PLASMA-CHEMICAL PROCESSING OF MINERALS TO NANO-DISPERSED POWDERS

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ABSTRACT. Nano-dispersed (ND) powder with particles size of 100-500 nm is obtained by plasma-thermal destruction of zircon. ND ZrO_2 with purity of 95-96 % is received by further leaching with NaOH. Nascent chemical elements, obtained by complex compounds destruction (manganese oxide concentrates, as an example) possess high chemical affinity towards oxygen, which causes reverse oxidative reactions to proceed instantly and leads to considerable difficulties in elements fixing in elemental state. The high chemical activity of ND metal powders, expressed as pyrophoreness, is overcome partially by suitable passivation. The disruptive oxidation of low-valence oxides to (for example, MnO to manganese and oxygen) represents the limiting stage of the entire thermal decomposition of oxygen-containing substances. ND Al_2O_3 is obtained by condensation of corundum (α-Al_2O_3) with granularity less than 50 μm. Depending on the process parameters its specific surface is in the range of 30-50 m^2/g. Meta-stable non-equilibrium phases (γ- and δ-Al_2O_3, as an example) are fixed at quenching rate $dT/d\tau$=10^5-10^6 K/s. The plasma-thermal destruction and/or re-condensation of complex compounds (ores, minerals, oxygen-containing salts, etc.) represents an effective method for their decomposition to lower compounds (oxides or even free elements) in ND state.

ПЛАЗМОХИМИЧНО ПРЕРАБОТВАНЕ НА МИНЕРАЛНИ СУРОВИНИ ДО НАНОДИСПЕРСНИ ПРАХОВЕ
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РЕЗЮМЕ. При плазмотермично деструктиране на минерала циркон е получен нанодисперсен (НД) прах с размери на частичките 100 - 500 nm, от който чрез излугване с NaOH е получен нанодисперсен ZrO_2 с чистота 95 - 96 %. Получените при деструктирането на сложни вещества (напр. манганооксиден концентрат) химични елементи в насцентно състояние, изключително трудно се фиксират в свободна елементна фаза, поради високия си химичен афинитет към кислорода и мигновено протичане на обратни окислителни реакции. Високата химична активност на НД метални прахове, проявена като пирофорност, частично се предотвратява чрез подходящо пасивиране. Лимитиращ стадий на пълното термично разлагане на кислородсъдържащи вещества е деструктирането на нисшите оксиди (напр. MnO до елементен Mn и кислород). При кондензиране на корунд (α-Al_2O_3) с гранулометрия под 50 μm е получен НД Al_2O_3 със специфична повърхност 30-50 m^2/g в зависимост от условията на процеса. При скорост на закаляване $dT/d\tau$ =10^5-10^6 K/s са фиксирани метастабилни неравновесни фази (напр. γ- и δ-Al_2O_3). Плазмотермичното деструктуриране и/или прекондензиране на сложни вещества (руди, минерали, кислородсъдържащи соли и др.) е ефективен метод за разграждането им до по-нисши съединения (напр. оксиди или дори до химични елементи) в НД състояние.

Introduction

High energy parameters of low temperature plasma (LTP) represent the main prerequisite for realizing the numerous processes of thermal destruction of many substances: natural raw materials – ores and minerals, oxides, carbides, etc. (Vissokov and Panayotova, 2003; Vissokov, 2004; Vissokov, 1984; Vissokov, 1987). Oxides or substances in elemental form are the main products of the thermal destruction of ores and minerals. Their further processing is realized by classical methods.

First announcements in the periodical and patent literature on the application of plasma heating to separate ores bearing ilmenite, beryl, and zircon dated from 1956-1963 (USA Patent, 1963; Berson, 1973). Raw materials are processed in plasma installation equipped with electric arc plasmotron, with cathode made of graphite. The anode is made of blend of the processed material and graphite in the amount ensuring enough high conductivity. At ignition of high intensity arc between cathode and anode, the latter is evaporated. Mixture of nano-disperse oxides (with particle size in the range of 35-50 nm) of titanium, beryllium, aluminum, silicon, uranium and zirconium is obtained at cooling (but not air quenching). Final products separation is realized by fraction condensation or by hydrometallurgical treatment of oxides. Oxides, treated in plasma, possess high chemical activity and dissolve easily in cold HCl.

