## EXPERIMENTAL AND APPARATUS

Construction of the reactor and its facing are of primary importance in high-temperature melting processes. In practice, “out-of-furnace” reduction processes for smelting master alloys of rare earth metals and alloys of infusible metals are carried out at temperatures close to 2800°C, and copper reactors with thick walls without protective coatings are widely used [7]. According to [8,9], also graphite, steel, and cast iron crucibles lined inside with magnesium or aluminium oxides have found industrial application.

The duration of aluminothermal reduction reactions of tantalum pentoxide is at raw materials mass of ~150 kg in the range of 90–120 s [6]. The short-term character of the process and thermal load in the reactor enable application of massive steel crucibles with a protective facing. However, without a protective facing a typical “grid of fatigue” is formed on the surface of the metal and the production capacity of the reactor falls.

In the present study steel crucibles with 50–100 mm thick bottoms were used for the aluminothermal meltings. The protective coatings inside the crucibles were plasma sprayed with microstrength >3500 MPa and adhesion >35 MPa. To avoid undesired impacts of hot slag and metal on the coating its surface was covered with a special layer of AlN–Ca(OH)<sub>2</sub>–Na<sub>2</sub>SiO<sub>3</sub> (AlN = aluminium with nitrogen content).

In our scale skilled tests tantalum pentoxide was heated at 900°C till permanent weight (Table 1). Other raw materials were used without any pretreatment. The content of gases adsorbed in aluminium powder was ≤1%. The specific surface of powdered aluminium measured by the BET method was 0.15 m<sup>2</sup>/g and bulk density ~1 g/cm<sup>3</sup>.

The procedure of the experiments was the following: the raw materials were mixed during less than 10 min and after that loaded into the steel crucible. The crucible was placed into the protective chamber equipped with a system of ventilation and hermetization and Ar gas input. The reaction was initiated by an electrical spiral placed into a special ignition mixture on the top of the feedstock, and the powerful ventilation system was switched on.

During the reductive meltings the temperature inside the crucible was registered. The distribution of the temperature field inside the furnace volume was computed previously [18]. The structure and phases of ceramic and

**Table 1.** Chemical composition and admixtures of raw materials

Chemical composition of calcium (grains ≤2 mm), mass%

Ca	Cl	N	Mg	Cu	Ni	Mn	Si	Fe	Al
≥98.5	0.20	0.10	0.25	0.05	0.01	0.01	0.01	0.02	0.30

Chemical composition of aluminium powder, mass%

Al <sub>2</sub> O <sub>3</sub>	Active Al	Fe	Si	Cu	Moisture
≤1	≥98	≤0.35	≤0.4	≤0.02	≤0.2

Admixtures of Ta<sub>2</sub>O<sub>5</sub>, ppm

Nb	F	Ti	Si	Mo	W	C	Mg	Mn	Al	Ni	Cr	LOI*, mass%
0.03	≤200	50	≤100	≤30	≤3	≤20	≤30	–	≤50	≤50	7	0.03

\* LOI, loss in the weight at 900°C.

Admixtures of Fe<sub>2</sub>O<sub>3</sub>, mass%

Mn	Cr	Ni	Si	CH <sub>4</sub> , CO <sub>2</sub> , O <sub>2</sub> , N <sub>2</sub>	Cu	V	Mo	W	Density, g/cm <sup>3</sup>
0.82	≤0.10	0.09	0.82	≤1	0.082	≤0.0	≤0.01	≤0.1	5.24

cermet coatings of the crucible were determined by a diffractometer DRON-2.0. The distribution of elements in the specimens was determined by a microanalyser "Cameca MS-46". The microstrength of the material was determined by the method of diamond finder suppression (EMCO Test Automatic Vickers) on a microstrength measuring instrument RMT-3.

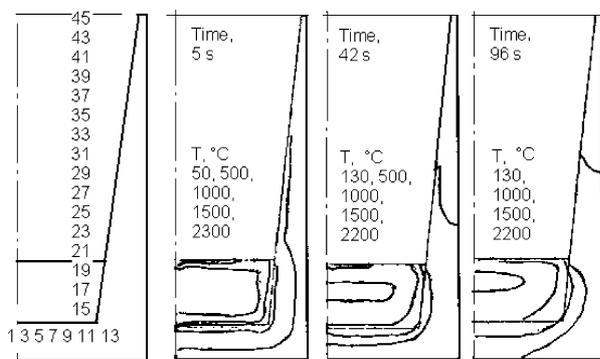
To follow the development of the different thermal zones during the reduction process of tantalum pentoxide a method of synchronous thermal analysis on a derivatograph Netzsch Gerätebau GmbH (Germany) was used. Four parameters were registered: increase in temperature (T), thermogravimetric parameter (TG), intensity of products destruction or velocity of mass change (DTG), and change in enthalpy (DTA).

Heating-up proceeded with the speed of 283 K/min up to 1473 K in the atmosphere of He. At the end of the cycle the temperature was kept constant during 60 min before cooling down to room temperature. For the graduation of the derivatograph thermograms of  $\text{Na}_2\text{SO}_4$  (1157 K) and  $\text{K}_2\text{SO}_4$  (1349 K) were used. The experimentally determined temperatures of the transition of phases for these compounds matched with the values published in the literature well. The accuracy of the temperatures of phase transition measurements was  $\pm 2$  K.

