

Plasma-arc production of synthetic rutile from leucoxene concentrate

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Abstract. Plasma production of synthetic rutile from leucoxene concentrate with high contents of SiO_2 is described. Concentrate was melted with carbon in laboratory plasma-arc furnace. Synthetic rutile with 3.6 % Si was produced. Experimental results and thermodynamic calculations are presented.

1. Introduction

The main Russian titanite ore resources exist in the form of the leucoxene oil-bearing sandstone which consists mainly of SiO_2 and contains TiO_2 up to 10 % (Yarega deposit). The enrichment of leucoxene ore is carried out in few stages. It is distillation from oil first of all and then ore is subjected to flotation. The concentration of TiO_2 raises up to 40-50 %. Further enrichment to 80-85% of TiO_2 is performed in autoclaves by treatment with hot H_2SO_4 . The autoclave treatment is complicated and ecologically dangerous [1-3]. The aim of the article is to show that the autoclave treatment can be replaced by carbon reduction without dangerous reagents. The essence of the process is reduction of SiO_2 to SiO. SiO will evaporate from concentrate at high temperature. The high temperature can be obtained by plasma-arc heating [4].

2. Thermodynamic calculation

The model system for thermodynamic calculation contained 0.75 mole TiO_2 , 1 mole SiO_2 and C. The amount of C was varied from 1 up to 4 moles. Calculation was executed by means of the program complex TERRA [5, 6] at pressure $p = 0.1$ MPa and temperature $T = 1000 - 4000$ K. It was considered that the condensed phase exists as oxide solution without heat of solution. The results are shown in figures 1 and 2. Figure 1 illustrates the composition of the system when amount of C equals 1 mole. The evaporation of SiO begins when temperature is over 2000 K. Almost all SiO_2 in system is reduced and evaporated when temperature is 3000 K. It is not good to heat the system more because the evaporation of titanium oxides also begins.

Not all amount of carbon in system is spent for reduction of SiO_2 . Some part of carbon is spent for reduction of TiO_2 to Ti_xO_y . It is useful to have 1.5 moles of carbon in the system for this reason. More carbon is not good because of formation of Si, SiC, TiSi which are not volatile. Figure 2 illustrates dependence of ϵ_{Si} upon contents of carbon and temperature of the system. ϵ_{Si} is the ratio of amount of Si in gas phase to total amount of Si in system. According to Figure 2 the optimal conditions are: C = 1.5 mole, $T = 2600$ K. Synthetic rutile contains 3 mass % of Si in this case. Gas phase contains ≈ 44



mass % CO and ≈ 56 mass % SiO, $\varepsilon_{\text{Ti}} < 0.01$. Theoretical energy consumptions (without losses) are 8.9 GJ/t of the concentrate.

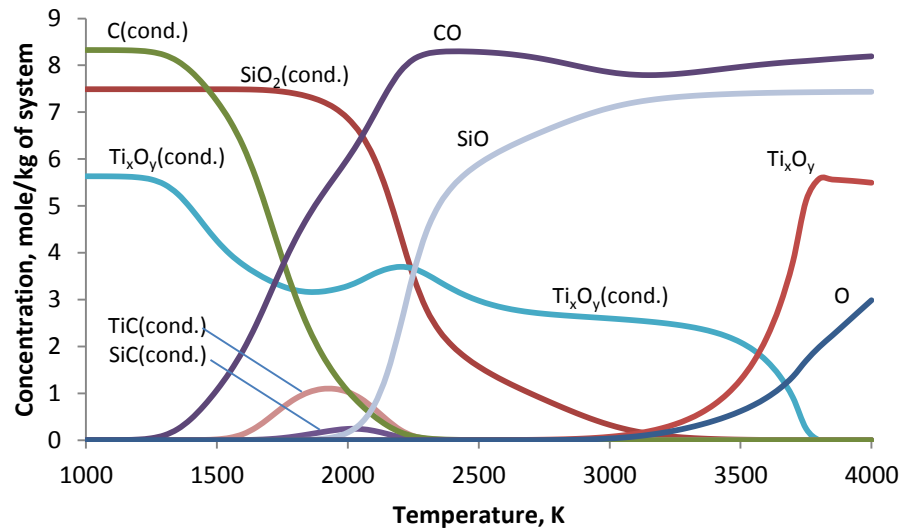


Figure 1. Equilibrium mixture of system $0.75 \text{ TiO}_2 + \text{SiO}_2 + \text{C}$ calculation results

