Translated from *Uspekhi Khimii*, **57**, 1419-1439 (1988) U.D.C. 669.094.22

Interaction of Refractory Metal Oxides with Carbon

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Certain characteristics of carbothermal processes involving the reduction of refractory oxides to the metal are surveyed with allowance for the structure of the outer and penultimate electron shells. The similarity and difference between the kinetics and mechanisms of reactions on the surfaces of the metal oxides and the carbon reductant are analysed.
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I. INTRODUCTION

The interaction of refractory metal oxides with carbon constitutes the basis of many metallurgical processes and of the technology for the preparation of materials for high-temperature engineering. The complexity of the mechanisms of these processes is due to the wide variety of the physicochemical properties of the elements formed in the reduction process and of their compounds. For this reason, carbothermal processes involving reduction to the metals have been the subject of continuous investigations and attempts to create a unique theory[1-10] from the standpoint of which it will be possible to predict and explain the role of the individual components of the reduction reactions.

The various views which have arisen hitherto concerning the mechanism of carbothermal reduction to the metals are related to the appearance of new promising trends in chemistry and to the employment of the advances achieved in them. Thus the application of the thermodynamic analysis to the study of metallurgical process has served as a basis for the development of ideas concerning the leading role of oxide dissociation reactions,[11] the development of catalysis led to the adsorption-autocatalytic theory,[1] studies on the evaporation and dissociation of substances led to the discovery of the oxide-sublimation mechanism of the reduction process,[4] mass-spectrometric detection of short-lived oxygen–carbon compounds demonstrated the active role of C_2O_5 as a reductant,[9,12] and the use of atomic-absorption analysis led to the discovery of the gas-carbide reduction mechanism.[13,14]

All these ideas reflect to different extents the phenomena observed in the study of reduction processes. As a result, many investigators have now adopted the view[4,5,9,12,15] that the mechanism of carbothermal reduction to the metals cannot be described from the standpoint of any single universal theory. This view is correct. However, it does not rule out the possibility of establishing general characteristics of the reduction of different groups of oxides having similar physicochemical properties (Ref.4, p.269).

The present review surveys data which have accumulated during the last decade on the high-temperature chemisorption of gases and the thermodynamics, kinetics, and mechanisms of the interactions of solid oxides of refractory metals with carbon. These processes take place simultaneously on the surfaces of both reactants and for this reason in the systematic treatment of the results the reduction process has been divided into two classes of reactions occurring on the surfaces of metal oxides and carbon reductants.

The characteristics of the variation of the properties of chemical compounds (including metal oxides) on passing from one compound to another are associated with the properties of the individual atoms. In order to elucidate the features of the kinetics and mechanisms of carbothermal reduction processes, it is therefore useful to examine the accumulated data with allowance for studies in the field of the systematic treatment of the elements.[16-19] The new version of the Periodic System of the elements[19] takes into account not only the limiting number of valence electrons but also the force characteristics of the latter, which are determined by the structure of the outer and penultimate electron shells. Together with group and type analogues of the elements, two new types of analogues have been differentiated in addition:[19] the shell analogues, i.e. those which not only refer to one subgroup but also have isotypical non-kinosymmetrical electron shells (for example, Ca–Sr–Ba, Zr–Hf, Y–Lu, etc.) and the shrink analogues—pairs of elements one of which (with the larger atomic number) has an orbital radius similar to or smaller than that of the preceding type analogue in the given group as a consequence of the *p*, *d*, or *f* contraction (for example, Ba–Ra, Si–Ge, etc.). The maximum similarity between the properties of certain elements has in fact been explained by their belonging to shell and shrink analogues.[19]

II. THERMODYNAMICS OF CARBOTHERMAL REDUCTION PROCESSES

Until recently, the method for the estimation of the probabilities of particular isolated reactions based on a comparison of their Gibbs free energies at the corresponding temperatures was widely used in the theoretical study of reduction processes. However, real reduction processes represent a set of interlinked reactions, which must be taken into account as an assembly of reactions.

Methods for the construction of phase and chemical equilibrium diagrams[20,21] and thermodynamic balances,[22] involving the solution of a system of equations for the equilibrium constants of the corresponding reactions under the conditions of a congruent transition

of the chemical compound from the condensed to the gaseous state, are used for this purpose.[8,23-25] On the basis of this approach, the carbothermal reduction process is represented by a set of reactions involving the dissociation of metal oxides and molecular oxygen to the constituent gaseous elements, the oxidation of CO to CO_2 by oxygen, and the regeneration of CO by solid by solid carbon.[26] The solution of the system of equations for the equilibrium constants of these reactions at a fixed CO pressure makes it possible to estimate the composition of the gas phase under conditions where the metal oxide is in equilibrium with the $O-O_2-CO-CO_2$ gas phase, which is in its turn in equilibrium with solid carbon. The equilibrium compositions of the gas phase in the interaction of SiO_2,[27] Al_2O_3,[28] Group IIA metal oxides,[29,30] and MnO [31] with carbon have been calculated by a similar method.

In the study of reduction processes in multicomponent systems, computer programs for thermodynamic calculations have been used in recent years.[32-36] Theoretical studies of the equilibrium compositions of condensed and gaseous phases in the interaction in the $Si-O-C$,[37,40] $Al-Si-O-C$,[41] $Al-O-C$,[10,42] $Ti-O-C$,[43,44] $Nb-O-C$,[45-48] $Zr-O-C$,[43] $Ce-O-C$,[49] and $Nd-O-C$ [10] systems have been carried out by these methods.

A decrease in pressure in these systems promotes the development of reduction processes with lower temperatures and intensifies the tendency towards decomposition of the condensed reduction products—towards the transfer of the substance to the gas phase.

The accumulated results of thermodynamic studies have shown that, under equilibrium conditions, the main gaseous reduction product is CO. The pressure of the remaining carbon oxides C_2O, CO_2, and C_3O_2 as well as the C, C_2, C_3, O, O_2, and O_3 components is more than 5 orders of magnitude smaller than the CO pressure. At pressures close to 0.1 MPa, the reduction of oxides to *s* and *sp* elements (BeO, MgO, CaO, SrO, BaO, SiO_2, and Al_2O_3) and MnO is accompanied by the formation in the gas phase of the vapours of the metals and their lower oxides as the reduction products. On the other hand, the reduction of oxides to the *d* and *f* elements (TiO_2, Nb_2O_5, ZrO_2, Ce_2O_3, and Nd_2O_3) is characterised by very low concentrations of the metal-containing reduction products in the gas phase. An increase in their concentration in these systems is observed only at high temperatures or as a consequence of the thermal decomposition of the intermediate compounds, in particular metal carbides.

The low equilibrium concentration of CO_2 in systems with metal oxides which are difficult to reduce does not provide grounds for the conclusion that it plays an insignificant role in reduction processes. However small the equilibrium CO_2 pressure, the probability of the interaction of metal oxides with CO in the presence of solid carbon increases at the temperatures where the carbon gasification reaction ensures an equilibrium CO_2 pressure lower than in an isolated reaction involving reduction with carbon monoxide.

