Reviews

Processing of mineral and technogeneous raw materials by carbothermal reduction

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Current studies dealing with the preparation of promising materials (most of all, ceramics) by carbothermal reduction (CR) of mineral and technogeneous raw materials is surveyed. Attention is concentrated on the mechanisms and kinetics of chemical reactions occurring during the CR process and on the effects of varying some factors during the reduction (temperature, duration of annealing, composition of the gas phase, ratio of the components, density of the blend, *etc.*) on the compositions and properties of the final products. Ways of optimizing particular technological schemes for the production of new materials by the CR method are discussed.

Key words: mineral raw materials; carbothermal reduction method; production of new ceramic materials; kinetics and mechanism of reduction.

According to statistical data, world production of materials for various purposes increases every year by more than 3%. Of these, ceramic materials occupy a leading position by total output and by cost price. In recent years, oxygen-free compounds have been widely used in the manufacture of ceramic materials. These compounds include binary and multi-component transition metal carbides, nitrides, borides, and silicides and their solid solutions, which possess unique properties: high melting points, hardness, and chemical inertness. Among the above-mentioned phases, compounds such as boron and silicon nitrides and carbides and complex compounds like sialons are of particular interest. Due to their abrasive properties and corrosion resistance, which are retained at elevated temperatures (higher than 1400 °C), these compounds are the main initial substances for the production of promising materials that are widely used for multiple purposes, as refractory, tool, and construction materials, *etc.*

However, at present, production of these materials is often based on multistage processes, involves unsolved environmental problems, and is characterized by high costs. The technological processes normally include extraction of pure oxides from ores and their subsequent reduction to metals or to oxygen-free compounds. The pyrometallurgical and chemical stages of this ore processing require a lot of energy and complex and expensive equipment; they involve evolution of large amounts of gases and dust, and the formation of liquid aggressive solutions that must be utilized.

The demand for the development of more efficient methods for the production of materials has resulted in the use of alternative methods for the digestion of raw materials that involve direct reduction of ores, concentrates, and technogeneous wastes with carbon.

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Carbothermal reduction (CR) of metal oxides formed the basis of the earliest technique for the large-tonnage manufacture of ferrous and nonferrous metals, alloys, and other substances. The kinetics and mechanism of CR have been studied quite extensively, and the results of these studies have been published in many monographs and papers. However, the vast majority of these studies were limited to the description of the reduction of metal oxides characterized by low heats of formation, for which CR occurs at moderate temperatures (700—1200 °C). Reduction of thermodynamically stable oxides requires higher temperatures (1200—1800 °C or even higher). A distinctive feature of high-temperature CR is the formation of stable intermediate compounds (oxycarbides, *etc.*) that mostly possess low diffusion permeability and thus decelerate the overall reaction. A further difficulty in conducting this process on an industrial scale is the fact that no special highly productive high-temperature equipment for continuous operation exists. Nevertheless, CR is attracting increasing attention from specialists producing new ceramic materials, because both the intermediate and the final reaction products are solid and because the possibility of conducting the process in a closed cycle makes it possible to capture completely the dust-like products and to utilize CO. Below we consider some characteristic examples in which the CR method was used for processing raw materials, in particular, for the preparation of the initial compounds used to produce ceramics, composites, and other materials for various purposes.

The problem of processing titanomagnesium placers by carbothermal reduction has been considered in a previous paper.[1] Titanomagnetites (TM) were used as the initial raw material; after magnetic separation, they had the following composition (%, w/w): Fe_2O_3, 46.7; FeO, 35.0; TiO_2, 8.4; Al_2O_3, 3.2; SiO_2, 3.0; MgO, 0.6; CaO, 0.3; MnO, 0.05.

The size of the initial TM particles was 0.4—1.5 mm. Boric acid was added to the concentrate, and reduction (at T 1200—1300 °C) occurred according to the following scheme:

$$TM + C + H_3BO_3 \rightarrow Fe + Fe_3C + Fe_2B + FeB + TiB_2. \quad (1)$$

The resulting ingots were ground into a powder with a particle size of 50—100 mm and used for plasma jet spraying onto construction-purpose parts. The slag, which contained the same components as the ingots, was used as an additive to wear-resistant construction materials.

Unfortunately, no data on the conditions of reduction of the oxides, on the ratio of the amount of the reducing reagent in the blend to the total amount of oxygen, or on the kinetics of CR were reported.[1] Therefore, it is impossible to explain why the composition of the ingots was identical to that of the slags since, if a reducing reagent is present in a sufficient amount, all iron should be concentrated in the ingots containing disperse segregations of iron and titanium borides.

In the paper under consideration,[1] an interesting way of using boron-containing datolite concentrate was proposed. Reduction yielded precipitation-hardened steel and glass ceramics. However, this stage of their work, like the first one, does not disclose the whole chemical process associated with variations in the synthesis conditions, *viz.*, increases in the reduction temperature and in the amount of the reducing reagent.

The characteristic features of carbidizing treatment of a tungsten concentrate were considered in another study.[2] Metallic tungsten or, when excess reducing reagent was used, tungsten carbide was detected in the final product. In the continuation of these studies, it would be of interest to reduce a mixture of tungsten and TM concentrates, which could give either ferrotungsten or iron hardened by precipitated $Ti_xW_yC_z$.

A similar approach to the production of a carbide-containing material was used by Chrysanthon *et al.*,[3] who carried out carbothermal reduction of columbite concentrate in order to obtain cemented carbides and composites with metallic (iron) matrices.

The kinetics and mechanism of the reduction of pure Nb_2O_5 by carbon in a vacuum have been considered in detail in the literature.[4,5] This reaction was found to occur by the following pathway:

$$Nb_2O_5 + C \xrightarrow{1000-1200\ ^\circ C} NbO_2 + CO \xrightarrow{1300-1400\ ^\circ C} \longrightarrow NbC + NbO_2 \xrightarrow{1500-1600\ ^\circ C} Nb + CO. \quad (2)$$

The rate-determining step of the process, which is written as follows

$$NbO_2 + 2\,NbC_x = 3\,Nb + 2\,CO, \quad (3)$$

is accompanied by heavy diffusional complications both at the atomic level (mutual diffusion of oxygen and carbon) and at the molecular level (diffusion of CO through micropores of the blend).

Reduction of Nb_2O_5 to the carbide occurs relatively readily according to the following scheme and ends at 1300 °C *in vacuo*:

$$Nb_2O_5 + C \rightarrow NbO_2 \rightarrow NbC. \quad (4)$$

The authors cited[3] used a columbite concentrate with an average particle size of 150 mm. The chemical composition of this mineral corresponded to the formula $(Fe,Mn)\cdot(Nb,Ta)_2O_6$. The effect of the particle size on the rate of the process was also studied. For this purpose, the concentrate was ground to a grain size of ~30 mm. Carbon black was used as the reducing reagent. The process was carried out in aluminum or graphite crucibles in an argon atmosphere, and the loss of mass was registered. The results of kinetic and structural studies[3] made it possible to distinguish two main stages in the reduction of columbite.