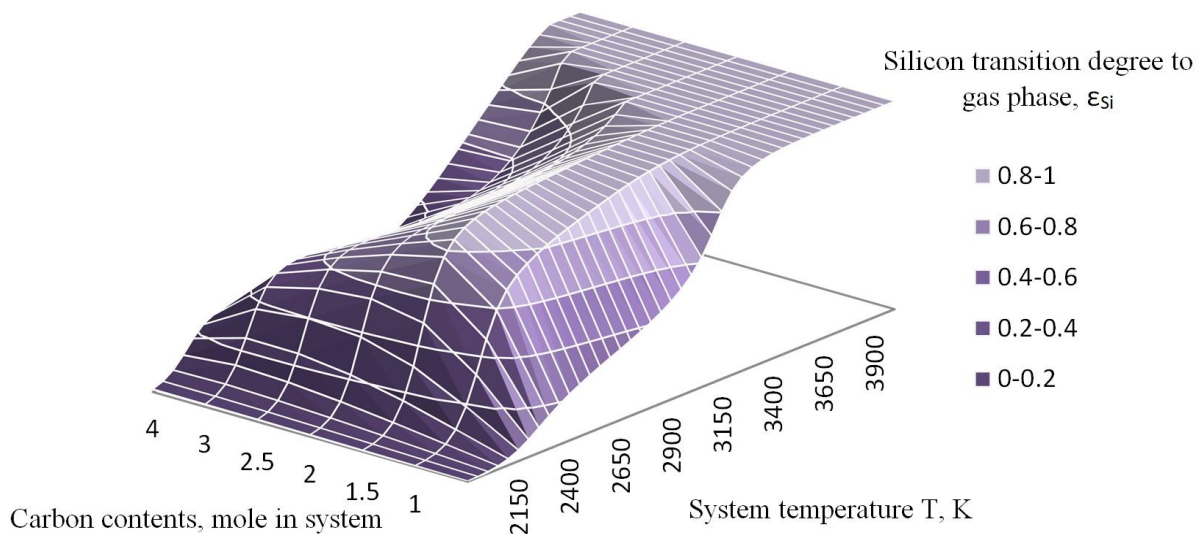


Figure 2. Silicon transition degree to gas phase ε_{Si} in dependence of system temperature T and carbon contents

3. Experiment technique

Experiments were executed at atmospheric pressure in laboratory DC plasma-arc furnace (figure 3). The furnace included copper cylindrical water cooled camera (1) with internal diameter 100 mm. Camera was closed from above by lid (2) through which graphite electrode (4) was entered by means of copper holder (3). Diameter of electrode was 50 mm. The lid was separated from camera by isolators (5) and gas collector (6). The gas collector served for supplying of argon under lid. The electrode was connected to a negative pole of electric source, the camera to a positive. The bottom of the camera was protected from extreme heating by graphite disc (7).

The electrode (4) had possibility of axial movement. Plasma arc (8) started when electrode (4) and disc (7) are brought in contact. The current of the arc was regulated by ballast resistance (9). Electrode

(4) and holder (3) had axial channels through which concentrate-carbon mixture was fed by feeder (10). The concentrate mixture formed the molten pool (11) while melting under arc heating.

There was an electromagnetic winding on the external surface of camera (1) (it is not shown on the figure), by means of which axial magnetic field ≈ 100 kA/m was created. The field promoted spatial stabilization of arc.

The sidewall of the camera (1) was equipped with window (12) for supervision over the process. The window was flushed by argon for prevention of a dust accumulation.

Argon was fed into electrode together with concentrate mixture. Argon served as transporting and plasma-forming gas. Hot gas products of the process (SiO, CO) mixed with Ar were transported to the heat exchanger (13) in which they were exposed to cooling. The cooled gas came to filter (14). Filter (14) was made as a combination of glass fabric and a steel grid of volume weaving. The total consumption of argon was 0.6 g/s: 70% in electrode, 15% on window, 15 % under lid.