## RESULTS AND DISCUSSION

### Temperature field in the crucible and protective coatings

The distribution of the temperature field across the height of the crucible is shown in Fig. 1. The measured values of temperature in the check-points matched with the computed ones well. The maximum temperature of the melt did not exceed 2850°C. Of the protective coatings tested the best behaviour was demonstrated by the multiple layer consisting of Nb–NbC–Nb–NbC–Nb–NbC–AlN [19,20].



**Fig. 1.** Temperature check-points on the inner surface of the crucible and the distribution of the temperature field.

At the moment the reaction starts a temperature gradient and thermal stress appear. The temperature of the inner wall of the crucible sharply increased (check-points 1–21) during the first stage of the process (~5 s), but after that the increase in temperature slowed down, and in 40 s the maximum temperature fixed on the bottom of the crucible did not exceed 2000°C (points 1, 7, 9). Elaboration and application of ceramic and special metal-containing coatings with the melting point significantly higher than the melting point of steel helped avoid thermal destruction of crucible metal and enabled its reuse up to 300 times provided that the coating was periodically restored.

X-ray spectroscopy of the distribution of elements in the protective coating indicated diffusion of the eutectoids formed in the porous structure of the coating, but no fusion of the coating and steel base took place. There were only narrow zones of diffused elements on the metal–coating interface. The content of nitrogen in the surface layer of the metal was 0.023–0.029% (mass) [19,21].

### Thermodynamic analysis of the process of aluminothermal reduction

Thermodynamic computations in this paper are based on the assumption about achievement of total thermodynamic equilibrium in the reactions. In practice, of course, achievement of absolute thermodynamic equilibrium is disputable, and therefore the term of "local thermodynamic equilibrium" was introduced. This term refers to the state when the time the reactions proceed is significantly shorter than the time for the input of the compounds into the local volume [10].

For the thermodynamic modelling of the process of tantalum pentoxide reduction a licensed computer simulation program "HSC Chemistry", elaborated by the company Outotec Oy, was applied. In 2007 a new version of this program (6.1) was published, containing 21 computation modules and 11 data bases to compute equilibrium of chemical reactions, heat balance, heat transfer, petrology, and imitation [22]. The majority of the modules use a combined thermochemical data base on enthalpy (H), entropy (S), and heat capacity (C) for more than 20 000 chemical compounds. The program "HSC Chemistry 6.1" does not contain a module for the computation of the reaction rates.

The dependence of the equilibrium constants  $K$  for reactions (1–6) on temperature in the range of 1000–3000°C is shown in Fig. 2. Computations were made per 1 mole of oxygen in the compounds of the feedstock ( $\text{Ta}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$ ) with the step of 10 K. All reactions proceeded completely, but  $\text{Fe}_2\text{O}_3$  reduced faster than  $\text{Ta}_2\text{O}_5$ . According to the depth of the progression of the reactions, metals can be arranged in the following order:  $\text{Al} < \text{Mg} < \text{Ca}$ . This conclusion was verified by the

chemical analysis of the products of the reductive melting [23].

Heating effects of reactions (1–6) depending on temperature are shown in Fig. 3. The breaking points on the curves correspond to the phase transitions:

- 1811 K – melting temperature of Fe;
- 2150 K – melting temperature of Ta<sub>2</sub>O<sub>5</sub>;
- 2327 K – melting temperature of Al<sub>2</sub>O<sub>3</sub>;
- 3105 K – melting temperature of MgO;
- 3172 K – melting temperature of CaO.

The highest “jump” in the heating effect took place in the formation of magnesium and calcium oxides in slag.

The heating effects of the reduction of Fe<sub>2</sub>O<sub>3</sub> with aluminium, magnesium, or calcium were significantly higher than the corresponding heating effects of Ta<sub>2</sub>O<sub>5</sub> reduction. The smallest amount of heat was released in reaction (2). Addition of Fe<sub>2</sub>O<sub>3</sub> to the feedstock increased the heat release in reactions and reduced the melting temperature of metal due to the formation of the Ta–Fe–Al alloy. Transition of iron oxide to the slag phase did not take place. According to the thermodynamic calculations, iron oxide was completely reduced with the formation of metallic Fe in the composition of the Ta–Fe alloy.

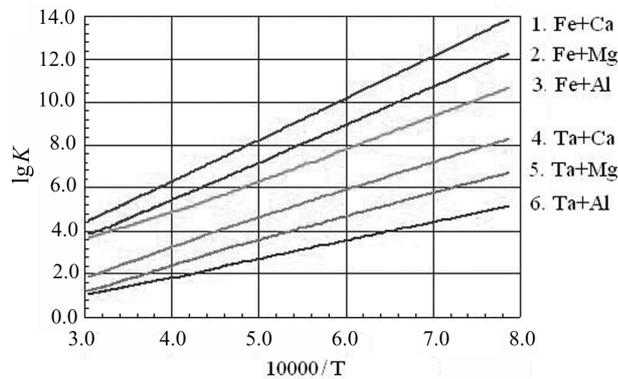


Fig. 2. Dependence of the equilibrium constants *K* of reactions (1–6) on temperature.