Similar process can be realized in highly frequency inductive (HFI) plasma. Separation of mixed oxides has been realized (Klausler, 1969; Knuppel, 1969; Kubanek, 1977; Lamprey, 1962; Maclin, 1967) at above-mentioned ores destruction in HFI plasma-chemical reactor (PCR) at enough high capacity of the plasmotron and relatively low consumption of the processed material.

The thermal destruction of minerals and ores under LTP is often based on the use of highly intensive arc, as described in some patents (USA Patent; USA Patent, 1964). The ore is mixed with carbon for ensuring conductivity. According to spectral analyses, the plasma jet bears vapors of the raw material and carbon. Mixture of oxides is formed at condensation in air. Oxides are separated by fraction condensation or secondary treatment of the mixture. Oxides condense as nano-dispersed particles (NDP) with high

chemical activity. The process was tested with some minerals: beryl, kaolin, rhodonite, zircon, serpentine, etc.

The aim of present work was to carry out investigations on the plasma-chemical destruction of zircon ($ZrSiO_4$), manganese oxide concentrate (mixture of manganese oxides) and re-condensation of corundum (α-Al_2O_3) to nano-dispersed powders.

Experimental and discussion

1. Plasma destruction of zircon

An industrial process for ZrO_2 production by plasma treatment of zircon was developed by TAFA (daughter of Yonark Smelters, USA) Company (Vissokov, 1987; Vissokov and Pirgov, 1998). The crystal lattice of zircon is destructed at 2050 K and mixture of oxides is formed:

$$ZrSiO_4 \rightarrow ZrO_2 + SiO_2. \qquad (1)$$

The mixture is treated with NaOH to obtain soluble salt, and ZrO_2 remains in the precipitate.

$$SiO_2 + NaOH \rightarrow Na_2SiO_3 + H_2O. \qquad (2)$$
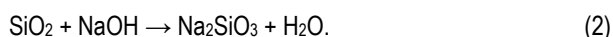
Our studies on plasma-chemical destruction of zircon were carried out in the plasma-chemical installation shown in Fig. 1 (Principal scheme) and Fig. 2 (General appearance). Bulgarian
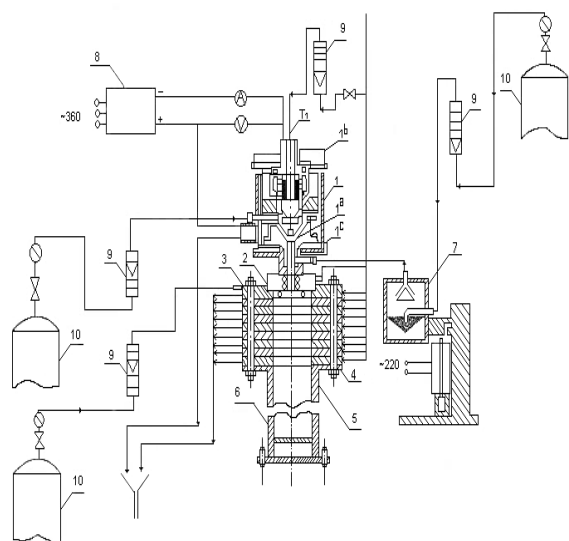

Fig. 1. Scheme diagram of plasma-chemical installation for preparation of nano-dispersed powders Electric-arc D.C. plasmotron; 1ᵃ. Thoriated tungsten cathode; 1ᵇ. Copper water-cooled anode; 1ᶜ. Plastic adjusting ring; 2. CW PCR; 3. Quenching device; 4. Copper water-cooled sections of the quenching device; 5. Powder-trapping chamber; 6. Filter; 7. Vibration powder-feeding device (if necessary, a piston type vibration powder-feeding device can also be used); 8. Current rectifier; 9. Flow-rate meters; 10. Bottles with plasma-forming, powder-carrying and quenching gases; T_1 – Temperature of inlet water; T_2 – Temperature of outlet water