In the first stage in which the weight of the sample decreases by ~1/3, columbite is reduced to a complex oxide (tannolite).

$$(Fe,Mn)\cdot(Nb,Ta)_2O_6 + (2 + 2y)C \rightarrow \rightarrow (Fe,Mn)_y(Nb,Ta)_{1-y}O_2 + (1 - 2y)(Fe,Mn) + 2y(Nb,Ta)C + 2CO. \quad (5)$$

In the second stage, the reaction occurs by the following scheme:

$$(Fe,Mn)_y(Nb,Ta)_{1-y}O_2 + (3 - y)C \rightarrow \rightarrow y(Fe,Mn) + (1 - y)(Nb,Ta)C + 2CO. \quad (6)$$

The data obtained[3] indicate that the kinetics of the process depends markedly on the degree of dispersity of the initial concentrate: as the size of the particles of the starting oxide decreases the reaction rate increases. In the same study,[3] the final product was partially sintered, due to the formation of a certain amount of an Fe—Mn—Nb—Ta—C liquid solution. It was found that the addition of 10% Ni increases the number of particles of the carbide constituent and decreases the number of particles in sintered samples, since NbC and TaC are more soluble in nickel (3.0 and 5.0% (w/w)) than in iron (1.0 and 0.5% (w/w), respectively). Apparently, the (Nb, Ta)C solid solution occurs under these conditions in an equilibrium with doped iron. The admixtures of Ni, V, and W also form solid solutions with (Nb,Ta)C.

The authors[3] concluded that direct reduction of columbite followed by processing of the final products allows production of composite materials with high mechanical strengths.

Taking into account the above data,[3] it can be suggested that "mild" reduction of columbite yields the (Nb, Ta)C solution and a Fe_xMn_y alloy as the main products. Since the physicochemical properties of these products are basically different,[4,5] they can be separated by the conventional magnetic method. Obviously, this increases the value of this technique for the processing of columbite, because it increases the range of materials obtained.

An attempt has been made[6,7] to separate the Al_2O_3 and SiO_2 present in clays by carbothermal reduction of clays.

It is noteworthy that a physicochemical justification of carbothermal reduction of pure aluminum and silicon oxides was reported as early as 1957.[8]

The separation of these oxide components of clay leading to the formation of new products (SiC and a silica-rich residue) is based[6,7] on a two-stage reduction scheme:

$$3Al_2O_3\cdot 2SiO_2 + xSiO_2 + (2 + x)C \rightarrow \rightarrow 3Al_2O_3 + (2 + x)SiO(g) + (2 + x)CO \rightarrow \rightarrow (2 + x)SiO(g) + (4 + 2x)C \rightarrow \rightarrow (2 + x)SiC + (2 + x)CO. \quad (7)$$

In these experiments,[6,7] a mixture of clay and carbon in a ratio of 90 : 10 (w/w) was crushed by a dry procedure in a mill with alumina grinding bodies. The mixture was reduced as a powder and as pellets (pressed at p = 35 MPa) at temperatures above 1500 °C.

The chemical analysis of kaolin is (%): Al_2O_3, 37.4; SiO_2, 47.1; CaO, 0.38; Fe_2O_3, 0.97; calcination losses (CL), 13.3. Other types of oxide raw materials were also used, for example, the ash dust from power plants. The pellets prepared were additionally covered by carbon black, and the reduction was carried out in a flow of argon or nitrogen (30 cm^3 min^{-1}).

Carbothermal reduction of kaolin was found to yield fine-grained β-silicon carbide and larger grains of α-Al_2O_3; in some cases, a glassy phase was also detected in the blend. The final product, consisting of Al_2O_3, SiC, and unreacted carbon, can be separated into individual phases by grading it into grain sizes. The excess carbon is removed by annealing the obtained fractions at 500—600 °C; the yield of the product amounts to ~80—100% and depends on the rate of heating, the temperature of the process, the velocity at which the gas is passed, the volume of the blend, the grain size, and the possibility of formation of a glassy phase.

Experiments on the processing of kaolin in a revolving furnace in a nitrogen atmosphere were also carried out.[6,7] However, reduction in the revolving furnace gave no two-phase samples (Al_2O_3 and SiC) under any of the conditions used. This is due to the complete change in the gas composition (CO_2 appeared) as well as to the formation of different solid products: silicon oxynitrides, sialons, and a glassy phase. It can be concluded[6,7] that the process conducted in a graphite tube furnace is the most promising technique for processing the clay to prepare Al_2O_3 and SiC.

It should be noted that in the study under consideration,[6,7] no results of chemical analysis of the reduced product separated by "grading" are given; it is only noted[7] that along with the carbon present in the blend, an additional amount of the reducing reagent was poured onto the pellets. In this case, SiC concentrates in the covered layer, due to the following additional reaction

$$SiO + 2C = SiC + CO. \quad (8)$$

However, neither the ratio of the amounts of silicon carbide in the pellet and in this layer nor its fractional composition were analyzed. The absence of these data makes impossible the selection of the optimal conditions under which the reaction yielding silicon oxide

$$SiO_2 + 2C \rightarrow 2SiO \quad (9)$$

would predominate in the bulk of the blend and the reaction giving silicon carbide

$$2SiO + 4C \rightarrow 2SiC + 2CO. \quad (10)$$

would occur predominantly in the near-surface layer.

Nevertheless, it clearly follows from the reported data[6,7] that the pressure in the gas phase, the temperature, and the porosity (grain size) of the blend are the crucial factors governing the reduction process and that

the reduction itself consists of two stages: the first stage yields silicon monoxide, and the second stage leads to silicon carbide. Therefore, when the overall pressure of the gas phase is constant, the reduction is extremely sensitive to variation of the partial pressure of silicon monoxide, which must be substantially higher than the sum of the partial pressures of all the other components of the gas phase (CO, CO_2, N_2). At the same time, it is obvious that excessive silicon monoxide pressure can result in its disproportionation ($2SiO \rightarrow SiO_2 + Si$) and thus change completely the above-described mechanism of the formation of SiC; in this case, this compound will be formed in the following reaction: $Si + C \rightarrow SiC$, and this reaction will occur in the bulk of the sample rather than on its surface. Therefore the density of the blend should be controlled during the process, in order to ensure free removal of the silicon monoxide formed.

This conclusion was also confirmed by the interesting results on the separation of SiO_2 and Al_2O_3 present in clay, reported in the above-considered study.[6] The researchers produced briquets from a mixture of a clay with carbon, in which the amount of carbon was sufficient to reduce all the SiO_2 present in the clay to SiO. After that, the briquets were covered with carbon black, which provided conditions for further reduction of SiO to SiC.

Calcination at 1500 °C in a flow of argon gave a product[6] consisting of an Al_2O_3 pellet and a surrounding layer of SiC, which were easy to separate.

A study dealing with the carbothermal reduction and nitriding of a mixture of SiO_2 and $Al_2O_3 \cdot 2H_2O$[9] aimed at the preparation of sialons $Si_{6-z}Al_zO_zN_{8-z}$ (where $0 < z < 4.2$) can also be classified with the above-considered series of works.