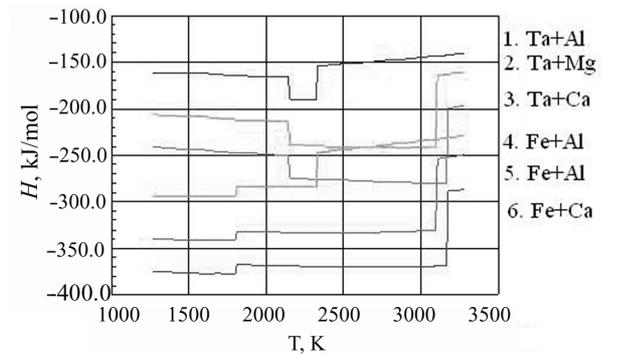
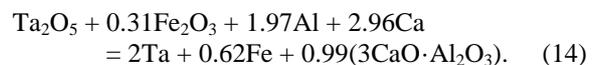
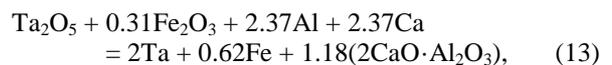
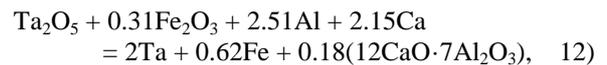
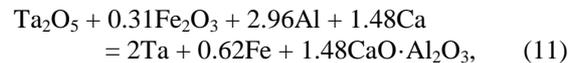
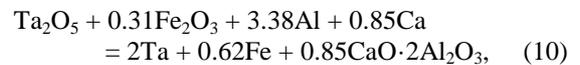
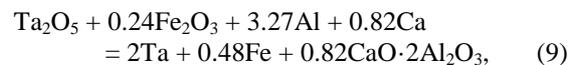
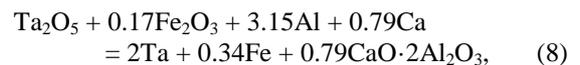
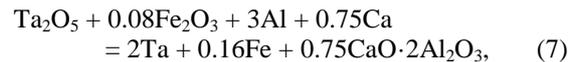


Fig. 3. Dependence of the heating effects *H* of reactions (1–6) on temperature.

Industrial application of only magnesium or calcium as the reductant of metals should be considered inefficient and even dangerous. Boiling temperatures of these metals are relatively low (Mg 1361 K; Ca 1757 K). In the “out-of-furnace” reduction process of Ta<sub>2</sub>O<sub>5</sub> with Mg and Ca the temperature reaches 3000 K. At this temperature vaporization of Mg evokes a jet out of the feedstock. As the melting temperatures of MgO (3105 K) and CaO (3172 K) are close to the melting temperature of metallic tantalum (3287 K), the separation of metallic and slag phases is incomplete, and the formation of compact ingot is impossible.

The use of a mixture (Al + Ca) as the reductant with an addition of Fe<sub>2</sub>O<sub>3</sub> enables to solve the main problems of the “out-of-furnace” process, that is to achieve a positive heat balance and an adequate physico-chemical state of the slag phase. In industry powdered aluminium, metallic calcium chips, or powdered mixture of Al–Ca are used for smelting niobium [3] and tantalum [6]. Reactions occur without preheating the feedstock. Niobium smelting takes 3–5 min and that of tantalum, 90–120 s. By changing the content of iron and aluminium in the feedstock, it is possible to reduce significantly the melting temperature of the Ta–Fe alloy [9].

Refining remelting of the product of aluminothermal reduction requires the minimum content of admixtures in the smelted metal. By changing the Al:Ca ratio in the feedstock, it was possible to achieve simultaneous reduction of Ta<sub>2</sub>O<sub>5</sub> and Fe<sub>2</sub>O<sub>3</sub> (7–14) under the conditions of the maximum heating effect. The slag system was designed for 50–70% (mass) content of Al<sub>2</sub>O<sub>3</sub> with the melting temperature close to 1800 °C.



Computation of the thermodynamic characteristics for reactions (7–14) with the step of 10 K was also

implemented per 1 mole of oxygen in raw materials ( $\text{Ta}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$ ), taking into consideration the stoichiometric coefficients in the reactions. The calculated equilibrium constants indicated that all these reactions proceeded sufficiently completely. At temperature of 3273 K, the values of  $\lg K$  smoothly increase in the row of reactions (7–14) from 1.34 to 2.09 with the growth of the iron oxide and metallic calcium content in the feedstock.

The “out-of-furnace” process of aluminothermal reduction of  $\text{Ta}_2\text{O}_5$  starts from the local heating of part of the feedstock up to the temperature of self-ignition. The heating effect of the reaction of self-ignition has to guarantee the melting of this local layer, heating-up of the adjacent layer, and compensation for heat losses.

Figure 4 illustrates the impact of temperature on the exothermic effect of reactions (7–14). In these reactions the impact is greater than in reaction (2) without iron oxide and metallic calcium. In the range of temperature of 2150–1000 K an increase takes place in the exothermic effect in the row of reactions (7–14). Conditionally it is possible to divide these reactions into two groups: (7–10) and (11–14). The difference is that in the reactions of the second group (11–14) the content of calcium in the feedstock is significantly higher.