Thus, in terms of the composition of the components of the equilibrium gas phase, the interactions of refractory metal oxides with carbon at pressures close to 0.1 MPa can be divided into two groups differing in the content of the vapours of metals and their lower oxides. The difference between them is correlated with the structure of the outer and pre-outer electron shells of the elements produced by the reduction process. The first group includes processes involving reduction to the *d* and *f* elements with the preferential formation of CO and the second involves the reduction of oxides to *s* and *sp* elements and manganese (from MnO) with the additional formation of the vapours of metals and their lower oxides.

III. CHEMICAL ADSORPTION OF CARBON MONOXIDE ON METAL OXIDES

The chemical adsorption of CO on the surfaces of metal oxides is not only one of the intermediate stages in the carbothermal reduction process but it also has independent importance in processes involving the catalytic oxidation of CO and the purification of exhaust gases. The results[50-53] which have accumulated in the field of heterogeneous catalysis and oxygen exchange involving metal oxides therefore make it possible to elucidate the mechanism of the chemical adsorption of CO and its role in high-temperature reduction processes.

The adsorption properties of metals and their oxides are determined to a large extent by their electrical properties and the participation of conduction electrons in the formation of complexes between the adsorbent and adsorbate. The higher their electrical conductivity, the greater their adsorption-catalytic capacity. In non-transition metal oxides, cations with outer s^2 and s^2p^6 electron shells are stable, because their electronic levels are not split by the atoms or molecules in the first coordination sphere. For this reason, the conductivity of the oxides of *s* and *sp* elements is very low. A similar stability of the electron shells of the cations has been observed also for transition metal oxides with ions having the configurations $d^0(Sc^{3+}, Ti^{4+}, V^{5+})$, $d^5(Mn^{2+}, Fe^{3+})$, and $d^{10}(Cu^+, Zn^{2+})$, which makes their catalytic properties similar to those of non-transition metal oxides.[54] The oxides of *d* transition metals, on the surfaces of which coordination-unsaturated cations with incomplete *d* orbitals (in which the number of electrons is not 5 or 10) are present, have the maximum catalytic activity. Such oxides are characterised by a higher crystal lattice energy than oxides with analogus ions having the s^2, s^2p^6, d^5, and d^{10} outer electrons. Lanthanide oxides with incomplete *f* orbitals (in which the number of electrons is not 7 or 14) also possess a considerable catalytic activity, for example, Nd_2O_3 [55] and ThO_2.[56] CO is adsorbed reversibly on zinc oxide at temperatures below 373 K.[53] At higher temperatures the adsorption is irreversible with formation of CO_2 molecules. Irreversible adsorption of CO has been recorded on the surfaces of Cr_2O_3, ZnO, CoO, and Mn_2O_3.[53] Under these conditions, the irreversibly adsorbed CO is bound to the surface of the metal oxide in the form of the "carbonate ion" CO_3^{2-}, which arises when CO interacts with the oxygen ions of the oxide lattice. On copper, cobalt, and nickel oxides, the adsorbed CO is capable of reacting not only with the oxygen of the oxide lattice but also with oxygen adsorbed on the oxide surface.

Depending on the temperature, the catalytic oxidation of CO on the surfaces of transition metal oxides proceeds via two mechanisms. At low temperatures it proceeds via an associative mechanism with formation of intermediate carbonate CO_3^{2-} structures,[57-59] which are decomposed by gaseous oxygen with formation of CO_2 molecules. With increase in temperature, the associative mechanism of the oxidation of CO passes to a multistage mechanism,[57-61] which is induced by the sharp decrease in the coverage of the metal oxide by surface carbonate ions and their rapid thermal decomposition with formation of CO_2 by reaction with the oxygen in the oxide lattice. The subsequent adsorption of oxygen from the gas phase leads to the disappearance of metal ions as the reduction products and to the formation of the radical-ions O_2^- on the surface of the metal oxide. As a result, the multistage mechanism represents alternate oxidation-reduction of the surface of the oxide catalyst. The temperature range corresponding to the change in the mechanism of the catalytic

oxidation of CO on oxides of metals in the Fourth Period (V_2O_5–ZnO) is 518–863 K,[60] while on TiO_2 this happens at 1173 K,[57] which is close to the temperatures of the onset of the surface diffusion of the metal oxide cations and anions.[62] In essence, the change of the mechanism of the catalytic oxidation of CO at high temperatures is induced by the involvement of reactions leading to reduction to the metal by the gaseous reductant.

The oxides of *s* and *sp* elements, which are dielectrics under normal conditions, exhibit the properties of semiconductors at high temperatures and low pressures.[63] As a result, conduction electrons, capable of participating in gas–adsorbent reactions, appear on their surfaces. Thus Group IIA metal oxides (BeO–BaO) and aluminium oxide (Al_2O_3) exhibit electronic conductivity at temperatures[63] close to the temperatures of the onset of appreciable interaction with carbon. A similar relation between the semiconducting nature of metal oxides and the temperature of the onset of interaction with carbon has been established in relation to the oxides V_2O_5, WO_3, and TiO_2.[4]

The isotope exchange observed in the study of the self-diffusion of oxygen in metal oxides[53] also indicates the occurrence of the high-temperature chemical adsorption of gases on the surfaces of metal oxides. The character of the adsorption of oxygen depends on temperature. At room temperature, oxygen is adsorbed in the molecular form, while at elevated temperatures it is adsorbed in various dissociatively adsorbed forms.[53]

The high-temperature isotope exchange of oxygen has been studied in the oxides SiO_2 [64] and Y_2O_3 [65] at 1123–1523 K and 1273–1773 K respectively. According to Finikov,[66] it is observed from 673 K to the melting point and in melts of oxygen-containing compounds. The mechanism of such reactions is based on the isotope exchange within a chemisorption complex of the type $M_x[O_nA-O_2]_y$, where M is the metal and A the element forming the anion in which O_2 combines with A via a chemisorption bond, and ^{18}O is redistributed in the exchange process between AO and O_2.

Thus, results accumulated in the field of the catalytic oxidation of CO indicate an important role for chemical adsorption of CO in processes involving the high-temperature reduction of refractory oxides. In contrast to the oxides of *d* and *f* transition metals, the CO chemisorption processes on non-transition metal oxides take place at very high temperatures, corresponding to the appearance of semiconducting properties in the oxides. It has been established[10] for the non-contact reaction of ZrO_2 with graphite at 2223–2323 K that, with increase in temperature, the intensity of the processes associated with the chemisorption of CO increases as a consequence of the increase in the number of active chemisorption centres formed owing to the increase in the concentration and mobility of the defects in the crystal lattices of the oxides.

IV. REACTIONS INVOLVING THE REDUCTION OF REFRACTORY OXIDES TO THE METALS

The interactions of metal oxides with carbon represent a definite class of chemical reactions whose common character and the differences between their properties are determined by the similarities and differences between the properties of the elements produced by the reduction process—the characteristic features of their variation as a function of the fundamental properties of atoms. Therefore the most common features of the kinetics and mechanisms of the high-temperature reduction processes in general and for individual groups of refractory metal oxides can be manifested in the analysis of the experimental data taking into account the distribution of the elements generated by reduction within the framework of the Periodic System.[18,19]

1. Reactions Involving Reduction to Group IIA Elements

The oxides of Group IIA metals interact with carbon to form a gas phase containing the vapours of the oxides and of the metals produced by reduction.[29,30,67–72] At p_{CO} = 0.1 MPa, the principal metal-containing component of the gas phase is the metal as the reduction product, whose partial pressure is higher by several orders of magnitude than that of the vapour of the corresponding metal oxide.[30] In the gaseous products of the reduction of barium oxide, the relative concentration of the oxide is somewhat higher than for the remaining group IIA metal oxides. With increase in temperature from 1773 to 2073 K, the fraction of BaO in the mixture of the metal-containing components of the gas phase diminishes from 26.09 to 5.73 vol.%.