It is known that sialons can be obtained from a mixture of SiO_2, AlN, and Al_2O_3[2,3] or by nitriding a mixture of SiO_2 and Al_2O_3 during its reduction.[4,8]

In this study,[9] sialon was obtained by heating a mixture of SiO_2 and $Al_2O_3 \cdot 2H_2O$ powders with carbon in a flow of nitrogen; attention was concentrated on the effect of the temperature of the synthesis on the formation of sialon. It was found that at 1350 °C, this reaction does not occur. Reduction and nitriding begins at 1470 °C to give silicon and silicon monoxide. The authors[9] set themselves the task of showing that the formation of SiO and its subsequent interaction with reaction products controls all the processes occurring during the reduction of SiO_2 by carbon and the formation of all resulting compounds. The formation of SiO, in its turn, is governed by a number of factors (the quantity and quality of carbon, grain size of the blend, the flow rate of N_2, duration of the heat treatment, the material of the crucible, and the temperature of the synthesis). The significance of these factors was studied in relation to the preparation of sialon. With allowance for vaporization of SiO, the process occurs by the following scheme:

$$3SiO_2 + 1.5(Al_2O_3 \cdot 2H_2O) + xC + \frac{x-4y}{3}N_2 \longrightarrow$$
$$\longrightarrow Si_{3-y}Al_3O_{10.5-x-y}\frac{N_{2x-4}}{3} +$$
$$+ xCO + ySiO + 3H_2O. \qquad (11)$$

where x is the number of moles of reacted carbon.

The blends were prepared[9] by mixing amorphous SiO_2, $Al_2O_3 \cdot 2H_2O$, and carbon black in a mill for 2 h in *n*-hexane; the excess of carbon was 0.8—1.4%. The mixtures were pressed into pellets with a diameter of 25 mm under a pressure of 30 MPa; the pellets were 2.6—5.2 mm thick, their weight was ~2.4 g and their relative density was 60%. Reduction was carried out at 1470 °C in a mullite tube furnace with SiC-heaters. The temperature was raised at a rate of 10 °C min^{-1}, N_2 was passed at a velocity (linear velocity R_{N_2}) of 0—490 cm^3 min^{-1}. This reduction carried out for 5 h at 1470 °C and at a flow rate of N_2 of 280 cm^3 min^{-1} gave products containing α-Al_2O_3, AlN-polytypes of sialon, and β-sialon. The elemental analysis of the final products as a function of the content of carbon in the initial blend is presented in Table 1. These data indicate that the proportion of nitrogen in the product increases in parallel with the content of carbon in the initial blend; the amount of residual carbon in the blend subjected to heat treatment increases simultaneously. In addition, it can be seen from the results obtained[9] that as the overall content of carbon increases, the compositions of the products synthesized deviate more and more from the expected (calculated) compositions; therefore, silicon is removed during heat treatment as SiO. According to reaction (11), when the total content of carbon in the blend, C_{tot}, is ~1.0%, "stoichiometric" β-sialon ($z = 3$) should be formed; however, compounds with z ~3.4 were obtained.[9] At the same time, when the proportion of carbon in the initial blend is high, the product contains more nitrogen than is needed for the "stoichiometric" β-sialon.

An important aspect in understanding the mechanism and kinetics of the reduction of SiO_2 mixed with other oxides is the role of the gas flow rate (N_2, inert gases).[10—13] The data[9] shown in Fig. 1 make it possible to follow clearly the effect of the N_2 flow rate (R_{N_2}) on the reduction and on the loss of SiO. For example, at

Table 1. Elemental composition (%) of the sialons formed depending on the content of carbon in the blend

Ca	Si	Al	C	N	O
0.8	23.8	32.8	1.3	18.7	23.4
0.9	25.1	31.6	1.9	20.6	20.8
1.0	25.6	31.4	3.0	222.0	17.8
1.2	26.8	30.4	46.0	25.5	12.7
1.4	26.7	28.2	9.6	26.1	9.4

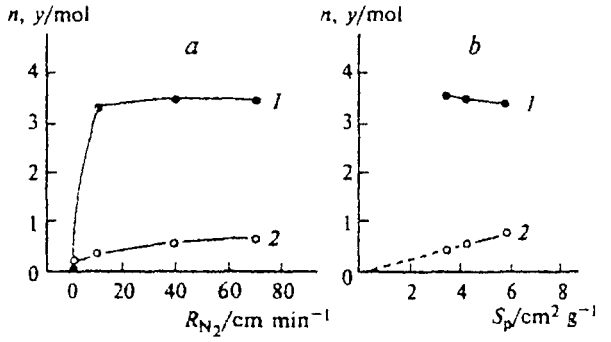

Fig. 1. Content of nitrogen (n) (*1*) and amount of "lost" SiO (y) (*2*) as functions of: *a*, nitrogen flow rate (R_{N_2}). Treatment for 3 h at 1470 °C, S_p = 4.3 cm^3 g^{-1} and C_{tot} = 0.9; *b*, specific interface area (S_p). Treatment for 3 h at 1470 °C (R_{N_2} = 40 cm min^{-1}, C_{tot} = 0.9).

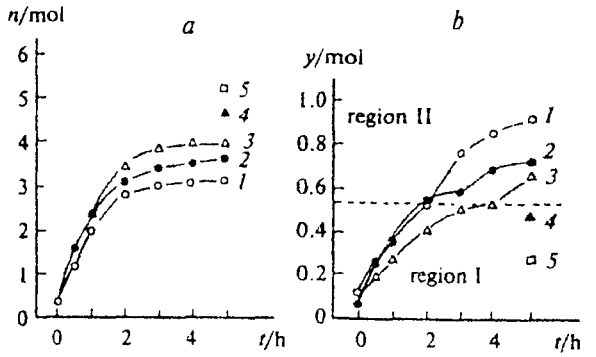

Fig. 2. Dependences of the content of nitrogen (n) (*a*) and of the amount of "lost" SiO (y) (*b*) on the duration of heat treatment (at 1470 °C) and on the amount of carbon added (moles): 0.8 (*1*); 0.9 (*2*); 1.0 (*3*); 1.2 (*4*); 1.4 (*5*); R_{N_2} = 40 cm min^{-1}; S_p = 4.3 cm^2.

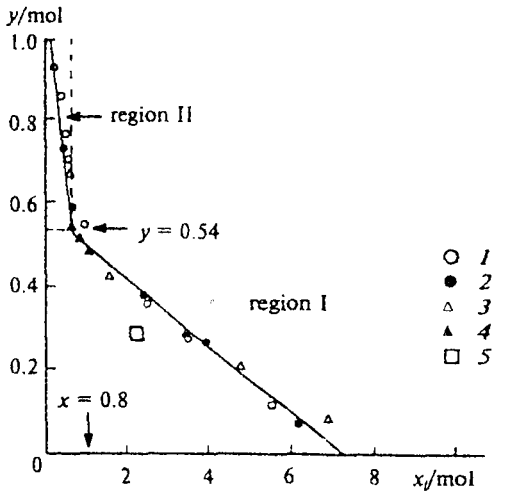

Fig. 3. The amount of SiO lost (y) as a function of the residual carbon (x_f) at various values of C_{tot} (mol): 0.8 (*1*); 0.9 (*2*); 1.0 (*3*); 1.2 (*4*); 1.4 (*5*).

R_{N_2} ~0, the reaction virtually does not occur, and at $R_{N_2} \geq 10$ cm^3 min^{-1}, the content of nitrogen in the product is ~3.5 moles, *i.e.*, the role of SiO and CO becomes noticeable. Previously,[13] it was found that even small changes in R_{N_2} enhance substantially the CO mass transfer in the reactor. Therefore, in the presence of a flow of N_2 (or, possibly, in an inert gas or hydrocarbon flow), the equilibrium in the reactions shifts toward the formation of the final products.