The amounts of iron oxide, aluminium, and calcium vary in reactions (7–14). In Fig. 4 two breaking points can be found: at 1811 K (melting of  $\text{Fe}_2\text{O}_3$ ) and at 2058 K (melting of  $\text{Ta}_2\text{O}_5$ ). This can be explained by the fact that the calcium aluminates  $m\text{CaO}\cdot n\text{Al}_2\text{O}_3$  are melting with insignificant enthalpy, and the melting temperature of  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  (2053 K) is close to the melting temperature of  $\text{Ta}_2\text{O}_5$  (2150 K). Calcium aluminates  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  (1878 K) and  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  (1698 K) have lower melting temperatures. Besides, the change in enthalpy  $\Delta H$  depends on the stoichiometric coefficient in front of the reactant.

During the melting processes corresponding to reactions (13,14) a jet out of the products from the reactor was observed. It was due to the vaporization of calcium in the feedstock, as vaporization of aluminium takes place at a higher temperature (2792 K), which is close to the melting point of the alloy. In [24] it was

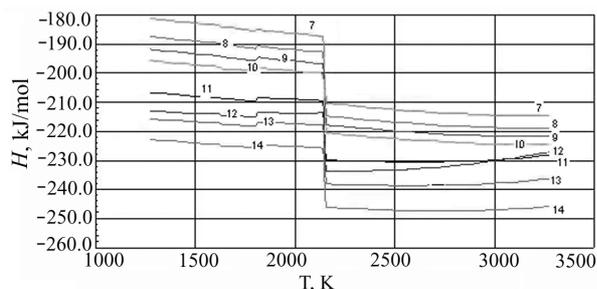


Fig. 4. Impact of temperature on the exothermic effect  $H$  of reactions (7–14).

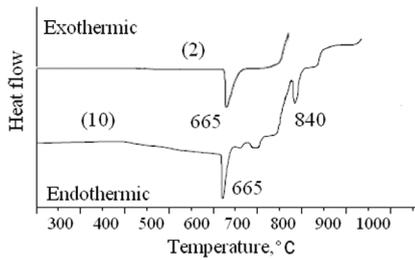
established that vaporization of the metal reductant leads to the spatial separation of the products. Vapour pressure interferes with coagulation, settling of metal particles, and formation of ingot and deteriorates the separation of metal and slag phases. During the pilot tests of tantalum smelting, it was established that the effect of the spatial separation of the products occurred if oxides with a small bulk density were used. Intensive vaporization of the melting products can be avoided by adjusting the fractional composition and amount of the reductant.

In the melting process with a significant excess of calcium and aluminium (reactions 12–14) the melting temperature of the slag fell to 1395 °C. The reaction rate and exothermic effect at this composition were very high. The feedstock was overheated, which caused it to jet out.

The calculated values of the equilibrium constant for reactions (7–14) in the temperature range of 1273–3273 K were verified by the experiments of reductive meltings. The content of aluminium and iron in the tantalum alloy corresponded to the results of thermodynamic computations. The content of tantalum oxide in the slag did not exceed 5%. The number of the negative phenomena accompanying the process of reductive melting was minimized by the right choice of the granulometric composition and ratio of feedstock components. According to the scale skilled tests (reactions 9–11) losses of metal with slag were insignificant. The alloy was obtained in the form of compact ingot with a very good separation of phases. The ratio of  $\text{Ta}_2\text{O}_5:\text{Fe}_2\text{O}_3:\text{Al}:\text{Ca} = 1:0.195:2.68:1.86$  in the feedstock in reactions (7–14) can be recommended for further studies.

### Differential thermal analysis

The results of the differential thermal analysis (DTA) of the process of  $\text{Ta}_2\text{O}_5$  and  $\text{Fe}_2\text{O}_3$  reduction with aluminium and calcium are presented in Fig. 5. Removal of the moisture from the feedstock can be followed at the starting stage of the process. No sintering of the components of the feedstock was established. Up to the temperature of 665 °C there was no change in the aggregation state of the aluminium powder. This is due to the passive film of oxides formed on the surface of aluminium in dry air or in the atmosphere of inert gas. The first endothermic peak (665 °C) is close to the melting temperature of technical aluminium, and the second one (840 °C) is close to the melting temperature of metallic calcium. The negligible change in the mass (TG analysis) can be explained by the presence of residuals of inorganic compounds from the previous production of feedstock components. At temperatures of 960–970 °C the heat release starts, which is the beginning of exothermic reactions leading to the reduction of tantalum and iron



**Fig. 5.** Results of the differential thermal analysis of the process of Ta<sub>2</sub>O<sub>5</sub> and Fe<sub>2</sub>O<sub>3</sub> reduction with the mixture of Al and Ca.

oxides and the formation of the alloy and the system Al<sub>2</sub>O<sub>3</sub>-CaO.

Differential thermal analysis, experimental measurements of the temperature field distribution in the reactor, and determination of the heat losses enabled to determine the temperature ranges for the formation of alloy and slag and vaporization of metallic reductants. Using the heat effects calculated with the program “HSC Chemistry”, the results of thermodynamic modelling, and information from the handbooks on metals and their alloys [24–27], we established the melting temperatures of slag, alloy, and the required preheating temperature for the feedstock (Table 2).