The reduction on the surfaces of metal oxides without contact with the carbon reductant is accompanied by the formation of only gaseous products.[29,30] The highest average rate of reduction, referred to unit geometrical surface of the metal oxide, is observed at p_{CO} = 0.1 MPa. The decrease in the rate of reduction when CO is replaced by an inert gas indicates the leading role of CO as the reductant. The interaction of MgO, CaO, SrO, and BaO with carbon at p_{CO} = 0.1 MPa begins at an appreciable rate at ~1773 K and that of BeO begins at 2173 K. However, the carbides CaC_2, SrC_2, and BaC_2 are formed on carbon only at temperatures close to 2073, 1973, and 1923 K respectively when the partial pressure of the reduction-product metals, transferred from the surfaces of the oxides to solid carbon, exceeds the dissociation pressure of the corresponding carbide. The appearance of BeC_2 on solid carbon is possible only above 2560 K.[29,30]

Thus the metal formed on reduction in the presence of solid carbon can be either removed with the effluent gases or can react with the carbon to form the carbide depending on the conditions.

When the CO pressure is reduced from 0.1 to 3.4×10^{-6} MPa, the degree of conversion of the oxides BeO, MgO, and CaO increases (Fig.1), passing through a maximum close to $p_{CO} \simeq 4 \times 10^{-3}$ MPa.[10,29] The decrease in the CO pressure in the system favours an increase in the rate of diffusion and mass transfer between the reactants, which compensates for the decrease in the CO concentration in the range $p_{CO} = 4 \times 10^{-3}$–0.1 MPa. At p_{CO} less than 4×10^{-3} MPa, the contribution of the reactions involving reduction by carbon monoxide diminishes and the role of the oxide dissociation reactions, forming a vapour–gas phase consisting of the atomic metal, its monoxide, and molecular and atomic oxygen, is enhanced.[73] The rate of reduction on the surfaces of metal oxides *v* is correlated with the partial pressure of the metal produced by reduction[30,74] and with the Gibbs free energy ΔG_T^0 of the overall reduction reaction:[72]

$$MO(solid) + C(solid) = M(gas) + CO(gas),$$

which is expressed by the equation

$$\lg v = a - b\Delta G_T^0 \qquad (1)$$

where *a* and *b* are coefficients.

In contrast to BeO and MgO, whose rates of reaction with carbon obey individual relations, the rate of reduction of CaO, SrO, and BaO obeys a common numerical relation of type (1) determined by

the great similarity of the physicochemical properties of the corresponding metals as shell analogue Group IIA elements.[19]

Under conditions where CaO is in contact with CaC_2, a eutectic is formed, its fusion at a temperature above 2100 K leading to intense dissolution of CaO in the $CaO-CaC_2$ melt, a diminution of the role of the reduction reactions via the gas phase, and the preferential development of reduction reactions between the $CaO-CaC_2$ melt and solid carbon.[68] A similar change of mechanism is observed when barium is obtained by reduction at temperatures above 1923 K,[30] ensuring the formation of BaC_2 on carbon in the initial stage.

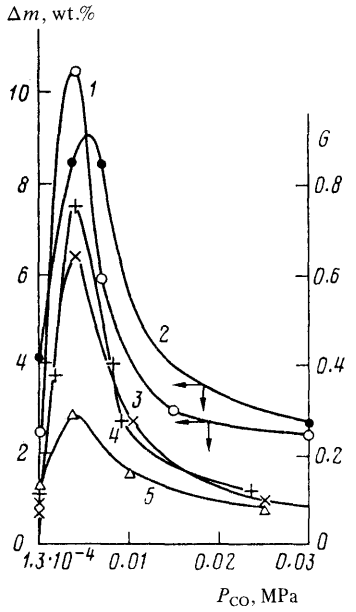


Figure 1. Decrease in the mass of metal oxides (Δm, wt.%) at a distance of 0.5 mm from graphite and in the degree of conversion of the oxides (G) in particulate mixtures with graphite as a function of the CO pressure: 1) Cr_2O_3 (1673 K); 2) CaO (2073 K); 3) SiO_2 (1773 K); 4) BeO (2223 K); 5) MgO (1873 K).[10]

2. Reduction to Aluminium

Among the oxides of Group IIIA elements, the most stable and refractory oxide is Al_2O_3. Its interaction with carbon takes place with formation of condensed (Al_3O_4, Al_4O_4C, Al_2OC, and Al_4C_3) and gaseous (Al, AlO, and Al_2O) products.[4,26,75] When Al_2O_3 was atomised in a graphite furnace, the presence of the carbide Al_2C_3 was detected together with aluminium in the gas phase by atomic-absorption analysis.[76–80] The ratios of the components of the gas phase ($c_{Al_2C_2}:c_{Al} = 10^2-10^3$) [77] calculated from the absorption spectrum of Al_2C_2 [13] conflict with the equilibrium concentrations of the components ($Al_2O_3:C:CO = 1:3:1$) [10] in the initial Al_2O_3-C systems[81] and with the results of the mass-spectrometric analysis of the evaporation products in the Al–C system.[82] According to the latter, $c_{Al}:c_{Al_2C_2} = 1050:1$. An analogous composition of the gas phase, mainly containing the metal vapour, has been observed in the mass-spectrometric analysis of the evaporation products of the carbides of *f* elements.[83] The results of the above studies[13,76–80] have been criticised[84] in a study where it was noted that the molecular spectrum obtained by L'vov and Ryabchuk[76] was arbitrarily attributed to the Al_2C_2 molecule (and not the AlC_2 molecule), while the estimate of the relative Al and Al_2C_2 concentrations, made on the assumption that the integral absorption coefficients of the corresponding atomic and molecular lines are similar,[13,79] is extremely inaccurate because the difference between the oscillator strengths even for atomic absorption lines can exceed 2–3 orders of magnitude. Therefore the concept of the gas-carbide reduction mechanism, which presupposes the transfer of carbon from the oxide surface by gaseous carbides of the type of MC_2 and its universal character regardless of the individual features of the oxide, experimental conditions, and the form of the products formed ultimately,[14] cannot be regarded as sufficiently well founded. Without contact between aluminium oxide and solid carbon at $p_{Ar} = 0.1$ MPa [85] and $p_{CO} = 0.1$ MPa,[28] condensed products (Al_4C_3) are formed on the surface of the reductant as a result of its interaction with the vapours of aluminium and its lower oxides.[86] The temperature of the onset of interaction at an appreciable rate is close to 2030 K at $p_{CO} = 0.1$ MPa,[28] at 1873 K at $p_{Ar} = 0.1$ MPa,[85] and at 1623 K in a high vacuum.[87] A decrease in the CO pressure from 0.1 to 3×10^{-6} MPa [10] promotes the acceleration of the reaction, which is particularly sharp at $p_{CO} < 4 \times 10^{-3}$ MPa (Fig.2).