(from Assenovgrad deposit) and Australian zircon with particles size less than 50 µm was used. Technical grade Ar (99 %) was used as plasma-forming and powder-carrying gas. Average mass temperature in the PCR was 1500-3000 K. The raw material consumption was 90 g/h. The consumption of plasma-forming Ar was 2 m³/h, and of powder-carrying Ar – 0.2 m³/h.

When cold-walls (CW) PCR is applied, a crust of melt is formed on the walls. Crust is not formed when a warm-walls (WW) PCR is used. Both reactors are with the same dimensions: length – 0.1 m, diameter – 0.02 m, cylindrical, made of stainless steel, water-cooled. The wall temperature in the WW PCR reaches 1500 K.
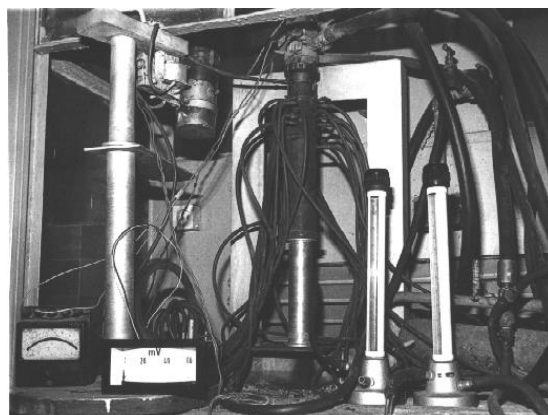

Fig. 2. General appearance of the plasma-chemical installation for preparation of NDP

Volt-ampere characteristic of the electric arc plasmotron with Ar as plasma-forming gas (0.792 g/s) is shown in Fig 3. It is known, that the discharge voltage of the electric arc depends on the plasma-forming gas and anode-cathode distance. In the range of 100÷500 A (Fig. 3), the discharge voltage decreases linearly with the discharge current increase.
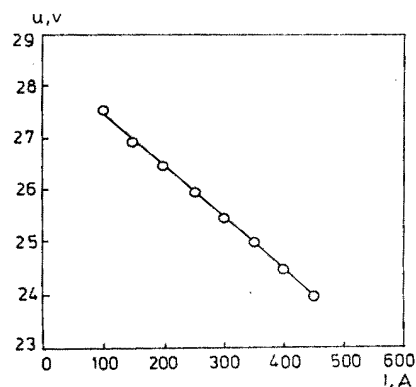

Fig. 3. Volt-ampere characteristic of the electric arc plasmotron with Ar as plasma-forming gas (0.792 g/s = 1.7 m³/h)

Linearity of U=f(I) determines the linear dependence of the plasmotron power P on the discharge current – P=f(I) – Fig. 4. At constant consumption of plasma-forming gas, the consumed power increases with the current increase, respectively – the average mass temperature of the plasma jet. The average mass temperature of the electric arc (Fig. 5) and of the PCR is found by calorimetric calculations (Vissokov, 1984; Vissokov and Pirgov, 1998).

Making use of the data, presented in Fig. 6, we can set enough accurately pre-determined values of the average mass temperature of the PCR, by varying the consumed electrical power, at constant consumption of powder-carrying gas and raw material.