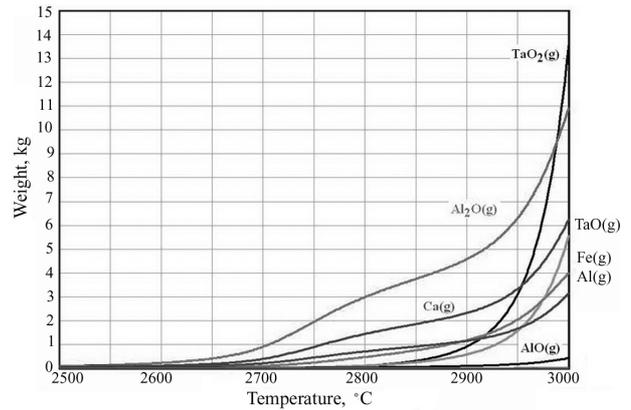
The maximum temperature required for the reduction of tantalum pentoxide ( $T_{max}$ ), established on the basis of the literature data [10,15], determines the overheating temperature of the products of melting according to the equation:

$$T_{max} \geq T_{min} + (200-250)^\circ\text{C}. \quad (15)$$

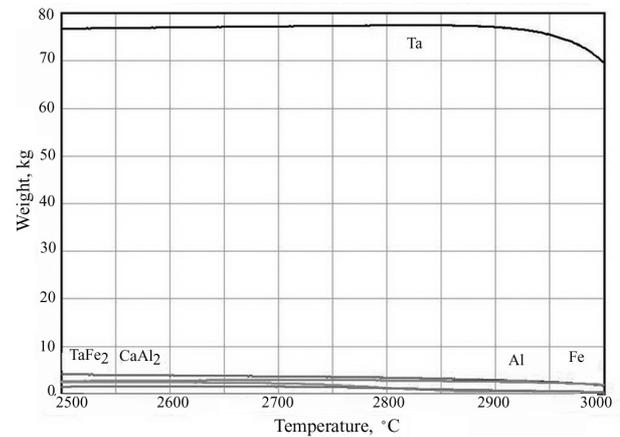
The results of thermodynamic modelling of the formation of the gaseous, metallic, and slag phases during the reduction process of Ta<sub>2</sub>O<sub>5</sub> and Fe<sub>2</sub>O<sub>3</sub> are presented in Figs 6–8. The initial ratio of Fe<sub>2</sub>O<sub>3</sub>, Al, and Ca in the feedstock was (in parts) 19.3 : 51.61 : 29.03.

**Table 2.** Temperature regimes of the reduction processes according to reactions (7–13)

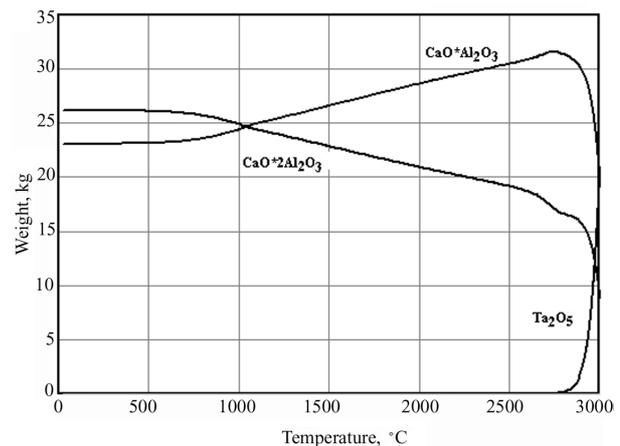
Reaction	Melting temperature of slag, $T_{slag}$ , °C	Melting temperature of alloy, $T_{min}$ , °C	Required temperature, $T_{max}$ , °C [10,15]	Calculated temperature of products settling, $T_{settling}$ , °C	Preheating temperature of reactor, $T$ , °C
7	1800	2800	3000	2650	350
8	1800	2640	2840	2670	170
9	1800	2560	2740	2690	50
10	1800	2500	2700	2810	No
11	1800	2400	2600	2900	No
12	1590	2500	2700	2890	No
13	1530	2550	2750	2870	No



**Fig. 6.** Impact of temperature on the composition of the gaseous phase.



**Fig. 7.** Impact of temperature on the composition of the metallic phase.



**Fig. 8.** Impact of temperature on the composition of the slag phase.

The gaseous phase above the feedstock consisted of Ar –  $2.4 \times 10^{-1}$ , O<sub>2</sub> –  $1.6 \times 10^{-3}$ , and N<sub>2</sub> –  $2.8 \times 10^{-3}$  (in

vol. parts). The ratio of the volume of the feedstock to the gaseous phase was 1:4. This composition was verified as an optimum one in the course of a series of scale skilled tests.