When Al_2O_3 and the carbon reductant are in contact under conditions where $p_{Ar} = 0.1$ MPa,[85] reduction reactions through the gas phase proceed on the sections of the oxide surface free from contact with graphite, while at the sites of contact diffusional interaction occurs with formation of a $Al_2O_3-Al_4C_3$ solution. Ultimately the reaction of Al_2O_3 at the sites of contact with the reductant terminates with formation of aluminium oxide carbides and carbide.[20,75] In mixtures with graphite at $p_{CO} = 0.1$ MPa in the temperature range 2073–2173 K, condensed products are not formed. Aluminium carbide is formed above 2173 K when the partial pressure of the reduction-product aluminium in the briquet exceeds the dissociation pressure of Al_4C_3. The formation of the $Al_2O_3-Al_4C_3$ melt on metallic aluminium intensifies sharply the reduction process as a result of the appearance of liquid "bridges" between aluminium oxide and graphite, which, by dissolving carbon, promotes the preferential development of reduction reactions with participation of the liquid $Al_2O_3-Al_4C_3-Al$ melt.[28]

The absence of carbon-containing phases on the surface of the specimen[28,85] precludes an unambiguous conclusion about the reduction mechanism. These ideas can be refined by employing experimental data for the reduction to the elements of the oxides of group analogues of aluminium.

3. Reduction to Group IIIB and IIIC Elements

The oxides of Group IIIB and IIIC elements possess high thermodynamic stability[83] and are very refractory.[88] At $p_{CO} = 0.1$ MPa, the temperature of the onset of their appreciable interaction with graphite lies above 2170 K. An increase in the content of carbon without an appreciable change of the parameters of the crystal lattices of the oxides has been observed in the products formed on the surfaces of the oxides during their interaction with

graphite through space in CO.[89,90] This justified the assumption[10] that reactions involving the chemisorption of CO and its disproportionation to CO_2 and C with subsequent substitution of part of the oxide oxygen by carbon and the formation of oxide carbide and carbide phases develop on the surfaces of metal oxides. The oxide carbide and carbide phases form a solution of the type of $M_2O_3-MC_2$, which has been observed on the surfaces of scandium,[89] yttrium, lanthanum, gadolinium, and lutetium[90] oxides at 2470, 2223, 2123, 2323, and 2373 K respectively, which are lower than the melting points of the metal oxides and carbides. As a result of this, the contribution of the reactions involving reduction through the gas phase diminishes and reduction reactions with participation of the $M_2O_3-MC_2$ melt, which take place under diffusion conditions without the formation of gaseous metal-containing products, become dominant. Such change of mechanism has been reflected, in our view, by the two maxima on the kinetic curves for the reduction of bricketted mixtures (Y_2O_3 + 7C).[91]

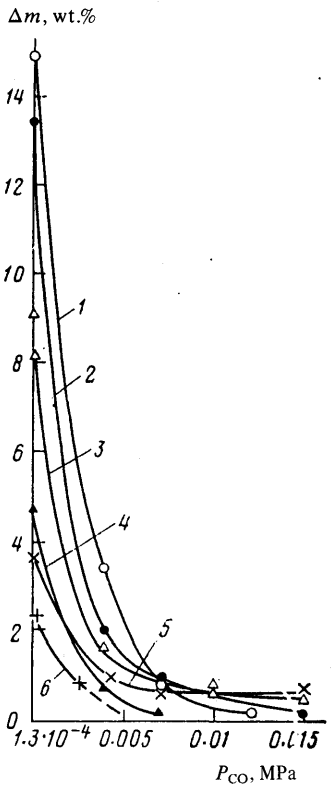


Figure 2. Decrease in the mass of metal oxides at a distance of 0.5 mm from graphite as a function of the CO pressure: 1) Al_2O_3 (2073 K); 2) La_2O_3 (1973 K); 3) Sc_2O_3 (2323 K); 4) Nd_2O_3 (1973 K); 5) Lu_2O_3 (2373 K); 6) Y_2O_3 (2223 K).[10]

At CO pressures in the space between the reactants less than 5×10^{-3} MPa, the rate of their interaction increases sharply (Fig.2). Under these conditions, the dissociation reactions of the oxides predominate with formation of the vapours of the atomic metals, their lower oxides, and atomic oxygen,[73] which react with solid carbon to give CO and the corresponding metal carbides. A similar character of the change in the degree of reduction of the oxide with decrease in pressure is observed in the reduction of aluminium,[10] which is a group analogue of the above metals.

When the reactants come into contact *in vacuo*, the interaction proceeds the gas phase up to a certain temperature with formation of the corresponding metal carbides on the carbon reductant and then, at temperatures significantly below the melting points of the metal oxides and carbides, reduction reactions with participation of the $M_2O_3-MC_2$ melt develop.

The rate of interaction of mixtures of lanthanum and gadolinium oxides with carbon *in vacuo* obeys a general correlation with the Gibbs free energy of the reduction reaction at the corresponding temperatures:[90]

$$M_2O_3+7C=2MC_2+3CO$$

This is associated with the similar chemical properties of the elements, determined by the identical numbers of valence electrons and the presence of the unfilled f^0 configuration and the stable f^7 configuration of the electrons. For the oxides of elements which are shell analogues of yttrium and lutetium, there is no similar relation in the temperature range 1900–2070 K owing to the difference between the mechanisms of the interactions with carbon which take place through the liquid and vapour–gas phases respectively. This is due to the difference between the appearance temperatures of the carbide oxide melts and the onset of the reduction through the liquid phase. Thus, when the reactants are in contact, the welding of Y_2O_3 to graphite, indicating the formation of the liquid phase, is appreciable already at 1923 K, while that of Lu_2O_3 is appreciable at 2373 K.[90]

4. Reduction to Group IVA Elements

Among the oxides of Group IVA elements, SiO_2 is the most stable and refractory. In the non-contact interaction with graphite in the presence of CO or argon or *in vacuo*, the maximum rate of reduction on the SiO_2 surface is observed at p_{CO} = 0.1 MPa.[27] A phase with a melting point close to 1823 K is then formed on the SiO_2 surface,[92] consisting of the $SiO-SiO_2$ solution.[93,94] As for the Group IIA oxides, a decrease in CO pressure[10,29] (Fig.1) promotes an increase in the rate of diffusion and mass transfer between the reactants, which compensates for the decrease in the CO concentration. At $p_{CO} < 4 \times 10^{-3}$ MPa, the contribution of reactions involving reduction by carbon monoxide diminishes and the role of SiO_2 dissociation reactions with formation of SiO and atomic oxygen,[73] which react with the carbon reductant affording CO and SiC, increases. The dominant role of the SiO_2 dissociation reactions persists in an inert gas in the presence of carbonaceous and non-carbonaceous reductants which are not in contact with the gas.[21,93]

The interaction of both liquid and solid SiO_2 with solid carbon at p_{CO} = 0.1 MPa takes place through the gas phase with participation of CO as the reductant without the formation of oxide carbide melts.[39]

The reduction of germanium, like that of its group analogue silicon, takes place through the gas phase with formation of the intermediate gaseous monoxide GeO. In the presence of solid carbon in the reducing medium, the reaction involving reduction by

carbon monoxide to gaseous GeO takes place on the GeO_2 surface, the monoxide being adsorbed on the surface of the carbon reductant and being converted into metallic germanium.[95-97]