A similar situation is observed for a SiO_2+C mixture in a flow of N_2. However, for large R_{N_2}, not only the carry-over of CO increases (which is favorable for reduction) but also the carry-over of SiO, whose presence disturbs the chemical equilibrium and markedly changes the composition of the final product (in the present case, sialon), because a certain portion of the SiO participates in the formation of sialon, and this process is not necessarily associated with mass transfer.[13]

Figure 1, *b* also presents the dependences of the content of N_2 and the amount of "lost" SiO on the specific surface area of the sample (S_p). It can be seen that the losses of SiO increase as the contact area of the grains increases, whereas the content of nitrogen in the blend remains virtually constant, *i.e.*, the amount of SiO formed in the bulk of the blend is not equal to its loss due to mass transfer; in other words, some of the SiO formed is not involved in the nitriding. Thus, the reported data[13] indicate that the amount of SiO carried away depends on the carrier gas flow rate and on the specific surface area of the grains.

The authors cited[13] also considered the dependence of the content of nitrogen (n) in sialon and the amount of SiO (y) on the duration of treatment. At 1470 °C and R_{N_2} = 40 cm min^{-1} (Fig. 2), nitriding occurs intensely for 2 h and then markedly decelerates. It also follows from Fig. 2 that carbon reacts with SiO thus decreasing its losses. Two regions of losses of SiO can be conventionally distinguished[13] (Fig. 3): the region with $y < 0.54$ moles (region I) and that with $y > 0.54$ moles (region II). These values correlate with the content of residual carbon (x_f) at various C_{tot} (0.8—1.4 moles). The plot (see Fig. 3) exhibits an inflection at x_f ~0.8 mol.

It can be concluded that the residual carbon controls the removal of SiO. In region I (in which the content of carbon is large), the formation of SiO, its capture, and its nitriding occur easily, while in region II, these processes are hampered.

In both cases, the arising SiO is reduced and nitrided according to the following equation

$$SiO + N_2 + C \rightarrow Si_3N_4 + CO, \quad (12)$$

while alumina is converted by the following equation

$$Al_2O_3 + N_2 + C \rightarrow AlN + N_2 + CO. \quad (13)$$

The scheme under consideration for the reduction and nitriding processes can be represented as follows:

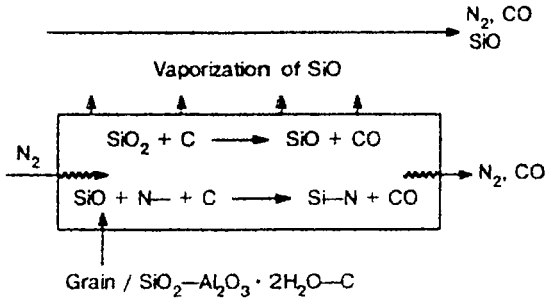

Figure 4 shows the correlation between the expected proportion of nitrogen, calculated from the equation

$$n = (x_a - 0.92x_t - 0.58)^{2/3} = (x_a - 0.2x_t - 1.13)^{2/3} \quad (14)$$

(where $x_a > 0.8$ moles, $x_t \leq 0.8$ moles), and the results of chemical analysis. It can be seen that the difference between the calculated and experimental values does not exceed ~0.3 moles, which proves the validity of using expression (14) in the calculations for such processes.

Unfortunately, the researchers[13] restricted themselves to discussion of the partial reaction of the reduction of SiO_2 by carbon, whereas the Al_2O_3 present in the blend was scarcely considered. In addition, they also did not take into account the intermediate products resulting from the reduction of Al_2O_3 and SiO_2 by carbon in a flow of N_2, *i.e.*, oxynitrides.

The authors[13] suggested that silicon nitride (and sialons based on it) are formed in the reaction SiO + C + N → SiN + CO, whereas in another study,[8] a different scheme was proposed; this scheme included disproportionation of the monoxide 2SiO → Si + SiO_2 followed by the reaction of silicon with carbon or nitrogen.

In this connection, it is appropriate to mention a study by Mackenzie *et al.*[14] devoted to the preparation of β-sialon by reduction of kaolinite ($H_4Al_2Si_2O_9$) and halloysite ($H_4Al_2Si_2O_9 \cdot H_2O$) by carbon in a nitrogen atmosphere. The intermediate compounds formed in the reduction were studied in detail by X-ray diffraction analysis and NMR spectroscopy. Based on the results obtained, a three-stage scheme was proposed for reduction of clay raw materials:[14]

1. Dehydration of the initial material at 1300 °C, in order to transform it into a mixture of mullite and silica (cristobalite)

$$3Al_2Si_2O_5(OH)_4 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 + 6H_2O.$$

2. Transformation of silica into silicon carbide at 1300—1400 °C

$$4SiO_2 + 12C \rightarrow 4SiC + 8CO.$$

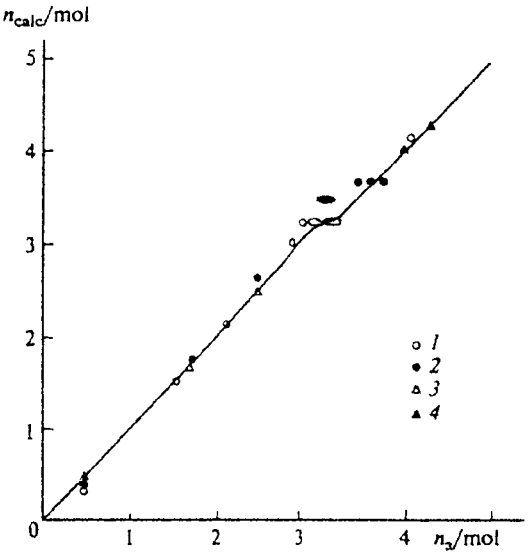

Fig. 4. Calculated (n_{calc}) and found ($n_э$) nitrogen contents (moles): 0.8 (*1*); 0.9 (*2*); 1.0 (*3*); 1.2 (*4*).

3. Reaction of SiC with mullite under nitrogen to give $Si_3Al_6O_{12}N_2$ (*x*-phase of sialon) with subsequent formation of β-sialon

$$3Al_2O_3 \cdot 2SiO_2 + SiC + N_2 \rightarrow Si_3Al_6O_{12}N_2 + CO,$$

$$Si_3Al_6O_{12}N_2 + 3SiC + 3C + N_2 \rightarrow 2Si_3Al_3O_3N_5 + 6CO.$$

It was noted[14] that β-sialon is not the final product of reduction: the reaction can proceed further with removal of Si and O(SiO) to give 15*R*-sialon. The latter is one of the polytypes with a laminated structure of the AlN type, and its general formula is $Si_{6-x}Al_{x+y}O_xN_{y+8-x}$.

In this paper, as in the above-discussed study,[13] initial mixtures of reactants containing 25% carbon (lampblack) in hexane were treated in a ball mill with ZrO_2 balls for 17 h. Then they were pressed into pellets 2 mm in diameter and placed in a tube furnace in Al_2O_3 crucibles. Heat treatment was carried out in a flow of pure N_2 (150 mL min^{-1}) for 10 min at temperatures of 1100 to 1400 °C, and for periods from 10 min to 24 h at 1400 °C. Formation of new phases and their relative concentrations were determined in ground samples by X-ray diffraction analysis. The problems of phase formation were discussed on the basis of the ^{27}Al and ^{29}Si NMR spectra recorded on a Bruker AMX 500 spectrometer.

