

ELECTRON MECHANISM OF REDUCTION PROCESSES IN BLAST AND FERROALLOY FURNACES

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ABSTRACT

Current interpretations of the solid-phase iron reduction theory are atom-molecule based. They view the reduction process as an exchange between oxide molecules and deoxidizer, i.e. oxygen atoms. However, there are neither atoms nor molecules in solid oxides or metals; there are just ions and electrons that bind the former. Thus, the oxidation-reduction reaction is not an exchange of atoms but that of electrons. Therefore, when viewing it in atom/molecule terms, formulating a consistent theory of processes that develop at a different — i.e. electron — level does not appear to be feasible. The electronic theory of reduction furthered by the authors describes electro- and mass transfer in gaseous and condensed phases, exchange of electrons between deoxidizer and oxide, redistribution of electrons between the cations and anions in the oxide lattice and transformation of the oxide lattice into a metal lattice, as well as the effect of pressure and temperature on the above processes. According to the theory, the extraction of one oxygen anion from the crystal lattice at the surface of an oxide would result in the creation of an anion vacancy and two free electrons bound to it. In complex and low-grade ores, vacancies and electrons tend to disperse across the oxide, build up and merge together near the cations the Fermi energy of which is below the chemical potential of electrons in the vacancies. The results obtained through experimental and real-life production of pig iron and ferroalloys were attributed to the charged particles of low-temperature plasma that are involved in redox reactions in the solid reagents layer. Plasma is formed as a result of the thermionic emission from the deoxidizer surface and the thermal ionization of gases. It is shown that the carbothermal reduction of active metals and iron from solid complex oxides can only be achieved with solid carbon. Through plasma, carbon is transferred to the oxide surface, and oxides — to the carbon surface. As a result, carbide shells form at the surface of both. Carbides contaminate the surface, they slow down and stop the reduction process. Melting and flowing of the shells switches the reduction process to a kinetic mode thus ensuring its efficient realization.

“... the mechanism behind chemical processes can only be explained on the basis of the physical theories describing the motion of reacting molecules and chemically reacting electrons” [1]

Reduction Viewed in Terms of Atoms and Molecules

The current metallurgical theory went through intense development in the first half of the previous century based on the understanding of chemical reactions as molecular processes, which had become established by that time. That's why metal reduction processes are described in terms of chemical reactions that take place between molecules and atoms at the interface between deoxidizers and oxides contained in the ore. The theory implies that reduction is achieved through an exchange of oxygen atoms between the molecules (atoms) of the deoxidizer and the oxide molecules. It is taken for granted that the products of the reactions are born at the same interface.

Based on the above views and considering that the oxygen atoms are taken from the oxide molecules one after another, academician A. A. Baikov made the following statement in the 1920s: Higher oxides should first transform into intermediate oxides, then into lower oxides before finally transforming into metal [2]. The principle of gradual transformation of higher oxides into metal via all possible intermediate stages is known as Baikov principle [3–9]; it forms the basis of the current atomic-molecular theory of reduction and is taken for granted.

In the production of pig iron and most of the ferroalloys, coke serves as the main deoxidizer that helps extract

iron and the target metals (such as chromium, manganese, silicon and others). That's why the reduction process is described with a reaction between a molecule of solid oxide of the ore and a carbon atom of solid coke producing an atom of solid metal and a gas molecule of carbon monoxide: $MeO_{\text{solid}} + C_{\text{solid}} = Me_{\text{solid}} + CO_{\text{gas}}$.

However, as the contact between solid bodies only exists in certain points, one cannot meaningfully explain the high rate of reduction observed in real life with the point contact area existing between the initial reagents, as such contact is extremely insignificant and keeps constantly changing in the course of chemical interactions. Besides, the first solid products of the reaction separate the initial solid reagents impeding the approach of atoms and molecules. The attempts to attribute the contact (direct) mechanism of solid-phase reduction happening at the rate observed to special atomic and molecular diffusion conditions present in the metallic layer separating the reagents, which were taken by scientists in the first half of the previous century, failed to come to fruition. That's why presently the contact mechanism of direct reduction of metals with carbon is almost out of consideration, at least with regard to the blast furnace process of iron reduction.