5. Reduction to Group IVB Elements

Group IVB includes titanium and its shell analogues—zirconium and hafnium, which is the reason for the significant difference between the properties of titanium oxides and the oxides of the remaining elements in this group. In particular, it is manifested by the presence of a whole series of lower valence oxides[63] and a wider range of homogeneity of the oxide carbides than for zirconium and hafnium.[98]

The interaction of TiO_2 with CO is characterised by a very low equilibrium CO_2 pressure and has been achieved at 1373 K up to a degree of reduction of 0.08 in a circulation apparatus in which CO_2 is frozen out with liquid nitrogen.[99] On the other hand, in the presence of solid carbon,[100,101] the process proceeds vigorously. The adsorption of CO on TiO_2 surface results in the formation of Ti_3O_5 and CO_2, which react with carbon to form CO. The dissolution of CO in the defective anionic oxide sublattice and the disproportionation of CO to CO_2 and C with the subsequent substitution of part of the oxide oxygen by carbon begins after the attainment of compositions close to Ti_2O_3. The contribution of the last reaction in TiO specimens increases with increase in temperature.[100] The mass of the specimens increases and the molar ratio of the inserted elements C:O increases from 0.975 at 1773 K to 1.285 and 1.975 at 1873 and 1973 K respectively.

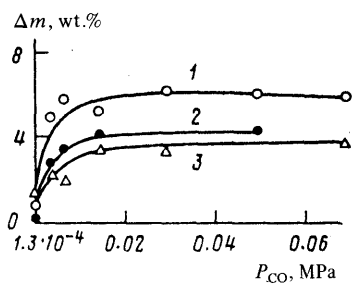


Figure 3. Decrease in the mass of metal oxides at a distance of 0.5 mm from graphite as a function of the CO pressure: 1) Nb_2O_5 (1623 K); 2) TiO_2 (1523 K); 3) Ta_2O_5 (1873 K).[10]

A decrease in the pressure of CO (Fig.3) and its replacement by an inert gas or a vacuum diminish the rate of reduction of TiO_2. In an inert gas, the dissociation of TiO_2 with formation of condensed products close in composition to $TiO_{1.9}$ predominates, whilst *in vacuo* the products have the composition $TiO_{1.87}$ [100]—the latter evaporate congruently, predominantly in the form of TiO and TiO_2,[73] and are converted into titanium carbide by reaction with solid carbon.

According to mass-spectrometric data,[12] the gas phase in the reduction of oxides of Group IVB and VB elements at $p_{Ar} = 1.33 \times 10^{-2} - 2.0 \times 10^{-3}$ MPa consists predominantly of CO and an insignificant amount of CO_2 in the range 573–1573 K. According to material balance, the overall composition of the gas phase formed is close to C_3O_2. A number of workers have therefore suggested[9,12,44,101,102] that the main reductant of titanium and other group IVB and VB elements is not CO but gaseous (or amorphous) carbon—one of the products of the decomposition of C_3O_2, whose condensate is observed on the cold parts of the furnaces. However, in the mass-spectrometric analysis of the gaseous products of the reduction to molybdenum C_3O_2 molecules have been detected experimentally at temperatures not exceeding 773 K.[103] The compound C_3O_2 is unstable and the possibility of its formation at the real reaction temperature is low.

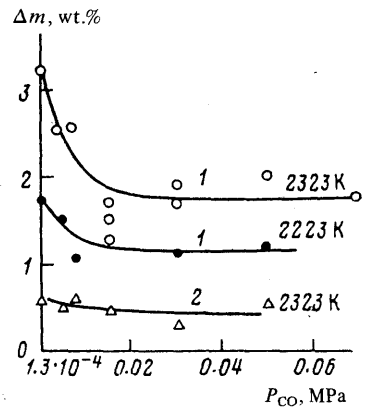


Figure 4. Decrease in the mass of metal oxides at a distance of 0.5 mm from graphite as a function of the CO pressure: 1) ZrO_2; 2) HfO_2.[10]

Zirconium and hafnium dioxides are the only thermodynamically stable solid oxides of these metals. At high temperatures (2223 to 2323 K) in the presence of carbon, they react with CO [10] to form carbides on the surfaces of the oxides. The decrease in the CO pressure to 0.01 MPa (Fig.4) influences only slightly the degree of reaction of the oxides as a consequence of diffusion-dependent obstacles arising as a result of the formation of the carbide phase. The acceleration of the interaction is observed at $p_{CO} < 0.01$ MPa in connection with the development of the dissociation reactions of the dioxides uncomplicated by the formation of any products on their surfaces and occurring via congruent evaporation from dioxides having a composition MO_{2-x} [100] predominantly in gaseous ZrO and HfO and oxygen.[73] The presence of the carbon reductant promotes a vigorous removal of the dissociation products from the surface of the oxide and the formation of ZrC, HfC, and CO on the carbon surface. At $p_{CO} = 0.1$ MPa, the amount of ZrC formed on the ZrO_2 surface increases with increase in temperature,[10] which is associated with the increase in the concentration of the active centres for

the chemisorption of CO as a result of the increase in the mobility of the crystal lattice defects in the oxides at temperatures above $0.5\,T_m$.† [62]

In vacuo, at relatively low temperatures (1523–1823 K) the reduction of particulate mixtures of the reactants also proceeds with participation of the CO adsorbed on the ZrO_2 and HfO_2 surfaces.[105–107] In the initial stage of the interaction, part of the oxygen in the anionic sublattice is removed and the oxides $ZrO_{1.98}$ and $HfO_{1.941}$ with a deficiency of oxygen are formed. In the last stage, the anionic vacancies in the lattices of the dioxides are filled with carbon, ensuring their conversion into the oxide carbide and carbide.[105,106] The formation of zirconium and hafnium oxide carbide melts is observed at 2373 and 2423 K respectively.[10]

6. Reduction to Group VB Elements

Group VB includes vanadium and its shell analogues – niobium and tantalum.[19] In contrast to the latter, vanadium forms a large number of oxides with a lower degree of oxidation and a β-phase with 15–25 at.% of oxygen.[63] In the reduction of the highest oxide to vanadium, oxides with lower degrees of oxidation are formed in succession as far as V_2O_3. In individual stages, the rate of reduction of V_2O_5 is limited by various elementary stages—in the reduction to V_2O_3 by the adsorption of CO with the subsequent diffusion of carbon and oxygen into the lattices of the oxides with formation of oxide carbide phases.[98,108]

The reduction to niobium is complicated by the formation in the condensed state of the intermediate lower oxide NbO_2 and variable-composition niobium oxide carbides.[98] For this reason, at a CO pressure above 2×10^{-3} MPa (Fig.3), the degree of conversion of Nb_2O_5 increases insignificantly owing to diffusion-dependent obstacles arising in the condensed phase.