Putting together all of the data obtained[14] it was possible to identify more precisely the sequence of chemical reactions occurring during the reduction of clay materials.

1. Formation of mullite and amorphous silica

$$3Al_2Si_2O_5(OH)_4 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 + 6H_2O.$$

2. Formation of silicon oxynitride in the presence of nitrogen and carbon

$$2SiO_2 + 3C + N_2 \rightarrow Si_2N_2O + 3CO.$$

3. Formation of the x-phase of sialon and β-sialon from mullite

$$3Al_2O_3 \cdot 2SiO_2 + N_2 + 12C \rightarrow \rightarrow Si_3Al_6O_{12}N_5 + 6AlN + SiO_2 + 12C;$$

$$Si_3Al_3O_3N_2 + 3N_2 + 9C \rightarrow Si_3Al_3O_3N_5 + 2AlN + 9CO.$$

4. Formation of silicon carbide

$$SiO_2 + 3C \rightarrow SiC + 2CO.$$

5. Formation of silicon nitride

$$3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO.$$

These researchers[14] also found some differences between the orders in which these phases are formed during the reduction of kaolinite and halloysite. For example, in the case of kaolinite, SiC and Si_3N_4 appear earlier, because they are formed directly from SiO_2 rather than from the x-phase of sialon, as occurs in halloysite samples:

$$2Si_3Al_6O_{12} + 7N_2 + 27C \rightarrow Si_3N_4 + 3SiC + 12AlN + 24CO.$$

The main distinction between halloysite and kaolinite is that the former contains a larger amount of silicon as cristobalite; it was noted[14] that the SiO_2 occurring in the bulk of this mineral disappears after 4 h of reduction as the amount of SiC increases. Conversely, in the case of kaolinite, which contains scarcely any free cristobalite, noticeable formation of SiC is detected much later (after no less than 1 h). Thus, the free SiO_2 in these materials is reduced at a higher rate than that bound in mullite.

The NMR spectroscopy data allowed the authors[14] to obtain interesting information concerning local structural transformations and the rearrangement of the interatomic interactions that accompany the processes in question. We shall mention the most important of these results.

1. In an early stage of reduction in which mullite is produced (T < 1300 °C), triply coordinated Al nodes are formed in the reaction mixture; this is due to the appearance of oxygen defects.

2. The first Si—N bonds are formed at low temperatures (1200 °C) in the region in which the oxynitride phase, which is being enriched in nitrogen as time passes, is in a quasicrystalline state. In the absence of carbon, the appearance of this phase is delayed to a temperature of 1400 °C.

3. Si—O bonds are retained in the reaction mixture for quite a long period after the mullite disappears, especially in kaolinite materials. The chemical shift corresponding to Si—O bonds suggests the formation of configurations similar to tetrahedral silicate groups with three bridging oxygen atoms between two tetrahedra, in which Al atoms can also be bound.

4. Si—C bonds arise in the later stages of reduction, especially when halloysite participates in the reaction. In the case of kaolinite, traces of SiC were also detected in the mixture after 10 min of the reaction, whereas, according to the NMR spectra, an individual SiC phase appears only after heating for 1 h.

5. Under the experimental conditions studied (1400 °C, 8 h), Al—N bonds are the last to be formed; they are detected much later than the sialon phases.

The latter conclusion is in good agreement with the results obtained previously for the reductive synthesis of AlN from Al_2O_3 carried out at 1773—1973 K in a flow of N_2.

In recent years, one more method for the production of new materials by carbothermal reduction has been intensely developed; this method involves the use of titanium-silicon concentrates, leucoxenes, as raw materials.

Among the wide variety of silicon-containing mineral raw materials, a prominent place is occupied by sandstones containing titanium leucoxenes. They normally consist of quartz (60—70 mol.%) and leucoxene (5—35 mol.%). Along with leucoxene, sandstones contain more than 40 other minerals,[15] which can be found, for example, in the Yaregskoe petroleum and titanium deposit. After enrichment and calcination, the concentrates obtained from the ores contain more than 80% titanium and silicon oxides. The chemical compositions of two samples of leucoxene concentrate (LC) are presented in Table 2.

Table 2. Chemical compositions of two samples of leucoxene concentrate

Sample	TiO_2	SiO_2	Fe_2O_3	Al_2O_3	MgO	Na_2O+K_2O	Nb_2O_5	P_2
1	48.0	40.7	2.50	2.40	0.78	Unknown	0.63	0
2	53.0	38.0	2.80	5.45	Unknown	0.75	0.091	0

Over the last 50 years, numerous attempts have been undertaken to process these concentrates using various chemical methods. Currently there are two competing methods, *viz.*, chlorination and sulfatization methods, which were developed mostly for the production of pigments. However, chemical methods require large expenses for waste utilization, and the slag contains almost 100% (w/w) TiO_2. Therefore, a technology for producing ceramic materials from these concentrates is more promising.

Digestion of LC concentrates using the carbothermal process has not been studied until recently.

The first studies along this line[16,17] included reduction of LC by carbon *in vacuo*. The samples were prepared by the following scheme:

— mechanical grinding of the initial components in a ball mill and grading them by screening through a 0.05 mm sieve;

— addition of a 5% aqueous solution of carboxymethyl cellulose (10%) to the blend as a binding agent;

— production of blanks as 5-mm-high disks with a diameter of 20 mm by pressing the material under a pressure of 100—150 MPa;

— drying the disks at 100—110 °C;

— annealing of the blanks in a vacuum of 10^{-3}—10^{-2} Pa at temperatures ranging from 1200 to 1500 °C.

Activated carbon with an ash content of less than 1% was used as the reducing reagent.

Heat treatment of these samples was accompanied by intense gas evolution in the 1200—1250 °C temperature range, which increased the pressure in the system. The annealing was completed after the initial pressure had been restored. After heat treatment, the loss of mass of the samples was determined. The results are presented in Fig. 5, which indicates that as the content of carbon in the blend increases, the initial oxides are reduced more intensely. When 20% (w/w) carbon is present, the mass loss is 62%. However, the detected mass losses cannot be explained by the formation of CO alone. The deviation of the experimental plot for mass losses (curve *1*) from the calculated curve (curve *3*) indicates that, together with CO, silicon monoxide, which is sublimed at 1025 °C,[18] is also removed. This is supported by the fact that a precipitate amorphous to X-rays and oxidized to SiO_2 upon calcination (1100 °C) is formed on the cold parts of the furnace.

Depending on the content of carbon, four sections in the curve of losses can be distinguished (see Fig. 5); these sections reflect different characters of the phase transformations. In particular, a decrease in the content of the α-cristobalite phase to low concentrations can be clearly followed in the fourth stage. In addition, as the content of carbon increases, the number of titanium-containing phases increases, and in the last stage (IV), mutual solutions of titanium oxide and carbide, oxycarbides, are formed, which is confirmed by the chemical analysis of the reduced blend that was preoxidized in air at 1100 °C (Table 3). These data indicate that under the conditions studied, at particular ratios of the oxygen in the oxides to the carbon in the initial blend, a material containing virtually no silicon can be obtained.