In connection with the above, the hypothesis raised by the French metallurgist L. Grüner [10] back in 1872 about

the key role of the intermediate reagent, i.e. gaseous carbon monoxide, in carbothermal reduction of iron, became widely recognized. According to his hypothesis, the following reaction takes place at the ore surface: $MeO_{\text{solid}} + CO_{\text{gas}} = Me_{\text{solid}} + CO_{2\text{gas}}$. Carbon dioxide, which forms at the temperatures exceeding 700...800 K [7], reacts with solid carbon following the Boudouard reaction and forming carbon monoxide: $CO_{2\text{gas}} + C_{\text{solid}} = 2CO$. A sum of these two reactions results in the reaction of direct reduction of metal with solid carbon: $MeO_{\text{solid}} + C_{\text{solid}} = Me_{\text{solid}} + CO_{\text{gas}}$.

This contact-free reduction process involving the intermediate gaseous reagent consumes solid carbon of the coke. That's why both textbooks and academic literature [3–6] also refer to this two-stage (or, bi-reaction) reduction process as direct reduction versus indirect gaseous reduction also involving carbon monoxide but happening at the temperatures below 700 K, when no regeneration of monoxide from dioxide is possible. Presence of the CO_2 molecules in the gaseous phase is taken as an indicator of indirect reduction, while the proportional concentration of CO and CO_2 in the gaseous phase indicates the progression of direct or indirect reduction.

It is also taken into account [4–7] that solid carbon is also involved in the reduction process when gaseous hydrogen acts as a direct reducing agent under the following reaction: $MeO_{\text{solid}} + H_{2\text{gas}} = Me_{\text{solid}} + H_2O_{\text{gas}}$. At the temperature above 1,083 K, the moisture delivered in the blast furnace with the burden and the blast air, as well as water resulting from the hydrogen reduction reaction react with solid carbon to produce CO and H_2 under the following reaction: $H_2O_{\text{gas}} + C_{\text{solid}} = CO_{\text{gas}} + H_{2\text{gas}}$. And although hydrogen serves as a direct reducing agent here, it regenerates with an almost full recovery meaning that hydrogen is only involved in the so-called transport reactions [11]. Because in this case it is only solid carbon that is consumed, the process of hydrogen reduction at the temperature exceeding 1,083 K is also defined as direct reduction [3–8].

At the temperatures below 1,083 K, hydrogen behaves less similarly to oxygen compared with carbon monoxide. That's why in this case the water vapour reacts with carbon monoxide as follows: $H_2O_{\text{gas}} + CO_{\text{gas}} = CO_{2\text{gas}} + H_{2\text{gas}}$, producing hydrogen. However, as the effect of carbon monoxide on the water does not extend further than reaching the equilibrium partial pressures and some of the water stays intact, the final products of the hydrogen reduction process, apart from the actual metal, include CO_{gas} and H_2O_{gas} . The proportional concentration of $(CO + H_2):(CO_2 + H_2O)$ in the blast furnace gas serves as an integral progress indicator of direct and indirect reduction processes. And since reducing gases can be regenerated with solid carbon, the following temperature ranges were assigned to distinguish between the two processes – reduction at the temperature above 800 K is considered a direct reduction, whereas what is defined as indirect reduction happens at lower temperatures.

According to the current understanding, the reduction of metals from solid oxides with the help of solid carbon

implies a contactless exchange of oxygen atoms between the oxides and coke, a gradual transformation of higher oxides into the metal via all the possible intermediate oxides, reduction reactions developing at the surface of solid reagents, compulsory involvement of gaseous molecules, regeneration of the gaseous molecules of direct deoxidizers with solid carbon, formation of a metallic phase where the reduction reaction occurs, i.e. at the oxide surface.

The “molecular” approach to the reduction process requires that one not only described how the solid reagents exchange molecules and atoms through the gaseous phase, but also analyzed how gas molecules interact with the molecules of solid bodies at the latter's surface and how molecules and atoms move to the reaction surface through solid reduction products and in solid oxides. They were predominantly Russian researchers who formulated a so-called adsorption-autocatalytic theory of iron reduction with carbon, which describes how the metal reduction occurs at the surface of solid oxides with the help of gas molecules. Under the theory, the intermediate agents include gas molecules of CO and H_2 [12–14], and the surface reduction process involves 3 stages: I – adsorption of the reducing gas on active centres (metallic nuclei), II – chemical reaction at the oxide surface, III – desorption of the product from the oxide surface.