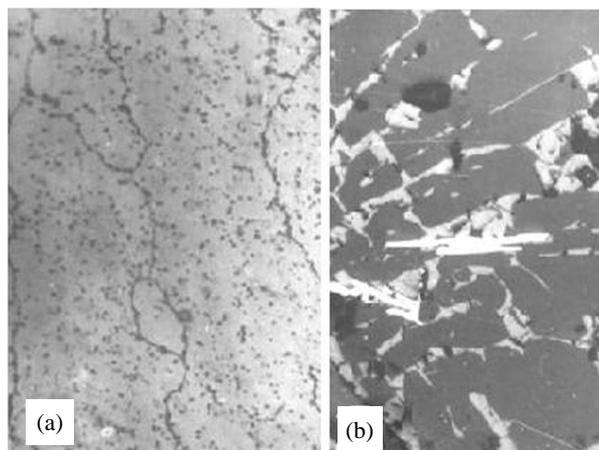
Thermodynamic calculations suggest that in the temperature range of 2000–3000 °C the slag phase should contain liquid  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  ( $T_{\text{melt}} = 1605^\circ\text{C}$ ) and  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  ( $T_{\text{melt}} = 1780^\circ\text{C}$ ). An increase in the temperature from 2900 up to 3000 °C leads to a sharp growth in the content of dissolved  $\text{Ta}_2\text{O}_5$ , i.e. the process will proceed in the opposite direction. After it is cooled down to room temperature, the slag contains  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  (53 mass%) and  $\text{CaO}\cdot\text{Al}_2\text{O}_3$  (47 mass%). Thermodynamic calculations of the slag composition at 25 °C agree well with the phase diagram of the system  $\text{Al}_2\text{O}_3\text{--CaO}$  for the concentration of about 73 mass%  $\text{Al}_2\text{O}_3$  [9]. This concentration corresponds to the average ratio  $\text{Al}:\text{Ca} = 2.8:1.5$  in the feedstock. The melting temperature of the slag in this range is  $\sim 1780^\circ\text{C}$ .

In the temperature range of 2500–2900 °C the equilibrium composition of the gaseous phase is mainly presented by the vapours of  $\text{Al}_2\text{O}$ , Ca, Fe, and Al (Fig. 6). Starting from 2850 °C the content of tantalum vapours in the gas in the form of  $\text{TaO}_2$  and TaO exponentially grows. This can be seen especially clearly at temperatures 2950–3000 °C. Vaporization of tantalum oxides and transition of  $\text{Ta}_2\text{O}_5$  to the slag phase lead to the diminishing of the tantalum content in the alloy at temperatures 2900–3000 °C [20]. At 2800–3000 °C the metallic phase is composed of tantalum, iron, and aluminium. The results of thermodynamic modelling agree with the results of the chemical analysis of the alloy and slag well (Table 3).

**Table 3.** Chemical composition (%) of the alloy and slag

Alloy denomination								
Ta	Nb	Al	Fe	N	O	C	Si	Ti, Ni, Cr, Mo, W, Cu
$\geq 88.5$	$\leq 0.03$	$\leq 5$	$\leq 6$	$\leq 0.01$	$\leq 0.08$	$\leq 0.02$	$\leq 0.013$	Residual
Slag denomination								
CaO			Al <sub>2</sub> O <sub>3</sub>			Ta <sub>2</sub> O <sub>5</sub>		
25–30			65–75			3–5		

Figure 9a is a photo of the macropolish of the alloy Ta–Fe–Al. Dark dots correspond to the pores. Etching with 10% HF reinforced this effect. Grain boundaries are clearly seen. On the phase diagram [28] in the triangle with Ta on the top (20 mole% Al and 20 mole% Fe) the phases  $\text{Ta} + \mu(\text{Ta}_7\text{Fe}_6) + \sigma(\text{Ta}_2\text{Al})$  are in equilibrium. Across the grain boundaries intermetallics TaFe and  $\text{Ta}_2\text{Al}$  are formed.



**Fig. 9.** (a) Alloy Ta–Fe–Al. Content of Al 5.6 mass%. Macro-polish. Etching with 10% HF. Magnification  $\times 170$ . Reflected light. Dots show porosity. (b) Slag of the reductive melting of  $\text{Ta}_2\text{O}_5\text{--Fe}_2\text{O}_3\text{--Al--Ca}$ . Magnification  $\times 150$ . Reflected light. Dark-grey area is  $\beta\text{-Al}_2\text{O}_3\cdot 2\text{CaO}$ . Bright-grey area is  $\text{CaO}\cdot\text{Al}_2\text{O}_3$ . White prisms denote the alloy  $\text{CaAl}_4$ .

Figure 9b is a photo of macropolish of the slag from the reductive melting of  $\text{Ta}_2\text{O}_5\text{--Fe}_2\text{O}_3\text{--Al--Ca}$ . White prisms correspond to the intermetallic  $\text{CaAl}_4$ . In general, for metallic Ca it is thermodynamically more favourable to react first with  $\text{Ta}_2\text{O}_5$  than with metallic Al. However, at the final stage of the reduction process intermetallics  $\text{CaAl}_4$  still appear. Small amounts of TaO and  $\text{TaO}_2$  as well as of Al and Ca remain in the liquid slag. At the end of the process the tantalum oxides cannot reduce to metallic Ta any more, and they form the so-called technological loss of Ta. Metallic Ca, which is not a metal forming an alloy with Ta, gets now an opportunity to form compounds with the residual Al in the slag phase. The Al content in the surface layer of the ingot contacting with slag is  $\sim 0.5\%$  higher than in the lower layer, which points to the presence of free Al in the slag [3].

For the estimation of the efficiency of the process of remelting (refining) the Ta–Fe–Al ingot in an electron beam furnace, coefficients of the separation of admixtures were calculated. It was found that in the temperatures range of 2850–3500 K effective removal of admixtures (Ti, Ni, Cr, Al, Fe) occurs. These findings match with the results of industrial-scale meltings [6,27].