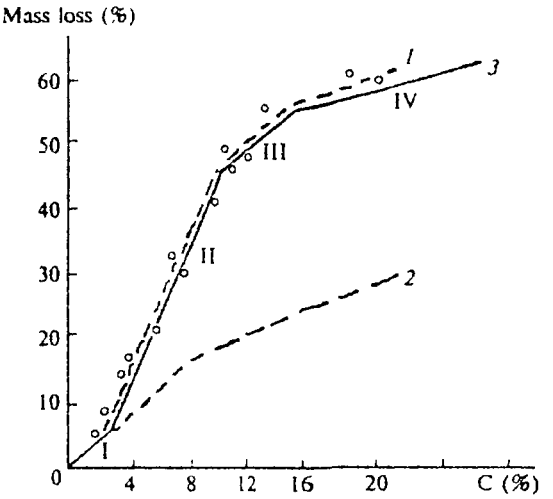

Fig. 5. Dependences of the mass loss on the content of carbon in the blend: experimental results (*1*); losses associated only with reduction of TiO_2 (*2*); losses calculated with allowance for the simultaneous reduction of TiO_2 and SiO_2 (*3*). I—IV are concentration ranges corresponding to various phases of formation.

The processes occurring during carbothermal reduction of LC and model oxide mixtures containing various proportions of carbon in an atmosphere of N_2 or *in vacuo* in the 1000—1600 °C temperature range have been studied previously.[19]

The thermal parameters of the reactions were obtained from DTA-TG data, and the phase compositions of the products were studied by X-ray diffraction analysis. To ensure the legitimacy of comparison of the data obtained, all blends were prepared under identical conditions by mixing acetylene carbon black with the corresponding oxides over a period of 1 h.

The finished blends were packed in tungsten crucibles. The syntheses were carried out at a residual pressure of no more than $1 \cdot 10^{-2}$ Torr; the samples were reduced in a flow of N_2 passed at a velocity of 0.1—0.2 L min^{-1}.

Table 3. Comparison of the chemical compositions of leucoxene concentrate (LC) and samples obtained by carbothermal treatment

Sample	Chemical composition (mol.%)									
	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	Na_2O	K_2O	P_2O_5	CL*	C in the blend
LC	37.88	52.90	5.37	2.80	0.004	0.11	0.64	0.142	0.55	0
116	36.40	54.80	4.48	2.96	0.010	0.06	0.54	0.130	0.16	4.00
118	32.36	58.95	4.51	2.96	0.020	0.06	0.45	0.116	0.22	5.90
120	26.08	65.20	4.646	3.14	0.015	0.03	0.44	0.108	0.17	7.70
124	6.08	84.86	3.79	4.60	0.007	0.05	0.02	0.108	0.31	20.00

* CL stands for calcination losses.

Table 4. Parameters of the reduction of Ti and Si oxides and phase compositions of the annealed samples

Reaction	Composition	Atmosphere	T/°C	t/h	Phase composition of the sample	Degree of conversion
(1)	TiO_2 + 3C	Vacuum	1300		TiC, Ti_2O_3	
			1350		TiC, (Ti_2O_3, TiO — traces)	
			1400		TiC, (TiO — traces)	
			1450	2—4	TiC	0.98
(2)	SiO_2 + 3C	Vacuum	1400		α-SiC, SiO_2	
			1500		α-SiC, (SiO_2 — traces)	
			1600	6—10	α-SiC	1.00
(3)	SiO_2 + 2C	Vacuum	1400		α-SiC, SiO_2	
			1500		α-SiC, (SiO_2 — traces)	
			1600	6—10	α-SiC	>1.00
(4)	TiO_2 + 2.5CN_2	N_2	1300		Ti(C, N), (Ti_2O_3 — traces)	
			1450	2	Ti(C, N)	0.96
(5)	SiO_2 + 2C	N_2	1300		SiO_2N_2, SiO_2	
			1450	2	β-S_3N_4	

The parameters of reduction and the phase compositions of the mixtures of individual oxides with carbon, annealed under various conditions, are listed in Table 4.

The data for reactions (1)—(5) given in Table 4 are in agreement with those described in the literature[19—21] and also with the results of the studies considered above. The Si—C—O system has also been described in earlier papers.[22—25] Some unusual features of reactions (4) and (5) carried out in a flow of N_2 were found. These reactions are characterized by the fact that the temperatures of formation of the final products are lower than those in reactions (1)—(3). In addition, in reaction (5), silicon oxynitride was detected as an intermediate compound; this compound has not always been observed in studies dealing with this reaction. Finally, excess mass loss associated with sublimation of silicon monoxide was clearly recognized in reaction (3) (see Table 4); this fact has also been observed in a number of other studies including those discussed in this review.

In the second series of experiments, model mixtures of silicon and titanium dioxides were studied under the same conditions (Table 5).

It follows from Table 5 that no principal differences between reactions (1)—(4), involving model mixtures of titanium and silicon dioxides in contact with carbon, and the corresponding reactions involving individual titanium and silicon dioxides were found (see Table 4). The nature of the intermediate compounds indicates that the TiO_2 and SiO_2 incorporated in the mixtures are reduced in parallel independently of each other. This is also true for the leucoxene concentrate, whose reduction pathway is similar to that for model mixtures of titanium and silicon dioxides. In this series of studies, a decrease in the temperature of reduction of mixtures of titanium and silicon dioxides and leucoxene in an atmosphere of N_2 was also observed.

The synthesis in the Si—Ti—O—C—N system occurs in the absence of thermal analogies (the DTA curves showed no thermal effects in the temperature range studied). Therefore, we can assume that the high rates of reduction of titanium and silicon oxides is due to the formation of intermediate reaction products, Ti and Si oxynitrides.

Mechanism and kinetics of CR of oxides

In the studies considered in this review, researchers analyzed CR of oxide-containing concentrates with fairly complex compositions and of technogeneous wastes giving solid and gaseous products rather than CR of pure oxides that are difficult to reduce (DRO). This hampers extremely any detailed consideration of the kinetics and mechanism of the processes involved, since the presence of other metal oxides has a substantial effect on the rate of reduction and on the composition of products. It has been established that an iron admixture in the reaction giving sialons and silicon carbide has a catalytic effect. Nevertheless, the main stages of CR of complex oxide-containing products obey the regularities established for individual oxides.

Vast information on the mechanism of CR of easily reducible (≤ 1200 °C) oxides (ERO) of Fe, Cu, Ag, Ni, and other metals has been reported in the literature. However, many oxides with high heats of formation (including those considered above) are reduced at T > 1200 °C. The corresponding reactions of DRO are characterized by some specific features.[27] In this case, in addition to the effects of the gas phase, the activity of oxides and reducing agents, and the physical state of the blend (grain size of reactants and porosity of the blend), a significant role belongs to the processes of macro- and microdiffusion of oxides included in the blend and carbon (nitrogen).