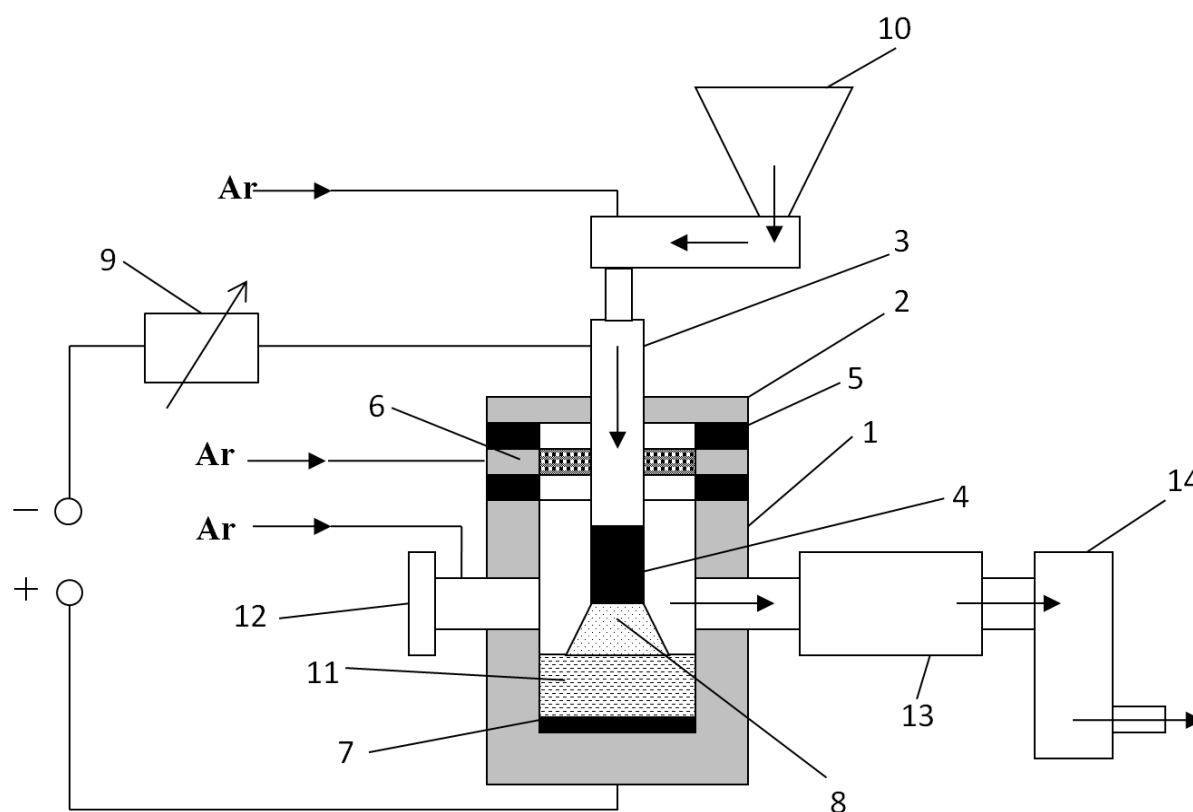


Figure 3. Plasma-arc furnace

Two condensed products were received after each experiment: ingot and powder. Ingot located on the bottom of camera, powder located on the upper part of camera, in the filter and in the heat exchanger. The condensed products were collected and weighed. It was not noticed that graphite disc (7) reacted with melt (11). The difference of mass of charged concentrate mixture and condensed products was thought to be a gas. It was assumed that this gas consists mainly of CO. Only powder from filter was analyzed. Its amount was about 10 % from total mass of powder. It was considered that this powder was not contaminated with initial concentrate.

The analysis of the Ti and Si concentration in products was carried out by atomic emission method with the inductive coupled plasma (AES-ICP) on spectrometer ICAP-6500 Duo (Thermo Scientific, USA) with the software of ITEVA. For definition of elements a standard sample Merck ICP multi element standard solution XVI was used.

The composition of the condensed powder was determined by measurement of a specific surface by isotherms of adsorption of gas on a surface of samples. For definition of nanopowders specific surface the analyzer of a specific surface TriStar 3000 was used (Micromeritics, the USA).

The morphology of ingot and powder material was analyzed on optical and electronic microscopes: on raster dual-beam microscopes of Helios 650 and Versa 3D (FEI Company), and also on the translucent electronic microscope of Tecnai G2 F20 (FEI Company) with adapter for the power dispersive x-ray analysis of a chemical composition.