As a result of the reduction by carbon monoxide, oxygen vacancies accumulate in the highest Group IVB and VB metal oxides and are partly filled with carbon atoms. Oxides with a lower degree of oxidation are then formed with a small amount of incorporated carbon. The CO adsorbed on the surfaces of vanadium and niobium monoxides can be absorbed, as in the case involving titanium monoxides,[100] by the defective lattices of the monoxides[102] and can also disproportionate to CO_2 and carbon atoms which fill the oxygen vacancies. This infringes the stoichiometry and causes a shift of the overall composition of the monoxide to the heterophase region of the M–O phase diagram and its decomposition with formation of an oxide with a higher degree of oxidation and the metallic phase. The metal reacts with CO and is converted into oxide carbides.[101,102,109] The absence of vanadium and niobium monoxides from the reduction products is associated with the fact, according to Shvikin,[5] that the rate of their conversion into oxide carbides having crystal lattices isostructural with those of the monoxides greatly exceeds the rates of the preceding reduction stages.

The reduction of Ta_2O_5 to tantalum is in many respects analogous to the reduction to hafnium,[10] which is due to the similarity of their properties since they are neighbours along the Period.[19] Like zirconium and hafnium dioxides, Ta_2O_5 reacts with carbon and is converted into oxide carbides with a cubic structure in accordance with the scheme described above for ZrO_2 and HfO_2, by-passing the monoxide formation stage.[98,107] The stability and composition of the oxide carbides depend on the temperature and the CO pressure in the system. An increase in the CO pressure at a specified temperature promotes not only their stability but also the expansion of the region of homogeneity, while a decrease in the CO pressure and an increase in temperature tend to increase the carbon content in the oxide carbides and bring the composition closer to that of the corresponding tantalum carbide. In the absence of contact with the solid carbon, the degree of conversion of Ta_2O_5 into the product increases with increasing CO pressure (Fig.3). However, at $p_{CO} = 2 \times 10^{-2}$ MPa, this process slows down as a consequence of the diffusion-dependent obstacles arising in the layer of products. Thus at 1873 K in the absence of contact with graphite in CO,[10] the carbide $TaC_{0.6}$ is formed on the Ta_2O_5 surface and then reacts further with the highest oxide, forming gaseous TaO and TaO_2. These oxides are adsorbed on the surface of solid carbon and are reduced to TaC. At temperatures close to 1973 K, under conditions where Ta_2O_5 is in contact with solid carbon, the interaction takes place with participation of the oxide carbide melt.[10]

7. Reduction to Group VIB Elements

Among the oxides of Group VIB elements, Cr_2O_3 is the most stable.[19,88] Its interaction with solid carbon proceeds in the initial stage with participation of CO as the reductant.[2,10,110,115] This is confirmed by the acceleration of the reduction when graphite is replaced by more active forms of carbon reductants, accelerating the gasification of carbon,[110,111] and also by the formation of reduction products on the surface of the oxide in the absence of contact with solid carbon at $p_{CO} = 0.1$ MPa.[110,112] A decrease in CO pressure in the space between the solid reactants which are not in contact with one another intensifies the reduction of Cr_2O_3 (Fig.1) [10] owing to the increase in the rate of diffusion and mass transfer which compensates for the decrease in the CO concentration. However, at $p_{CO} < 4 \times 10^{-3}$ MPa the degree of conversion of Cr_2O_3 diminishes sharply due to the decrease in the CO concentration and the oxide dissociation reactions develop preferentially, occurring at rates lower than in the reduction with carbon monoxide. The oxide Cr_2O_{3-x}, in which the concentration of oxygen corresponds to the lower limit of the region of homogeneity,[116] is formed under these conditions in the initial stage. This is followed by congruent evaporation with formation of atomic chromium and the vapours of the lower oxides CrO and CrO_2 and oxygen,[73] which react with solid carbon to give the carbide Cr_3C_2 and CO. At $p_{Ar} = 0.1$ MPa [116] and *in vacuo* ($\sim 4.6 \times 10^{-8}$ MPa), the interaction of the Cr_2O_3 specimens and solid carbon, which are not in contact, in the range 1373–2073 K [117] also includes the oxide dissociation stage.

When the solid reactants are involved in contact interaction *in vacuo* at 1773 K,[117,118] the carbide phase grows into the oxide specimen at the sites of contact between them. However, the role of this process is small owing to the extremely small area of contact in mixtures of reactants compared with their overall surface area.[2]

The interaction of Cr_2O_3 with carbon intensifies sharply at temperatures above 1773 K [116] where the reduction on the surface of chromium oxide results in the formation of the metallic Cr–C melt, which, creating a liquid contact between the reactants, ensures the preferential development of the reactions involving the reduction by the carbon dissolved in the metallic phase.

† T_m is the melting point (Ed.of Translation).

8. Reduction to Group VIIB Elements

Among the Group VIIB elements, manganese and its alloys have been obtained by the carbothermal reduction. The most stable manganese oxide is MnO, which has been detected as part of the composition of complex intermediate compounds in the reduction of concentrates and ores.[2,119,120] In a free state, without contact with solid carbon at p_{CO} = 0.1 MPa,[31] MnO reacts in the temperature range 1473–1623 K with the CO adsorbed on its surface, forming gaseous metallic manganese and CO_2. At temperatures in excess of 1623 K, the carbide Mn_7C_3 is formed on the surface of the carbon reductant. The replacement of CO by an inert gas greatly diminishes the rate of the reduction reactions on the MnO surface as a consequence of the sharp decrease in the contribution of reactions with participation of CO and the development of MnO dissociation reactions with the preferential formation of atomic manganese and molecular oxygen.[73] At temperatures close to the fusion of Mn_7C_3 (~1623 K), the contribution of the reactions of MnO with CO diminishes[31,121] owing to the formation of liquid Mn_7C_3 carbide bridges between the solid reactants and the development of reactions involving reduction by the carbon dissolved in the liquid metallic phase.

9. Reduction to Metals with Participation of Metals

Analysis of the accumulated experimental data shows that at certain temperatures reactions with participation of melts play a leading role in carbothermal reduction processes. The intensification of the reduction processes observed under these conditions is due to a number of factors; the closer contact between the fused metal oxide with the solid carbon (SiO_2 [39]); contact between the solid metal oxide and the carbon dissolved in a metallic melt (Cr_2O_3, MnO [2,31,116]); the dissolution of the initial reactants in the melt with subsequent interaction in the liquid phase (CaO,[68] Al_2O_3,[28] Group IIIB elements[89,90]), and also the stirring of the melt by the evolved gas. Under these conditions, when ionic activity is appreciable, the interaction becomes electrochemical in character. These processes have been studied in detail in the reduction of slag melts to iron, manganese, and chromium. The mechanism of the reduction of melts of this type is represented as the sum of the cathodic and anodic half-reactions, which takes place on different sections of the surface[122]

$$M^{n+1}+e=M^{(n-1)+}$$
$$M^{n+}+ne=M$$
$$C(Solid)+O^{2-}=CO+2e$$

The electron exchange necessary to maintain the electroneutrality of the phases takes place through solid carbon.

The Table presents the appearance temperatures of the melt menisci around the metal oxide specimens in their contact interaction with graphite at different CO pressures. Under these conditions and also at higher temperatures, the reduction reactions in the liquid phase assume the leading role.