Table 5. Phase compositions of the annealed samples of titanium and silicon dioxide mixtures

Reaction	Composition	Atmosphere	T/°C	Phase composition of the sample*
(1)	$TiO_2 \cdot SiO_2$ + 6C	Vacuum	1400	TiC, SiC (SiO_2, TiO — traces)
			1500	TiC, SiC (TiO — traces)
			1600	TiC, SiC
(2)	$TiO_2 \cdot SiO_2$ + 4C	Vacuum	1400	TiC, SiO_2 (SiO_2, TiO — traces)
			1500	TiC, SiO_2 (SiO_2, TiO — traces)
			1600	TiC, SiC
(3)	$TiO_2 \cdot SiO_2$ + 6C	N_2	1300	Ti(C, N), SiO_2, Ti_2O_3 (Si_3N_4, Si_2ON_2 — traces)
			1450	Ti(C, N) SiC
(4)	$TiO_2 \cdot SiO_2$ + 4C	N_2	1300	Ti(C, N), SiO_2, Ti_2O_3 (Si_3N_4, Si_2ON_2 — traces)
			1450	Ti (C, N) SiC
(5)	"LC" + 6C	Vacuum	1400	TiC, SiO_2 (SiO, TiO — traces)
			1500	TiC, SiC (TiO — traces)
			1600	TiC, SiC
(6)	"LC" + 4C	Vacuum	1400	TiC, SiO_2 (SiO, TiO — traces)
			1500	TiC, SiO_2 (SiO, TiO — traces)
			1600	TiC, SiC
(7)	"LC" + 6C	N_2	1300	Ti(C, N), SiO_2, Ti_2O_3 (Si_3N_4, Si_2ON_2 — traces)
			1450	Ti(C, N), SiC
(8)	"LC" + 4C	N_2	1300	Ti(C, N), SiO_2, Ti_2O_3 (Si_3N_4, Si_2ON_2 — traces) Ti(C, N), SiC

* Actually it was titanium oxycarbide with a low carbon content.[26]

Before considering the roles of individual parameters of the CR of DRO, we should determine the main stages of the process and their rate-determining steps, taking into account the fact that these stages often occur in parallel at different rates rather than following one another in a definite order. They frequently compete with one another, and their separation in a particular time interval is possible only if one of the stages obviously predominates.

The following main stages can be distinguished.

Contact interaction of oxides with carbon. It has been repeatedly emphasized in the literature[28] that the reaction of ERO with carbon begins at fairly low temperatures, whereas the gasification reaction (C + CO_2) begins at relatively high temperatures (~800 °C). This appears to be due to activation of carbon and ERO during the preparation of the blend, *i.e.*, this can be a consequence of the mechanochemical reaction involving the carbon atoms inserted into the outer layers of oxide grains. This is directly confirmed by the fact that in some cases, bound carbon was detected in a blend; for example, in the blend consisting of carbon and TiO_2, its content amounted to several percent. X-ray diffraction analysis shows only some broadening of the TiO_2 lines, which points to distortion of the dioxide lattice. This assumption is also supported by the data of Mackenzie *et al.*,[14] who reported that during the primary stages of the interaction of SiO_2 and Al_2O_3 with carbon, the coordination number of Al decreases to three, due to the appearance of oxygen vacancies. The presence of these defects causes the formation (upon contact with carbon and nitrogen) of pseudocrystalline compounds (solid solutions), oxycarbides and oxynitrides. An increase in the content of these compounds leads to transformation of the crystal structures of the initial oxides to give new structures typical of oxycarbonitrides.[26] These solid solutions are fairly sensitive to the partial pressure of N_2 and CO, and the process of their formation is largely determined by the activity of carbon in the blend. Since the composition of oxycarbonitrides arising during reduction depends on many factors, they cannot, as a rule, be prepared in a pure state, although many of these solid solutions are of considerable scientific and practical interest.

Role of the gas phase. As the process goes on, the oxide—carbon contact interaction, which is fairly significant in the initial stages of CR, is broken off, and further reduction mostly involves the gas phase (the CO present in the system). In the case of ERO, the composition of the gaseous products of reduction and their

interaction with the oxide have been studied quite extensively;[3] this can be expressed by the following scheme:

$$MeO + CO = Me + CO_2 \quad (15)$$

$$C + CO_2 = 2CO \quad (16)$$

$$MeO + C = Me + CO \quad (17)$$

Attempts to extend this scheme to the reduction of DRO have not been confirmed experimentally. It was found[8] that in the case of DRO, reactions (16) and (17) do occur, whereas reaction (15) scarcely proceeds in the presence of CO alone even when the proportion of CO_2 is much lower than its equilibrium concentration. To explain this fact, a number of models have been proposed. For example, an adsorption-catalytic theory of reduction was suggested in relation to the reactions involving ERO;[3] however, it failed to describe the mechanism of high-temperature reduction of DRO and, more importantly, to explain this process without reaction (15).

Taking into account the fact that DRO are reduced in the presence of solid carbon, it has been suggested that volatile suboxides and subcarbides exist. No direct experimental evidence for the existence of these oxide and carbide forms has been obtained yet (except for several volatile oxides). However, the dependence of the sizes of metal-containing particles in the final products of high-temperature reduction on the size of the initial oxide particles can serve as evidence supporting the existence of volatile subcarbides that "carry" reducing reagents to oxides. Based on the above and some other factors, it was assumed[28] that at high temperatures, volatile carbon suboxides, in particular C_3O_2, exist in DRO—carbon systems; this is not at variance with the available data on the macrokinetics of the reduction of DRO and allows the adsorption-diffusion mechanism of their reduction to be presented in a more general form.

According to this model, unstable forms of carbon suboxide ($CO_{1\pm x}$), which are adsorbed on the metal oxides and carbon, arise during CR. The formation of these species on the surface of solid reactants is due to the presence of CO in the reaction area. The composition and the rate of formation of these suboxides are determined by the rate of diffusion from the bulk to the surface of particles, while desorption and the lifetimes of these species (the path length of $CO_{1\pm x}$) are determined by the reaction conditions (temperature, pressure, relative activities of reactants, *etc.*). Therefore, the process of reduction of oxides by carbon can be represented as reaction of metastable desorbed complexes with the oxide and carbon surfaces:

$$[CO_{1+x}] + [CO_{1-x}] = CO. \quad (18)$$

This model is consistent with the obtained experimental data interpreted within the framework of the adsorption-diffusion theory and makes it possible to extend this theory to the reduction of DRO.

According to the model under consideration, the rate of reaction (18) is limited by the formation of CO_{1+x} complexes on the surface of oxides, because diffusion of oxygen ions to the outer layers of oxides and reaction products is more difficult than the formation of complexes on the carbon surface. This fact can account for the deposition of carbon on cold surfaces of the reaction vessel, especially in those cases where the reaction occurs rapidly *in vacuo* or in an intense inert gas flow:

$$CO_{1-x} \rightarrow CO + xC. \quad (19)$$

Apparently, reaction (19) also occurs during annealing of oxides of carbide-forming metals in graphite furnaces in which high-melting oxides undergo contactless reduction and metals are carbidized.

In discussing the role of the gas phase in CR of DRO, one should take into account the effect of the velocity of gas flow on the rate of reduction. It is known that for a constant density of the pressed blend, the velocity of the gas flow has the greatest effect on the initial stage of the process; as the degree of reduction increases, the role of this factor sharply decreases, due to the increase in the porosity of the sample.

The rate of CR also depends on the volume of the sample, which determines the rate of diffusion of gaseous reaction products through the blend pores. As an example, we present in Figs. 6 and 7 the dependences of the rate of reduction of Ta_2O_5 by carbon on the reaction time (at various gas pressures) and on the density (the degree of porosity) of the blend, according to the data reported previously.[29] It can be seen from Fig. 7 that when a certain density of the blend is attained, the rate of CR dramatically decreases.