According to the thermodynamic analysis, the temperature range of 2800–2900 °C can be recommended for effective reduction of  $\text{Ta}_2\text{O}_5$ . At these temperatures the pickup of tantalum in ingot is maximum. Iron and aluminium reduce the melting temperature of tantalum alloy to 2200–2300 °C. This promotes effective settling of metal drops, formation of a compact ingot, and a good separation of phases. The calculated pickup of

tantalum to ingot was 94%. Experimentally measured values were close (93.8–94.5%). This proves that the program “HSC Chemistry 6.1” is a very useful tool for thermodynamic analysis and optimization of “out-of-furnace” aluminothermal processes and also indicates actual achievement of local equilibrium conditions for fast metallothermal reactions.

## CONCLUSIONS

- Possibility of using steel crucibles with erosion-resistant multiple protection plasma sprayed layers for the reduction of Ta<sub>2</sub>O<sub>5</sub> was proved. On the basis of a series of scale skilled tests it was found that the multiple Nb–NbC–Nb–NbC–Nb–NbC–AlN coating had the best durability. At repeated restoration of this layer the number of operating cycles of the steel crucible was approximately 300. The maximum temperature of the metal and slag in the process of reduction reached 2850°C.
- During a series of meltings simultaneous reduction of tantalum pentoxide and iron oxide was studied. A mixture of powdered aluminium and metallic calcium was used as the reductant. Thermodynamic analysis of the process at different compositions of the feedstock was carried out. Melting temperatures of the alloy and slag were determined. The results of thermodynamic modelling agreed with the data of chemical analysis of the metal alloy and slag well. According to the experimental meltings (reactions 9–11) losses of iron, aluminium, and calcium with the slag were negligible. The alloy was obtained in the form of compact ingot with a good separation of phases.
- Differential thermal analysis of the feedstock for the reduction process of the Ta<sub>2</sub>O<sub>5</sub> and Fe<sub>2</sub>O<sub>3</sub> mixture was carried out. The starting temperature of exothermal reactions was in the range of 960–970°C.
- The program “HSC Chemistry 6.1” proved to be a very useful tool for thermodynamic analysis and optimization of the “out-of-furnace” aluminothermal processes and also indicated actual achievement of local equilibrium conditions for the fast aluminothermal reactions. The best operation parameters (pickup of tantalum 93.8–94.5%; <5% losses of Ta<sub>2</sub>O<sub>5</sub> with slag) were achieved when the process proceeded according to reactions (9–11).

## REFERENCES

1. Bose, D. K. and Gupta, C. K. Extractive metallurgy of tantalum. *Mineral Processing and Extractive Metallurgy Review*, 2001, **22**(4–6), 389–412.
2. Zelikman, A., Korshunov, B., and Elyutin, A. *Niobium and Tantalum*. Metallurgiya, Moscow, 1990 (in Russian).
3. Gorkunov, V. and Munter, R. Calcium–aluminothermal production of niobium and mineral composition of the slag. *Proc. Estonian Acad. Sci. Chem.*, 2007, **56**, 142–156.
4. Tsegel'nik, É. Tantalum. *Journal of Atomic Strategy*, 2006, 20. ProAtom, St. Petersburg (in Russian). <http://www.proatom.ru/modules.php?name=onas>
5. Linnupõld, L. Complex environmental impact of technological processes of Silmet JSC and estimation of correspondence of applied technology to the requirements of BAT. Report No. E1131. Tallinn, 2009 (in Russian). [www.sillamae.ee/public/files/S%2013.03.07%20rus.doc](http://www.sillamae.ee/public/files/S%2013.03.07%20rus.doc)
6. Parshin, A. and Plotnikov, V. Elaboration and introduction of aluminothermal technology for the production of tantalum ingots and powders with application of electronbeam refining. Joint Report. VNIHT, Moscow, 1984, (in Russian). Archives AS Sillmet-Chemical Factory, Sillamäe (Estonia), No. A-115c (in Russian).
7. Orlov, V. M., Kryzhanov, M. V., and Sukhorukov, V. V. Magnesiothermic reduction of tantalum pentoxide. In *Abstracts of the International Conference “Chemistry of solids, monocrystals, nanomaterials, nanotechnology”, 11.–16.10. 2009. Kislovodsk, Russia*, 65–68.
8. Lyakishev, N. (ed.). *Phase Diagrams of Twin Metallic Systems. Handbook*. Mechanical Engineering, Moscow, Vol. 1, 1996; Vol. 2, 1997 (in Russian).
9. Phase diagram of the system CaO–Al<sub>2</sub>O<sub>3</sub>. In *Schlackatlas*. Stahleisen Verlag GmbH, Düsseldorf, 1981.
10. Zelikman, A., Korshunov, B., and Elyutin, A. *Metallurgy of Refractory Rare Metals*. Metallurgiya, Moscow, 1986 (in Russian).
11. Nair, K. U., Mukherjee, T. K., and Gupta, C. K. *Production of Tantalum Metal by the Aluminothermal Reduction of Tantalum Pentoxide*. Metallurgy Division, Bhabha Atomic Research Centre, Trombay, Bombay, India, 1975.
12. Polak, L. (ed.). *Kinetics and Thermodynamics of Chemical Reactions in Low-temperature Plasma*. Collection of papers. Institute of Oil-Shale Synthesis, USSR Academy of Sciences, 1965 (in Russian).
13. Malkin, O. A. *Relaxation Processes in Gas*. Atomizdat, Moscow, 1971 (in Russian).
14. Pupyshev, A. A. Application of thermodynamics for description, analysis, studies and control of thermochemical processes in sources of atomization and excitement of spectrums. Doctoral Thesis. Ural State University, Yekaterinburg, 1994.
15. Lyakishev, N. P. *Aluminothermal Processes*. Metallurgiya, Moscow, 1978.
16. Pliner, J. and Ignatenko, G. *Reduction of Oxides with Aluminium*. Metallurgiya, Moscow, 1967 (in Russian).
17. Belov, G. V. *Thermodynamic Modelling: Methods, Algorithms, Programs*. Nauchnyj mir, Moscow, 2002 (in Russian).
18. Obabkov, N., Gorkunov, V., Munter, R., and Beketov, A. Computation of the temperature field in the furnace of aluminothermal reduction. *Sci. Proc. Riga Technical*