The adsorption-autocatalytic theory is usually enhanced with a diffusion-kinetic theory [15], which claims that the reduction process is controlled by the way the reagents approach the oxide surface where the reaction takes place. The theory suggests that the high rate of reduction observed in real life can be attributed to a possible fast counter diffusion of the CO and CO_2 gas molecules in metal and oxides via micropores, the size of which is comparable to the size of the molecules. This is a so-called Knudsen diffusion.

Thus, the atomic-molecular theory of reduction is based on the principle of gradual transformation of oxides into metal, the adsorption-autocatalytic theory of gas reduction, and the diffusion-kinetic theory of gas molecules moving through micropores in solid metallic and oxide phases.

Myths and Problems of Atomic-Molecular Theories

The above theoretical assumptions are based on the results of a study that looked at the iron reduction from iron oxides or high-grade iron ores in terms of the blast furnace process. However, as a deoxidizer, carbon, in the form of coke, is also widely used in ferroalloy furnaces for the production of ferroalloys with active metals, including ferromanganese, ferrosilicium and others. That's why the carbothermal reduction theory should also be observed when producing the above ferroalloys. At the same time, in certain instances carbon monoxide lacks in strength as a deoxidizer and, in contrast to solid carbon, fails to deoxidize metals which are more active than iron, such as chromium [16]. However, while the above described provisions of the adsorption-

autocatalytic theory are not applicable to the production of ferroalloys, they are still used for describing the reduction processes taking place in ferroalloy furnaces [16–19].

Moreover, some of the assumptions stated above fail to find practical evidence. For example, it is a well-known fact that higher blast temperature and pressure in the furnace lead to better performance of the blast furnace by increasing the throughput, reducing the coke consumption etc. [6, 20, 21]. However, it is completely obvious that a higher temperature makes atoms and molecules move more actively thus affecting the adsorption, which, according to the adsorption-autocatalytic theory, should produce the opposite result. And according to the Le Chatelier principle, a high gas pressure in the furnace should impede the key reaction of direct reduction: $MeO_{solid} + C_{solid} = Me_{solid} + CO_{gas}$, as, per this reaction, the condensed phases produce gas.

The current reduction theory equally fails to account for either the heat-induced structural changes experienced by solid bodies or the changing behaviour of molecules and atoms resultant from heat and rising gas pressure. Indeed, a higher than a 1,000-degree rise in the temperature of solid bodies and a higher than a 2,000-degree rise in the temperature of gases observed in modern blast furnaces cannot but impact the crystal structure of solid bodies and the behaviour of gases.

The Knudsen diffusion-based theory is not without a flaw either. As mentioned earlier, when in the beginning of the previous century researchers tried to understand if it would be possible to make the reagents fast approach the reaction site, they looked into the possibility of inducing a fast diffusion of atoms or ions in solid oxides and solid metal. At the same time, researchers clearly established that the observed rate of reduction could be attributed to neither atomic nor ionic diffusion. And the diffusion-kinetic theory explains such a high rate with a counter diffusion of coarse two- and three-atom molecules of CO and CO₂ traveling through the micropores, which are still technically undetectable, even using most advanced instruments.

To eliminate the obvious discrepancies between the existing theories and in the attempt to “adapt” them to particular cases of extracting particular metals from particular ores in particular conditions, researchers have attempted to find more consistent evidence to support these theories. Thus, the authors of the papers [16–19] are working on developing a “gas-phase/solid-phase” reduction mechanism, while the authors [22–24] are looking to substantiate a so-called dissociative adsorption theory by considering the processes of adsorption and dissociation being a part of one mechanism, which implies the unthinkable idea that they might take place in the same conditions. Since one cannot explain the reduction of chromium with the presence of CO for the thermodynamic conditions, one considers that the deoxidizer function is performed by gas radicals (CH_{4gas}, CH_{3gas}, CH_{2gas}, CH_{gas}, C_{gas}, H_{gas}) [16–19] or intermediate oxides of carbon (e.g. the “suboxide” C₃O₂ [18, 25, 26]), which

move the carbon of the deoxidizer to the oxide surface while producing a highly active carbon C*^{*}; the vapour of the reduced oxides or the vapour of lower oxides produced as a result of dissociation of the former [27–30], which move the target component to the surface of the solid deoxidizer developing a direct (contact) reduction (a “gas-carbide” variant of the theory). In other words, it is assumed that, depending on the chemical activity of the target metal, the types of ores and deoxidizers used, different metals in different conditions follow different reduction mechanisms, and because of this there can be no single reduction theory [31].