Plasmotron characteristic, presented in Figs. 3-6, show that the plasma-chemical process can be carried out with enough

security and accuracy by smooth increase in consumed electrical power, at constant consumption of raw material, plasma-forming and powder-carrying gas.
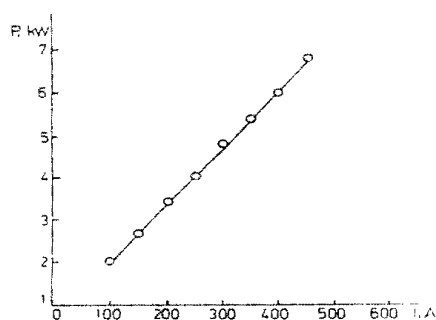

Fig. 4. . Watt-ampere characteristic of the electric arc plasmotron with Ar as plasma-forming gas (0.792 g/s = 1.7 m³/h)
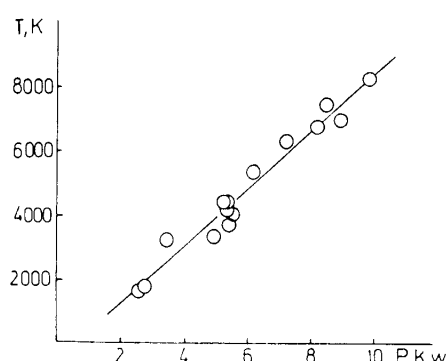

Fig. 5. Average mass temperature of the electric arc plasmotron as function of consumed electric power
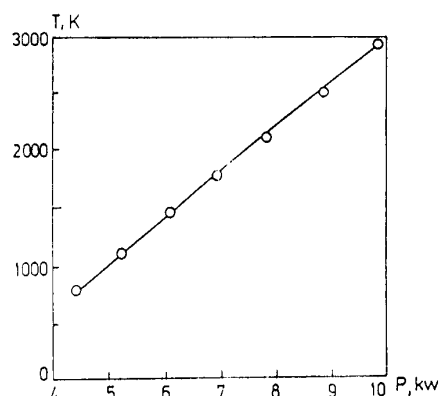

Fig. 6. Average mass temperature of the PCR as function of consumed electric power

Vibration-type powder-feeding device is used when the plasma-chemical process is carried out with a single-component raw material (as is the case with plasma destruction or plasma re-condensation). The device has conical bottom where the raw material is placed. Powder-carrying gas is supplied to the top of the cone. Powder cloud is formed and supplied to the plasmotron nozzle. The whole powder-feeding device vibrates with frequency of 50 Hz and amplitude 0.2 mm in order to ensure regular feeding with powder. Depending on the process specificity and necessary amount of NDP, the experiments duration was in the range of 3÷30 min.

Experiments for zircon destruction were made with the described installation. NDP was subjected to X-ray analysis. Major peaks of ZrO_2 and $ZrSiO_4$ can be distinguished, while SiO_2 appears as amorphous phase. The latter converts to soluble Na_2SiO_3 via reaction (2) at temperature of 500 K and use of 50 % NaOH solution. Fine-dispersed ZrO_2 with quality of 95-96 % was obtained. The main admixture is non-destructed $ZrSiO_4$. In our opinion, even without SiO_2 leaching, the obtained mixture of ZrO_2 and SiO_2 can be used as refractory or abrasive material, for chemicals preparation, as coloring reagent for ceramics, etc. Materials made of ZrO_2 are thermally resistant up to 3000 K, and those made of destructed zircon – up to 2000 K.

Calculations made by Yonark Smelters company pointed that specific capital investment for the plasma process are lower, compared to the conventional process, and the specific energy consumption is 7.92, against 33.12 MJ/kg for conventional furnaces. Plant with capacity of 4500 t/annum, at specific energy consumption of 10.8 MJ/kg was launched by the Company in 1977. Other silicate ores (thorite, sillimanite, calamine, chrysocolla, etc) can be processed in a similar way (Vissokov, 2004; Vissokov, 1987).

2. Plasma destruction of manganese oxide concentrates

First results on Mo obtaining by thermal destruction of MoS appeared in 1961 (Scholz et al., 1961). The process can not be realized in practice because of many technical difficulties, reaching the necessary high temperature – one of most important. Numerous experiments with plasma destruction of MoS_2 were made in 70-es of the previous century. NDP was obtained by Ar plasma destruction of molybdenite (92 % MoS_2 and 8 % SiO_2) where 90 % destruction was achieved (Huska et al., 1969). Experiments were carried out in installation with capacity of 10 kW and frequency of 4 MHz. Patent and periodical literature lacks data on plasma destruction of Mn, Fe, Co and Zn oxides and/or sulfides aimed at obtaining ultra-disperse pure Mn, Fe, Co, Zn, etc.