10. Reduction of Complex Refractory Metal Oxides

The reduction of complex refractory oxides to the metal takes place consecutively in conformity with the thermodynamic stabilities of simple metal oxides forming part of the composition of the complex compound. Thus in the reduction of chromium ores containing chromium spinelides and chromites, the spinelides are initially reduced to iron and chromium, while at higher temperatures chromites are reduced to the metals with formation of MgO and $MgAl_2O_4$ spinel.[123] The reduction of $MgAl_2O_4$ spinel to magnesium at 2020 and 2170 K without contact with graphite at p_{CO} = 0.1 MPa takes place with participation of CO as the reductant.[124] A solid solution of Al_2O_3 in the spinel is formed as a result on the surface of the complex oxide. After the attainment of the limit of the region of its homogeneous composition, Al_2O_3 is segregated in an independent phase. The reduction reaction at the spinel–reducing gas (CO) interface take place under diffusion conditions and its rate depends on the ratio of the specific surfaces of the initial reactants.

Temperatures of the appearance of melt menisci in the contact interaction of metal oxides with graphite.[10]

Oxide	T, K	p_{CO}, MPa	Oxide	T, K	p_{CO}, MPa
Al_2O_3	2223	0.1	ZrO_2	2373	$3\cdot10^{-2}$
Sc_2O_3	2273	$1.3\cdot10^{-4}$	HfO_2	2423	0.1
Y_2O_3	2123	$1.3\cdot10^{-4}$	Nb_2O_5	1773	0.1
La_2O_3	1823	$1.3\cdot10^{-4}$	Ta_2O_5	1973	0.1
Nd_2O_3	1973	$1.3\cdot10^{-4}$	CaO	2073	$5\cdot10^{-2}$
Gd_2O_3	2073	$1.3\cdot10^{-4}$	SrO	2023	0.1
Lu_2O_3	2373	$1.3\cdot10^{-4}$	BaO	1973*	0.1
Cr_2O_3	1823	0.1	MnO	1623**	0.1
TiO_2	1923	0.1			

*According to data in Ref.30.
**According to data in Ref.31.

The interaction of the aluminosilicates with carbon also takes place in stages. In the initial stage of the reduction, gaseous SiO is formed and reacts with the carbon reductant to give silicon carbide.[125] This process is controlled by diffusion through the layer of the microporous product—α-Al_2O_3.[126] The contribution of the mullite dissociation reactions to the reduction process increases with decrease in pressure in the system. Under these conditions, the dissociation of Al_2O_3 at a lower rate than that of the formation of gaseous SiO is observed together with the thermal decomposition to gaseous SiO and solid Al_2O_3. Thus CO retains the role of the reductant in the reduction of complex oxides to the metals. When CO is diluted with an inert gas and *in vacuo*, the contribution of the reduction by carbon monoxide diminishes and the role of the metal oxide dissociation reaction increases. The reduction processes on the surfaces of solid oxides are associated with diffusion-dependent obstacles as a consequence of the segregation in an independent phase of the oxides which are more difficult to reduce to the metals.

Analysis of the accumulated experimental data shows that, in the absence of liquid phases, the interaction of solid metal oxides with carbon proceeds through the gas phase via a mechanism including reactions involving reduction by carbon monoxide and the dissociation of metal oxides. The contributions of these reactions to the overall reduction process depend on the composition of the gas phase between the reactants. At p_{CO} in excess of 4×10^{-3} MPa, the

reactions involving the reduction by carbon monoxide play a leading role, while at p_{CO} less than 4×10^{-3} MPa, the dissociation of the metal oxide predominates in an inert gas and *in vacuo*.

The character of the variation of the mass of specimens of the oxides of Group IIA elements, SiO_2, and Cr_2O_3 out of contact with graphite as a function of the CO pressure (Fig.1) indicates the presence of common features in the change of the reduction mechanism. An analogous similarity (Fig.2) has been observed for the oxides of aluminium and its group analogues (in Groups IIIB and IIIC). The formation of carbon-containing phases in chromium oxides and the oxides of Group IIIB and IIIC elements justifies the assumption that carbon monoxide is also a reductant in relation to SiO_2 and Al_2O_3. The absence of carbon-containing phases on the surfaces of oxides of Group IIA elements, Al_2O_3, and SiO_2 at p_{CO} = 0.1 MPa, interpreted by some investigators as an argument in support of the oxide-sublimation mechanism of the reduction process, is associated with the fact that, in contrast to the refractory oxides of *d* and *f* elements, the oxides of *s* and *sp* elements under the conditions of real processes are incapable of substituting part of the oxygen in the anionic sublattice by carbon atoms and of creating conditions for the appearance of carbide and oxide carbide phases.

At temperatures in excess of $0.5\,T_m$ of the metal oxides, the contribution of the reactions involving reduction by carbon monoxide on the surfaces of the solid metal oxide increases as a consequence of the increase in the concentration and mobility of the crystal lattice defects responsible for the increase in the number of centres for the chemisorption of CO.[10] The dissociation reactions become the mains ones under the conditions of a low-temperature plasma.[127]

The composition of the products of the reduction by carbon monoxide depends on the nature of the elements produced by the reduction process. The reduction of the oxides of *s* and *sp* elements and manganese with a stable $3d^5$ electron shell of the metal atom takes place via the chemisorption of CO and its subsequent oxidation by the oxide oxygen to CO_2 with formation of the vapours of the metals and the lower oxides. On the oxides of *d* and *f* elements, the chemisorbed CO disproportionates predominantly to CO_2 and carbon, which is oxidised by the oxide oxygen and also partly fills the oxygen vacancies. The kinetics of the reduction reactions on the surfaces of solid oxides of the shell analogue elements under different initial conditions obey the general correlation with the Gibbs free energy of the reduction reaction. At the corresponding temperatures, the interaction through the gas phase is limited as a consequence of the appearance of carbide oxide or carbon-saturated metallic melts.

V. OXIDATION REACTIONS OF SOLID CARBON

Reactions of two types take place on the surfaces of carbon reductants: the gasification of carbon and the formation of metal carbides in the interaction with the vapours of metals and their lower oxides. The high-temperature carbon gasification processes have been described in detail by Golovina.[128] The gasification of carbon has a multistage mechanism, which includes the chemisorption of CO_2 and the formation of intermediate complexes on active sites of the surface:

$$C + CO_2 \rightleftharpoons C(O) + CO(gas), \quad (2)$$

$$C(O) \rightleftharpoons CO(gas). \quad (3)$$

where C(O) is an intermediate complex.

At p_{CO_2} close to 0.1 MPa, the gasification reaction in the temperature range 1300–1650 K takes place not only on the surface of the carbon material but also throughout its volume. In the range 1700–2400 K, the reaction shifts to a narrow zone at the reductant surface. In this temperature range, the specific rate of the reaction is seen to diminish, passing through a minimum at 2000–2300 K as a consequence of the diffusion-dependent inhibition in the gas phase, which arises with increase in the absolute rate of oxidation of carbon. The rate of reaction depends on the number of active centres adsorbing CO_2 molecules. The decrease in the rate of reaction at 2000–2300 K, when the desorption of CO is rapid and the role of the reverse reaction (2) is small, has been attributed to the thermal deactivation of the reductant surface. At temperatures in excess of 2400 K, the depth of the reaction zone and the specific rate of the reaction again increase as a consequence of the development of the self-diffusion of carbon from the bulk phase to the reaction centre and the increase in the concentration of defects, whose number reaches a maximum at temperatures close to those corresponding to a change in the state of aggregation of the substance. This stimulates an increase in the degree of chemisorption of CO_2 and in the rate of reaction as a whole. The sublimation of graphite begins to play an appreciable role under these conditions. The disordered "amorphous" part of the reductant is then sublimed in the first place.