It should also be noted that neither the basic assumptions of the existing reduction theory, nor any of its numerous variants designed to improve and add to the theory, fail to consider the key developments of the reduction process — i.e. the transformation of the crystal lattice when oxides become metals. These developments are inherent in any reduction process and are a common feature for any reduction scenario.

We believe that the drawbacks and inconsistencies of the current theory are due to the fact that oxidation-reduction reactions are not when molecules exchange atoms but rather when ions exchange electrons, the motion and distribution of which (including those within the ionic structures of oxides and metals) are governed by the laws of quantum physics rather than Newton’s laws. The existing reduction theories attempt to apply molecular laws to describe processes that develop at a deeper structural level. Solid bodies contain neither molecules nor atoms. Molecules and atoms are only distinguishable in gases, while the crystal lattice of both oxides and metals consists of ions bound by “valence” electrons. Distinguishing separate molecules or atoms in a crystal lattice with ionic or metallic bonding does not appear to be possible [32–34].

Even if we take a very simple crystal lattice (like the one of NaCl) with ionic bonds, every sodium cation is bonded with 6 chlorine anions through its single valence electron, while every chlorine anion is bonded with 6 sodium cations (**Fig. 1, a**). In a body-centered lattice (like that of CsCl), every cation is bonded with 8 anions (**Fig. 1, b**) through one valence electron, while in closest packings (face-centered cubic and hexagonal close-packed lattices) every ion is interacting with 12 ions of the opposite sign. Closest packing is common for oxygen anions which are always coarser in oxides (**Fig. 1, c**). Cations, which have smaller sizes, are found in tetra- and octapores. And it is not uncommon when, together with reducible cations (e.g. iron and chromium), the same pores contain non-reducible metal cations, such as those of magnesium and aluminium in chromium spinel (**Fig. 1, d and e**). That’s why when iron and chromium are reduced as part of the carbon ferrochromium production, no reaction is possible between carbon and iron oxide molecules or chromium oxide molecules.

Therefore, the general reduction theory should describe not only the mechanism of mass transfer between the deoxidizer and oxides, i.e. the motion of molecules

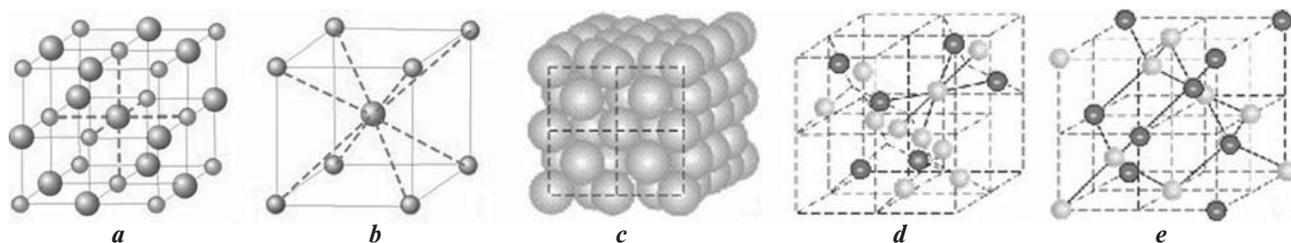


Fig. 1. Distribution of ionic bonds between ions of a simple cubic (*a*) and body-centered cubic (*b*) crystal lattice with one valence electron; closest packing of oxygen anions in 8 primitive unit cells of spinel (*c*), cations of reducible and non-reducible metals in okta- (*d*) and tetrapores (*e*) of the anion sublattice of spinel