Thermodynamic properties of substances participating in a certain stage of the whole process determine the nature of chemical transformations taking place at temperatures of several thousands degrees. If reliable data on thermodynamic constants are available, the optimal temperature conditions, reaction thermodynamic probability, extent of raw materials conversion until the equilibrium and energy parameters of the process can be preliminarily assessed. We applied the classical approach for calculating the processes free enthalpy, entropy, free energy, equilibrium constant and thermodynamic probability for the thermal destruction of manganese oxide raw material, which follows the sequence:

$$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO \rightarrow Mn . \qquad (3)$$
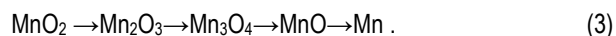
Calculations were made for the process, described with the equation (4), which is the limiting stage of the chain destruction process (3):

$$MnO \leftrightarrow Mn + O. \qquad (4)$$

Standard entropy and enthalpy of substances in gaseous state were used, because of the fact that at high temperatures (~10^4 K) of the plasma reactions all substances are in vapor state. Values of the equilibrium constant of the thermal

dissociation process (4), found for different temperatures are presented in Table 1.

Calculations made show that the dissociation reaction (4) proceeds to the right towards Mn production at very high temperatures (4000-5000 K).

Table 1. *Equilibrium constant and change in free energy for the thermal dissociation of MnO under Ar plasma conditions and different temperatures*

T, K	$\Delta G_T, .10^{-3}$	lg K_P	K_P
2000	39.4	-4.28	$5.25.10^{-5}$
2500	25.4	-2.20	$6.30.10^{-3}$
3000	11.3	-0.818	0.125
3500	-2.85	0.177	1.505
4000	-17.2	0.935	8.60
4500	-31.5	1.52	33.00
5000	-45.9	2.0	100.00
6000	-64.8	2.26	181.50

Manganese oxide concentrate used as raw material contains up to 99.9% manganese oxides and represents mixture of MnO_2, Mn_2O_3 and Mn_3O_4. Depending on its color, the raw manganese oxide is divided to black and brown - Table 2.

Table 2. *Manganese content in the raw material*

Component	Contents in black raw material, mass %	Contents in brawn raw material, mass %
Mn_{Total}	67.6	69.5
Mn^{2+}	43.1	48.9
Mn^{4+}	23.0	19.4

Granularity of the raw material, determined with metallographic microscope, is as it follows: less than 1 μm – 72.7 %, 1÷2 μm – 21.1 %, 2÷3 μm – 3.0 %, 3÷5 μm – 1.9 %, 5÷7 μm – 0.6 %, 7÷10 μm – 0.2 %, The raw material can be easily introduced into the reactor with the vibration powder-feeding device, at powder-carrying gas (Ar) consumption of 0.3 m^3/h and 1g/min carried powder. In order to decrease the particles adhesion, the raw material is dried at 353÷373 K and metal pellets are placed in the vibration feeding device. The specific surface of initial powder and final NDP was determined by Kljachko-Gurvich method (Kljachko-Gurvich, 1961) – Fig. 7,
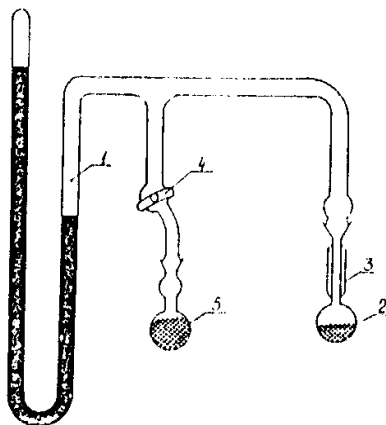