Carbon reductants differ significantly in their crystal structure, the type and size of pores, and the character of their distribution. The rate constants obtained for the oxidation reactions of reductants[129,130] as well as the estimation of the reactivity with respect to CO_2 [131] are valid only for specific reduction conditions. A general treatment of the results accumulated in this field established[129] that one of the main parameters determining the rate of reaction with the gas is not only the activation energy *E* but also the pre-exponential factor *A* in the Arrhenius equation, which changes on passing from one kind of material to another and obeys the relation

$$\lg A = \lg A_0 + \alpha E$$

where A_0 and α are coefficients. The relation obtained for porous (cokes, semicokes, different types of coal, anthracites) and nonporous (carbon black, carbon fibres, pyrographite) materials is universal and applicable to different textures of the material. It can be used to estimate the reactivities of reductants in relation to CO_2 in the absence of data on the size of the reaction surface. It is sufficient to know what the gas medium is and to determine the apparent activation energy for the oxidation of the reductant.

In the reduction of *s* and *sp* elements on the reductant surface, reactions with participation of the vapours of metals and the lower oxides and leading to the formation of carbides take place in addition. Therefore, if the reductant surface is blocked by the reaction products, the oxidation of carbon passes from the kinetic to diffusion conditions[90,131] with a change in the size of the specific surface.[132] Under these conditions, the growth of the layer of products, especially SiC,[132] is caused by the counterdiffusion of the metal ions and carbon along the grain boundaries and microstructural defects. The rate of diffusion of the metal ions, for example of the silicon ions in SiC, is then higher by several orders of magnitude than that of carbon ions, which promotes the preferential growth of the reaction front into the bulk of the reductant and the formation of a pseudomorphic analogue of the carbide from the carbon.

Silicon[132] is formed on the surface of the particles of the carbon reductant only after the complete conversion into silicon carbide. The partial pressure of SiO in the system should then be significantly greater than in its formation from SiO_2 and carbon.

The chemical reactivity of the reductant in relation to the metal oxide is a complex function of factors acting simultaneously (the porous structure, the specific surface, and the degree of order in the crystal structure of carbon), whose influence cannot be taken into account separately.[131] Two principal forms are present in the macrostructure of cokes—finely dispersed crystalline regions with a well developed system of pores and non-porous amorphous regions. The greater the number of crystallite intermediate forms in the microstructure and the greater their defectiveness, the larger the surface area of the reductant and correspondingly the higher its chemical reactivity.[133,134] A clear dependence of the reactivity of the reductant in relation to SiO_2 on the specific surface is observed only for petroleum cokes.[135] In other types of reductants, it depends little on the specific surface. The reactivity of different types of carbon blacks in relation to SiO_2 [135,136] depends on the degree of order in the structure. Many carbon blacks having a high specific surface are extremely compact and there is a film of high-molecular-weight products preventing the diffusion of silicide forming agents into the bulk of the particles.

In practice, the reactivity of the reductant is estimated from the intensity of its interaction with CO_2.[131] However, this method does not take into account the specific features of certain metals, whose reduction is accompanied by the formation of carbides blocking the surface of the reductant. The methods proposed for the estimation of the reactivity of the reductant from the change in the mass reacting with gaseous SiO,[137–140] with SiO_2,[131] and with CaO [141] reflect the overall result of the interaction and do not allow the determination of the influence of the surface area on the intrinsic reactivity of the reductant, which is estimated quantitatively from the ratio of the rate constants for isotypical reactions (k/k_0) carried out under identical conditions, where k_0 is the rate constant for the reaction of one of the substances in the reaction series.[142] Overall, the influence of the surface of the reductant and of its reactivity on its chemical activity in relation to the metal oxide being reduced (for example, SiO_2) has been estimated[39] from the quantity

$$A = S k$$

where S is the initial surface of the reductant ($m^2\ kg^{-1}$) and k the rate constant for the reaction of carbon ($kg\ m^{-2}\ s^{-1}$).

Thus the chemical activity of the reductant depends on two factors acting simultaneously, its specific surface and its reactivity. The activity of the reductant can therefore be increased not only by selecting the necessary degree of dispersion and hence the specific surface of the reductant[139,143,144] but also by increasing its reactivity. The latter is achieved by introducing mineral admixtures,[131,133,135,145] by mechanochemical treatment together with the metal oxides to be reduced,[12,146] and by γ-irradiation,[147] which ensures the appearance of oxide–carbon–oxygen complexes at additional defects in the carbon structure.

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It follows from the analysis of the data described that the observed difference in the interaction of refractory metal oxides with carbon are correlated with the differences in the fundamental properties of the metal atoms generated in the reduction process, which are reflected in the Periodic System of the elements. This made it possible to deduce a general basis for the description of the interactions of solid metal oxides with carbon, according to which they proceed via an adsorption-dissociative mechanism including reactions involving reduction by carbon monoxide in combination with reactions involving the gasification of solid carbon by its dioxide and the dissociation of the metal oxide. At CO pressures in the space between the reactants in excess of 4×10^{-3} MPa, the reactions involving reduction by carbon monoxide develop preferentially. The contribution of the metal oxide dissociation reactions to the overall reduction process is insignificant under these conditions. On decrease in the CO pressure to less than 4×10^{-3} MPa, *in vacuo*, and in an inert gas, the metal oxide dissociation reactions make the main contribution to the reduction process.

The differences in the interaction of certain metal oxides with carbon at p_{CO} close to 0.1 MPa depend on the properties of the oxides, which are determined by the electronic structure of the reduction product metal atoms. Thus the reduction of the oxides of *d* and *f* elements by carbon monoxide in the presence of solid carbon is accompanied by the liberation of CO_2 to the gas phase, while the reduction of the oxides of *s* and *sp* elements results in addition in the evolution of the vapours of the metals and their lower oxides, which block the surfaces of the carbon reductants by the corresponding carbides. The CO adsorbed on the surfaces of the oxides of *s* and *sp* elements is oxidised by the oxygen of the oxides to CO_2, while on the surfaces of the oxides of *d* and *f* elements it disproportionates to CO_2 and carbon, which is oxidised by the oxide oxygen and partly fills the oxygen vacancies, forming solutions of carbon in the oxides and carbon-containing phases. The existence of groups of oxides for which there are general correlations between the rate of reduction and the Gibbs free energy of the reduction reaction has been established in relation to the oxides of elements, which are shell analogues of calcium, strontium, and barium, and also lanthanum and gadolinium oxides.

The chemical activity of the reductant depends on the two factors acting simultaneously: its specific surface and its reactivity. The latter can be increased by introducing mineral admixtures, by mechanochemical treatment, and by γ-irradiation.

It is noteworthy that many ideas about the interaction of CO with the surfaces of solid metal oxides require confirmation by refined experimental methods. It is essential to accumulate qualitatively new information about the elementary steps in the reduction process by employing research methods from adjacent fields of science. Overall, the views formulated on the mechanism of the reduction process make it possible to estimate the interrelation between the individual stages of the processes, to select the optimum compositions of the gas phase, the carbon reductants, etc., and to influence the intensity of technological processes.

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