The phase composition was examined by method of the X-ray phase analysis on the Ultima-4 diffractometer (Rigaku, Japan) with use of the program complex MAUD developed on the basis of the modified Ritveld's method and PDXL with the PDF-2 database (Powder Diffraction File).

The carbon contents in samples was measured on the CS-600 analyzer (Leco, USA) by method of burning of samples in oxygen flow with the subsequent definition of the carbon contents in gas phase by means of infrared spectrometry.

Camera (1), lid (2), holder (3) and heat exchanger (13) (figure 3) were cooled with water and calorimetred. The temperature of gas after heat exchanger was near the room temperature

4. Experiment results and its discussion

Concentrate was a loose oxide material with a size of particles ≈ 1 mm. Chemical composition: Si-17.0, Ti-32.8, Al-1.65, Fe-2.07 mass %. Chemically pure carbon (%C > 99.9%) with size of particles 0.3 - 0.5 mm was used as a reducing agent. Charge mixture was prepared on Turbula C20 setup. Three experiments differing in amount of carbon in charge mixture and plasma arc power were carried out. The parameters of experiments and properties of products are presented in table 1.

Table 1. Parameters of experiments and properties of products

Parameters	Melting No.1	Melting No.2	Melting No.3
Contents of carbon in charge mixture, mole C/mole Si	1.8	3.4	3.4
Plasma arc power, kW	10.3	10.0	18.5
Plasma arc current, A	332	334	691
Charged mass of concentrate mixture, g	437	327	327
Masses of products, g			
- ingot	202	148	150
- powder	103	72	73
- gas (calculated as difference)	132	107	104
Content in ingot, mass. %			
Si	8.8	7.3	3.6
C	0.9	10.0	9.12
Content in powder from filter, mass. %			
Si	33.7	45.7	47.5
C	3.3-7.24	6.29	4.05

The content of silicon in ingots was significantly less than in an initial concentrate in all experiments. The increase of contents of carbon in charge mixture in melting No.2 and power of

plasma arc in melting No.3 promoted desiliconization of concentrate. So, in melting No.3 the contents of silicon in the ingot was 3.6% against 8.8% in melting No.1. The contents of silicon in powder increased on the contrary.

Analysis of ingot on optical microscope has shown the existence of two phases. The microstructure of ingot is given in figure 4. Dark fields correspond to silicon oxide, light – to titanium oxide. The eutectic on basis of titanium oxide is distinguishable: areas containing dot inclusions of SiO_2 .