It should be noted that the presence of gases such as argon, acetylene, or hydrogen markedly decreases the

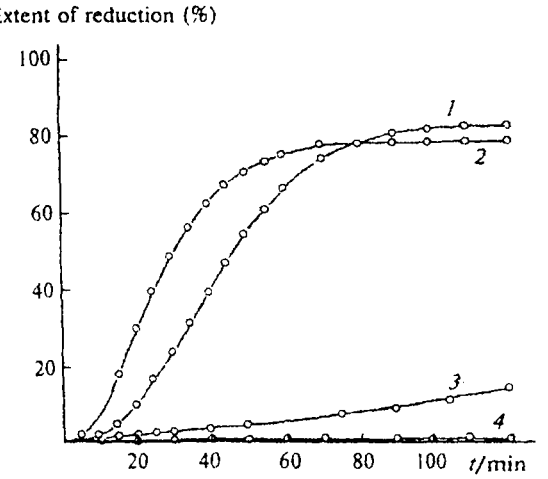

Fig. 6. Time dependences of the rate of reduction of Ta_2O_5 at various pressures in the gas phase: rough exhaust (*1*); rough exhaust and diffusional pump (*2*); accumulation of the reaction products (*3*); atmosphere of CO (*4*).

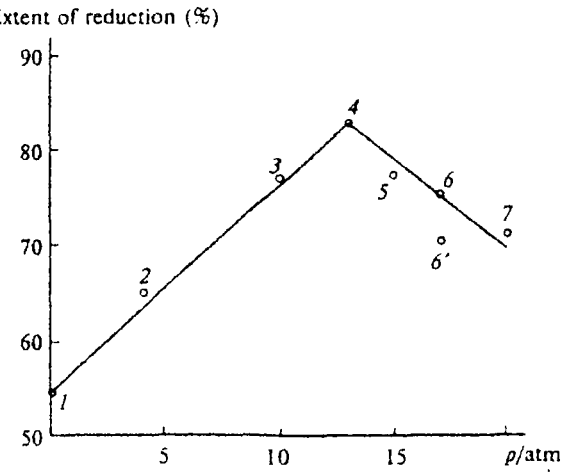

Fig. 7. Dependence of the rate of reduction of Ta_2O_5 on the pressure used for compaction of the blend (p). *1—7* are the sample numbers (reduction was carried out for 100 min).

rate of reduction. In the studies considered above, reduction was usually carried out in a flow of nitrogen. Moreover, the reaction does not occur at 1200 °C without N_2 and starts even at low flow rates of N_2. This can be explained in the following way.

The introduction of N_2 in the reaction area sharply decreases the partial pressures of the gaseous components participating in the reduction, because

$$p_{over} = p_{CO} + p_{SiO} + p_{Si} + p_{CO_2} + p_{N_2}.$$

Then at a constant overall pressure, $p_{over} = 1$ atm, we neglect the small values of p_{SiO} and p_{CO_2} and thus obtain $p_{CO} = (p_{over} + p_{N_2})$. This fact, in its turn, leads to the displacement of the reaction equilibrium toward the formation of products. From this it follows that the partial pressure of CO decreases with an increase in the N_2 flow rate (partial pressure), and, consequently, the reaction equilibrium shifts towards the formation of products. In addition, the introduction of N_2 in the reaction area and the decrease in the concentration of CO and SiO over the blend surface, stimulates the concentrational macrodiffusion of these compounds in the blend pores toward its surface and thus favors abstraction and mixing of the adsorbed complexes. Depending on the time they spend within the bulk of the blend, molecules of SiO and of desorbed complexes can either react with one another or partly leave the reaction area and decompose thus forming silicon, silicon dioxide, and carbon black deposits on cold parts of the furnace. As applied to silicon, this process can be described by the following reactions:

$$SiO_2 + C = SiO + CO,$$

$$SiO + C = Si + CO,$$

$$2SiO + N_2 + C = Si_2N_2O + CO,$$

$$Si + C = SiC,$$

$$2Si + N_2 = 2Si_3N_4.$$

In the case of leucoxene concentrate containing TiO_2, in addition to the reduction of dioxide by solid carbon (see Ref. 30), reduction of TiO_2 by silicon monoxide occurs according to the following scheme:

$$TiO_2 + SiO \rightarrow Ti_nO_{n-1} \rightarrow Ti_3O_5 \rightarrow Ti_2O_3 + SiO_2.$$

Thus, in the reduction of complex oxide mixtures containing SiO_2, not only can solid carbon act as a reducing reagent, but also gaseous SiO. The positive effect of the gas phase (N_2) on the reduction rate is manifested in more than the previously mentioned decrease in the partial pressure of the gaseous components; in addition, the rate of reduction of oxides in an atmosphere of CO_2+CO is markedly lower than that in the CO_2+N_2 mixture, which attests to activation of carbon by nitrogen.[8]

Crystallochemical mechanism of the CR of complex oxides

Crystallochemical transformation of simple ERO during CR is one of the important stages of their reduction by carbon. For M—O—C systems (M = Fe, Cu, Ag, Zn, *etc.*), these transformations have long been the subject of investigation.[8] The reduction of oxides of high-melting metals capable of forming complex oxycarbonitrides as intermediate products has been much less studied.

Previously[28] we surveyed studies dealing with the reduction of Ti, V, Nb, and Ta oxides. In particular, it was noted in these studies that in the case of carbide-forming metals, the known sequence of transformations of oxides during can CR is retained only in the stage of the reduction of the initial oxides to monoxides. Subsequently, monoxides are not detected among the reaction products; either carbides and nitrides or oxycarbides and oxynitrides are formed. This is due to the fact that the monoxides formed are extremely unstable toward contact with carbon; as a rule, they decompose to give higher oxides and metal: $MO \rightarrow M + MO_2$ (M_2O_3). After that, depending on the sort of particles that predominate in the metal environment, various reactions can occur. In the presence of carbon *in vacuo* (or in a flow of inert gases), carbides are formed; in a nitrogen flow of high concentration, nitrides are formed, and when CO is present in a high concentration, metal oxycarbide is produced. In mixtures of CO with N_2 or H_2, complex oxycarbonitride or oxycarbohydride compounds are formed in these systems.

The above solid solutions can also be obtained by other methods. For example, TiC_xO_y is formed by prolonged grinding of TiO_2 mixed with carbon in ball mills. Complex silicon and aluminum oxycarbides arise in the

beginning of the CR of SiO_2 and Al_2O_3 with carbon in a flow of N_2.[26] Certainly, the mechanism of their formation differs from that described previously and involves diffusional replacement of the oxygen atoms in the initial solid phase by other nonmetal atoms.

* * *

The purpose of the present work is to attract the attention of technologists to a long-known process, carbothermal reduction of oxide-containing ores and concentrates, which is a unique method for the production of new initial compounds (metal carbides, nitrides, or oxycarbonitrides) that can be useful for the development of new materials. The high service characteristics of the latter such as hardness, and wear resistance, along with their known plasticity and corrosion resistance, make these materials indispensable for re-equipment of many branches of industry, for example, metallurgy (refractories, coatings), machine building (abrasives, heavily loaded parts operating in aggressive media, *etc.*), the ceramics industry, and others.

Since the physicochemical properties of oxygen-free compounds and of the solid solutions based on them differ markedly from those of the conventional oxides of the same metals, these compounds can be completely separated and, therefore, complex processing of raw materials becomes possible. However, although the CR process has been satisfactorily physicochemically justified, highly productive equipment for CR processing lags far behind the requirements of the manufacture of powders of oxygen-free compounds. This holds up the development of the above-mentioned basic branches of industry.

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