- University “Material Science and Applied Chemistry”, Ser. 1. Riga, 2007, 100–110.
19. Obabkov, N. High-temperature composite anticorrosion and antierosion protective coatings for construction materials. Doctoral Thesis. Ural State University, Yekaterinburg, 2001 (in Russian).
  20. Gorkunov, V. and Munter, R. Production of silicon free master alloys in Estonia. *Sci. Proc. Riga Technical University “Material Science and Applied Chemistry”*, Ser. 1. Riga, 2007, 111–120.
  21. Beketov, A., Obabkov, N., Gorkunov, V., and Munter, R. Protective coatings for the graphite facing in calcium–aluminothermal processes. *Proc. Estonian Acad. Sci. Chem.*, 2008, **57**, 54–60.
  22. [http://www.outotec.com/templates/Search\\_9173.aspx?epslanguage=EN&find=HSC+Chemistry++6.1](http://www.outotec.com/templates/Search_9173.aspx?epslanguage=EN&find=HSC+Chemistry++6.1)
  23. Sokolov, I. and Ponomarev, N. *Introduction to the Metallothermal Processes*. Metallurgiya, Moscow, 1990 (in Russian).
  24. Miroshnikova, L. D. Tantalum oxides. *J. Inorganic Chem.*, 1989, **34**(1), 184–187.
  25. Shunk, F. A. *Constitution of Binary Alloys*. Metallurgiya, Moscow, 1973 (in Russian).
  26. Bennett, L. *Phase Diagrams of Alloys*. Mir, Moscow, 1986 (in Russian).
  27. Bakish, R. The substance of a technology: electron-beam melting and refining. *J. Min. Met. Mat. Soc.*, 1998, **50**(11), 28–30. Springer, Boston.
  28. Hunt Coy, R. and Raman, A. Alloy chemistry of  $\beta(\sigma U)$ -related phases. I. Extension and occurrence of  $\mu'$ -phases in ternary systems Nb(Ta)–X–Al. *Z. Metallknd.*, 1968, **59**(9), 701–707.

## **Tantaalpentoksiidi alumotermilise redutseerimise termodünaamiline modelleerimine ja pilootkatsed**

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ja Viktor Kober

Suur osa tantaali toodetakse tänapäeval põhiliselt klassikalises ahjuprotsessis, kus on vaja väljastpoolt soojust juurde tuua. Tunduvalt vähem on katsetatud ja rakendatud ahjuvälilist protsessi (“*out-of-furnace*” *process*), kus vajalik temperatuur saavutatakse reaktsioonide sobiva eksotermilise soojusefekti abil. Tantaali alumotermiline redutseerimine kulgeb temperatuuril  $\geq 2800^\circ\text{C}$  kestusega 90–120 s, kui toorsegumass ei ületa 150 kg.

Käesolevas töös on uuritud tantaal(V)oksiidi ja raud(III)oksiidi alumotermilist redutseerimist alumiiniumi- ning kaltsiumisegu abil. Raud(III)oksiidi juuresolek võimaldas suurendada protsessi eksotermilist efekti, tagada metalli ja šlaki hea eralduspind ning tantaalisulami eraldumine kompaktses sulatisena (plokina). Pilootkatsed viidi läbi terasest tiiglitest, mis olid vooderdatud erinevate kaitsekihtidega. Parima kestvusega kaitsekihiks osutus mitmekihiline vooderdis Nb–NbC–Nb–NbC–Nb–NbC–AlN, mis kanti peale plasmameetodil.

Et määrata süsteemi  $\text{Ta}_2\text{O}_5\text{–Fe}_2\text{O}_3\text{–Al–Ca}$  termodünaamilisi funktsioone, redutseerimisprotsessi soojusbilanssi ja arvutada saadud sulami ning šlaki tasakaalulisi koostisi, kasutati firma Outokumpu Research Oy arvutusprogrammi “HSC Chemistry 6.1, 2007”.

Protsessi termodünaamilise modelleerimise tulemusena määrati optimaalsed redutseerimisreaktsioonid (9–11), mis tagasid metalli ja šlaki hea eraldumise, tantaali 93,8–94,5% sisalduse sulamis ning <5%  $\text{Ta}_2\text{O}_5$  jääksisalduse šlakis. Läbiviidud pilootkatsed kinnitasid termodünaamiliste arvutustega saadud tulemusi ja eeldust lokaalse tasakaaluolukorra saavutamise võimalikkuse kohta, vaatamata kiiretele mittepõrduvatele reaktsioonidele redutseerimisprotsessis.