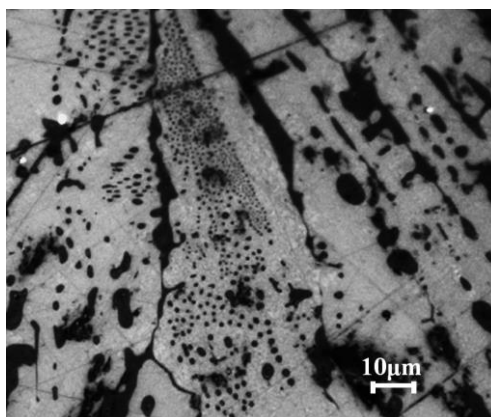


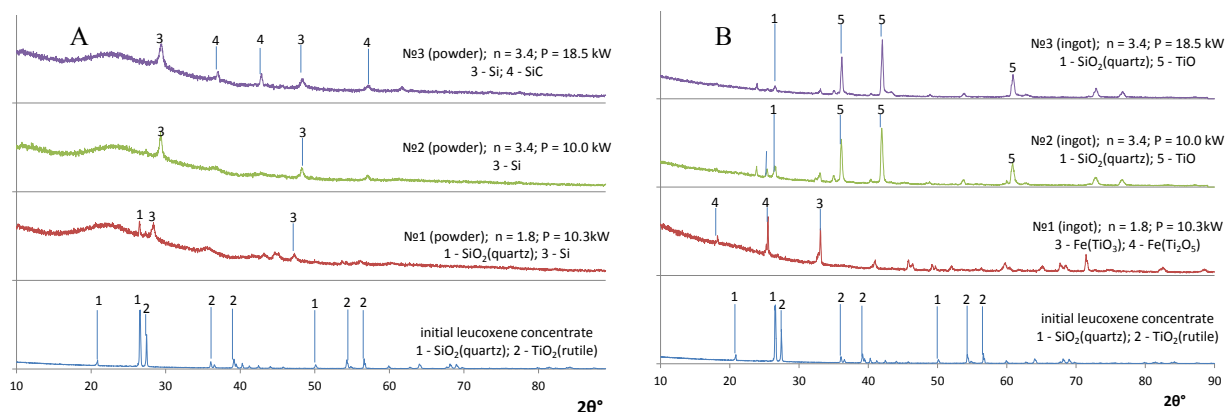
Figure 4. Microstructure of ingot

There are lines of quartz and rutile on the X-ray pattern of initial concentrate, whereas peaks of TiO_2 on the X-ray pattern of the ingot from melting No.1 are not found (figure 5). But there are peaks of less oxidized compounds: $\text{Fe}(\text{TiO}_3)$ and $\text{Fe}(\text{Ti}_2\text{O}_5)$. Quartz peaks in this sample are absent also. It can be explained by SiO_2 amorphization when hardening.

There are no peaks of Fe-bearing compounds on X-ray pattern of initial concentrate because these compounds have no peaks in realized range of θ .

There are no peaks of $\text{Fe}(\text{TiO}_3)$ and $\text{Fe}(\text{Ti}_2\text{O}_5)$ on X-ray patterns of the ingots from melting No.2 and No.3 at high contents of carbon in charge mixture. However there are TiO peaks which are absent on X-ray patterns of initial concentrate and ingot from melting No.1. Thus, the increase of carbon contents in charge mixture leads to titanium oxides reduction.

The peaks of Ti-bearing compounds are not revealed on X-ray patterns of powder. The pattern of melting No.1 with moderate amount of carbon contains the Si and SiO_2 peaks. SiO_2 peak disappears in pattern for melting No.2 with more amount of carbon in charge mixture. SiC peak appears in pattern for melting No.3 with high amount of carbon and high power of plasma arc.



The powder had microstructure as if it had condensed from gas phase. It was presented generally by fibres about 10 nanometres thick and up to 1 micron long (figure 6). The specific surface of powder was $\approx 70 \text{ m}^2/\text{g}$. There were spherical particles in size of 20 – 100 nanometres (figure 7). Fibres and spherical particles had layered structure with impurity of Al and Fe. Spherical particles, for example, could have the two-layer structure including the kernel enriched with Ti. The upper layer of the particle is enriched with Si (figure 8). The contents of silicon in some particles is significantly higher than deduced from the results of chemical analysis. The reason is: chemical analysis gives the average structure of great amount of particles. So, separate groups of particles might contain up to 90 mass.% Si. Thus, the contents of Si in various particles can significantly differ. The contents of impurities (Fe, Al) is about several percents at figure 8. It coordinates with the results of chemical analysis: 7.11 % Fe and 1.6 % Al for melting No1.