Fig. 7. Scheme of the device for specific surface determination by Kljachko-Gurvich method: 1- manometer, 2- ampoule with sample, vacuum-jacket of the ampoule with sample, 4-vacuum-valve, 5- ampoule with activated carbon

which is based on the nitrogen adsorption on the particles surface at the liquid nitrogen temperature. The accuracy is in the range of 10÷-15 % (lower than the accuracy of the classical BET method), but the method is faster. The method can be applied with good accuracy when the total surface of the analyzed sample (S) is in the range of 7÷15 m^2. In our case S=5.8 m^2/g for the black raw material and 5 m^2/g – for the brown manganese oxide material.

Thermal destruction experiments were made with plasmotron nozzle of 5 mm. Plasma-forming Ar consumption was 2.0-2.5 m^3/h and powder-carrying Ar consumption – 0.3 m^3/h. Current was changes in the range 200 ÷ 400 A, with a step of 100 A. Quenching was made by Ar jets spraying (at consumption 1.2÷1.4 m^3/h) and over water-cooling surface. Numerous experiments were made under described conditions, but each time the powder fed through the nozzle melted, formed ingots plugged the nozzle and process stopped. That means that the diameter of the anodic opening considerably influences the gas jet dynamics and processes of powder distribution and mixing with the gas jet. The process proceeds without problems at nozzle diameter of 7 mm. Experiments with black manganese oxide raw materials, quenching over water-cooling surface and with nozzle diameter of 7 mm were made. Process parameters are presented in Table 3. Experiments showed that when the quenching is over water-cooling surface, the reaction product is a mixture of NDP and solids that adhere on the quenching chamber walls.

In order to improve the conditions for reaction products condensation, which are very important for obtaining powders with highly developed specific surface, we studied more effective quenching method – simultaneous quenching over water-cooling surface and by cold gas spraying. Process parameters are presented in Table 4, where samples numbers 1 and 2 are of black and numbers from 3 to 5 – of brown manganese oxide raw material.

Table 3. *Parameters of plasma-chemical thermal destruction of black manganese oxide raw material at quenching over water-cooling surface*

Sample No	1	2	3	4
I, A	250	300	350	400
U, V	30	19	22	24
W, kW	7.5	5.7	7.7	9.6
S, m^2/g	4.8	2.3	-	6.1
Ar-pl-f, m^3/h	2	2	2	2
Ar-p-c, m^3/h	0.3	0.3	0.3	0.3

Ar-pl-f – plasma forming argon; Ar-p-c powder carrying argon

Table 4. *Parameters of plasma-chemical thermal destruction of manganese oxide raw material at simultaneous quenching over water-cooling surface and by cold gas spraying*

Sample No	1	2	3	4	5
I, A	400	400	200	300	400
U, V	29.5	26.5	30.0	30.5	27.0
W, kW	11.8	10.6	6.0	9.15	10.8
S, m^2/g	18.0	37.4	15.5	18.4	14.1
Ar-pl-f, m^3/h	2.4	2.5	2.5	2.5	2.5
Ar-c-g, m^3/h	1	1	1	1	1
Ar-p-c, m^3/h	0.30	0.30	0.35	0.40	0.40

Ar-pl-f – plasma forming argon; Ar-c-g – argon used as cold gas; Ar-p-c powder carrying argon

After destruction, the obtained NDP samples were analyzed chemically and by X-Ray analysis. It turned out that samples contain mainly MnO. The amount of Mn^{2+} increases and that of Mn^{4+} decreases in treated samples compared to the raw material. The concentration of Mn^{2+} in the raw material is 43.1 % and in thermally destructed – 57.2 %; the concentration of Mn^{4+} in the raw material is 23 % and in thermally destructed – 10.5 %. Carrying out the plasma destruction at higher power consumption (respectively – higher temperatures) and application of simultaneous quenching over water-cooling surface and by cold gas spraying ensures production of powders with higher specific surface and higher MnO concentration, compared to the raw material. Without additional measures, the elemental Mn content in the final product is less than 6 %. This is due to the fact that the obtained Mn possesses high chemical activity and reacts with the O_2 from the air. Proceeding of the reverse reaction of the equilibrium (4) can be suppressed by addition of H_2 or H-bearing compounds in the PCR.

3. Plasma re-condensation

Evaporation of coarse-disperse or with micron dimensions raw material under LTP conditions and subsequent condensation of vapors represents and effective method for NDP producing. American Vitro Laboratory's Company has studied for many years the plasma re-condensation as a method for producing NDP of refractory materials, including oxides, carbides, metals and multi-component systems [4]. Particles size is in the range of 10-100 nm. Nano-dispersed oxide powders are obtained in recurrent semi-industrial installation with capacity of 4.5÷9.0 kg/h. Other materials, described above, are produced in pilot installations.

Nano-dispersed powders of W, Mo, Ti, Ni, Al and ZrO_2 were produced in plasma-metallurgy laboratories of the "A. A. Baikov" Metallurgical Institute at Russian Academy of Science by plasma evaporation of conventional metal powders and vapor condensation in warmed up gaseous jets. Electron-microprobe analyses showed that size of produced particles is in the range of tens nanometers. Particles are spherical, with large specific surface and high chemical activity. Work under inert atmosphere allows keeping the chemical purity of products.

Our studies on thermal destruction of Fe_2O_3 under conditions of LTP produced by Ar electrical arc lead to production of finely-dispersed iron powder with particles size in the range of 100-500 nm. Particles are spherical with high affinity towards O_2 from the air (expressed as pyrophoreness). Product intensive oxidation to Fe_2O_3 occurs at lack of measures for the final product passivation (usage of nitrous atmosphere with O_2 contents of 0.1÷0.2 vol. %).

Experiments on re-condensation of α-Al_2O_3 with particles size less than 50 μm under LTP conditions were carried out in the installation shown in Figs. 1 and 2. Argon was used both as plasma-forming and powder-carrying gas with flow of 2 m^3/h and 0.3 m^3/h correspondingly. The average mass temperature of the PCR was 4000 K. Nano-dispersed Al_2O_3 was obtained, with specific surface in the range of 30÷50 m^2/g. Combined quenching with cold air jets (with flow up to 20 m^3/h) and over water-cooling surface was applied. The quenching rate $dT/d\tau = 10^5\text{-}10^6$ K/s was achieved that lead to formation of particles with size less than 100 nm and non-equilibrium crystal structure. Fast quenching allows meta-stable modifications fixing. δ-Al_2O_3 is formed faster than α-Al_2O_3 that is stable at temperatures higher than 1300 K. The fact is explained with the increased tetrahedral co-ordination of Al with the temperature raise. This co-ordination predominates also in the liquid Al_2O_3. It could be supposed that this co-ordination is preserved at quenching and determines appearance of δ-Al_2O_3 when, under quasi-equilibrium conditions, time is enough for octahedral co-ordination formation that is prerequisite for α-Al_2O_3 appearance. The phenomenon can be explained also in another manner: Crystallization nucleus can be formed only at such extent of overcooling when γ- and δ-Al_2O_3 are stable, because, at phase transition temperature, the crystallization heat can be enough to raise the material temperature only for coarse particles. Peaks intensity shows that γ-Al_2O_3 is the main constituent of the nano-dispersed Al_2O_3 and the share of δ-Al_2O_3 is considerably lower.

Conclusion

Plasma-chemical destruction of complex substances (ores, minerals, oxygen-bearing salts, etc) represents an effective method for their decomposition to lower compounds. Plasma re-condensation of refractory materials represents an effective method for producing finely-dispersed and ultra-dispersed powders.

Summarizing the studies on NDP obtaining in neutral LTP medium, we can highlight the plasma-chemical method is suitable for producing products with particular properties. For obtaining certain materials this is the only possible method. The industrial implementation of plasma-chemical production of NDP will be determined by technology, quality of products obtained and economics.

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