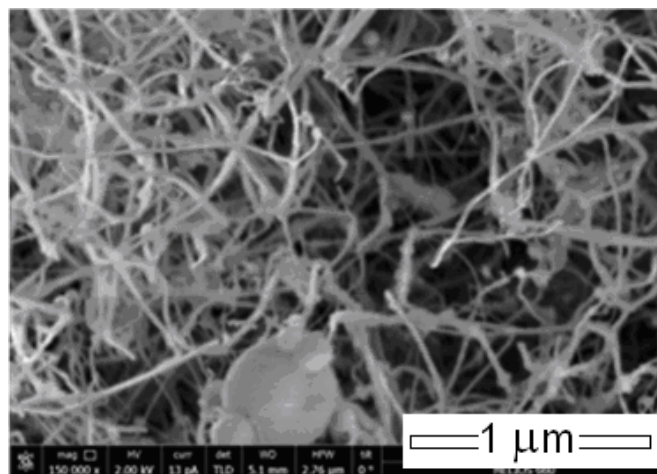


Figure 6. The typical microphotography of condensed powder

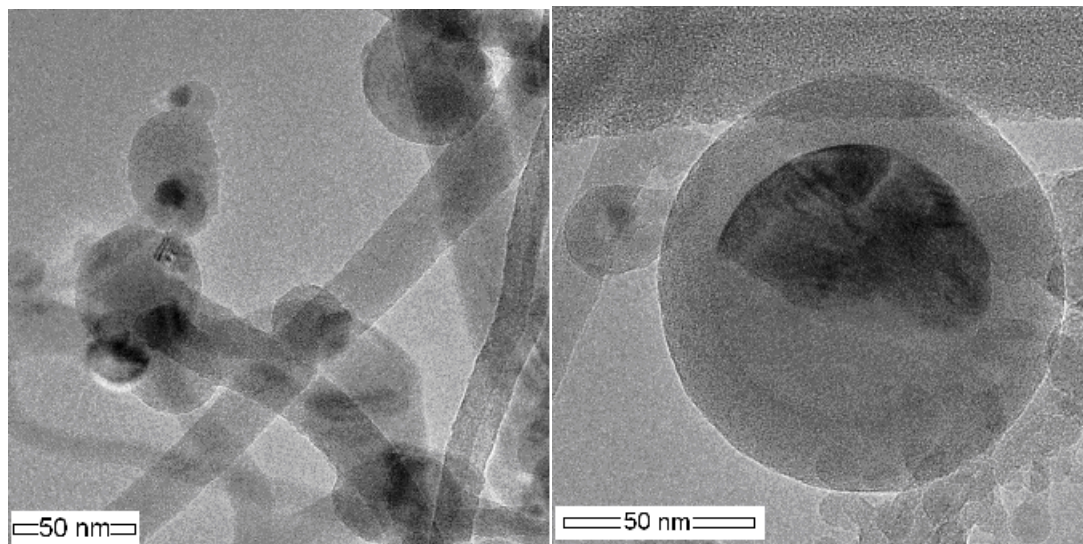


Figure 7. Microphotographs of spherical particles

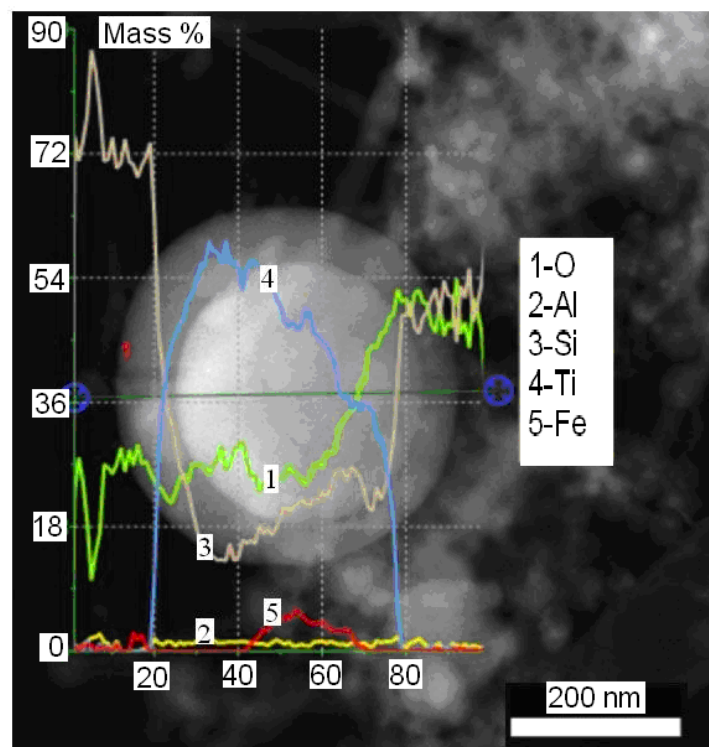


Figure 8. Composition of a spherical particle

The power of plasma arc exceeded the power of cooling at size $\Delta Q \approx 2,5$ kW. This testifies that endothermic processes took place in the furnace: formation of oxide melting pool $\approx 1,5$ kW and formation of siliceous fraction ≈ 1 kW.

5. Conclusions

The possibility of plasma-arc production of synthetic rutile from leucoxene concentrate is shown. Synthetic rutile with 3.6% of silicon was produced in laboratory experiments at energy consumption 20 - 40 GJ/t of concentrate and specific productivity of plasma furnace 20 t/(m³·day). The additional product in the form of ultra-disperse powder on the base of silicon was produced. The base of powder is fibers 10 - 50 nanometers thick and about 1 micron long.

The optimal thermodynamic conditions of plasma-arc reduction of leucoxene concentrate are: C = 15 % in mixture with concentrate, T = 2600 K. Synthetic rutile contains 3 % of Si in this case. Gas phase contains ≈ 44 % CO and ≈ 56 mass % SiO. Theoretical energy consumptions (without losses) are 8,9 GJ/t of concentrate.

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