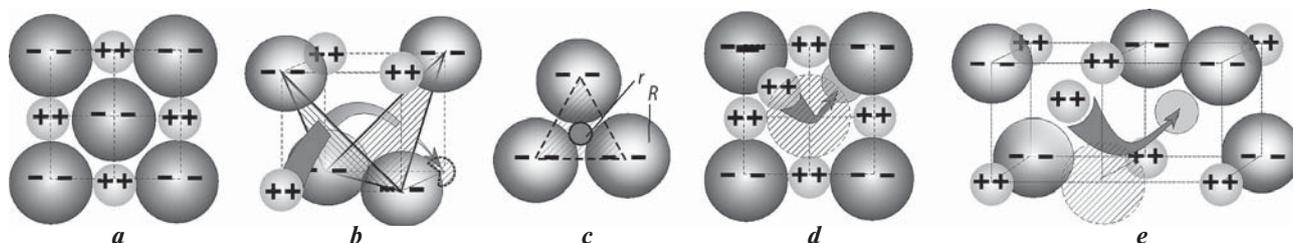


Fig. 2. Cation traveling to the neighbouring vacant node of spinel: *a* – spinel's primitive unit cell plane; *b* – cation's path; *c* – a “narrow” window in the 3-anion plane; *d*, *e* – cation traveling through anionic vacancy

and atoms in the gas phase or the motion of cations and anions in condensed phases, but also the mechanism of electron exchange between the deoxidizer and the metal cations, the redistribution of electrons between cations and anions in the oxide lattice and the transformation of the oxide crystal lattice into the metal crystal lattice, as well as the impact of external factors (*P* и *T*). That's why the goal of this research is to summarize the results of our investigations and analyze the available literature to get a better insight into the reduction processes that are inherent in the production of pig iron and ferroalloys.

Mobility of Ions in the Oxide Crystal Lattice

The above mentioned unsuccessful attempts to explain the contact reduction mechanism with solid carbon can be attributed to the fact that the mobility of ions in the oxide crystal lattice was viewed in the same terms as the one in the metal lattice. Besides, particle size was viewed as the key factor when analysing the velocity of travel. And because cations are much smaller than anions, it was logically concluded that cations would predominantly have a higher diffusion rate. However, the analysis proved otherwise [35–38].

Unlike it is with metals, the ionic lattice of oxides consists of particles that have not only different sizes but also different charges and different node occupancy in the cation and anion sublattices. Thus, the 8 primitive unit cells of spinel, which comprise a full set of anion and cation sublattice nodes, contain 32 oxygen anions, 64 tetrahedral and 32 octahedral pores, which may house cations. Only 24 out of 96 pores are filled with cations – 16 octahedral and 8 tetrahedral pores, while 72 pores are empty. One would think that such amount of potentially vacant pores would most certainly stimulate cation diffusion,

especially considering the fact that rising temperatures make normal spinels turn into inverted ones, in which doubly and triply charged cations exchange places.

However, to transfer into any vacant node, a cation has to squeeze through the narrow “window” ($r = 0.15R$, where R – anion radius) between the oppositely charged particles (Fig. 2, *a–c*) twice. Considering that the nodes of the anionic sublattice are filled up, such transfer may not be highly probable. At the same time, as a result of thermal oscillations anions, which are so close to each other that they can come into contact, can easily jump from one anionic node to any neighbouring node even if there are no vacant anionic nodes. The conditions for a cation to transfer into a vacant cation node considerably improve even if there is just one anionic vacancy (Fig. 2, *d* and *e*). Thus, cationic diffusion is basically determined by the presence and the number of anionic vacancies rather than the cation sizes or the number of cationic vacancies.

Anionic vacancies are present in any oxides and in any conditions. They mainly include Frenkel and Schottky vacancies occurring due to the thermal motion of ions; impurity vacancies occurring due to the presence of impurity cations that are charged less than the basic cations; and vacancies occurring as a result of poor stoichiometry of oxides caused by changing partial pressure of gaseous oxygen [39–43]. When the partial pressure of gaseous oxygen drops, the oxygen may transfer from the oxide into the atmosphere following the reaction: $O^{2-} = O + V_a + 2e^-$, resulting in an anionic vacancy and two “extra” electrons (Fig. 3) formed in the oxide. The latter occur because the oxygen cannot take away from the oxide the metal atom electrons that it caught, as this would break the balance between the positive and negative charges within the oxide. Newly formed charged anionic vacancies, or

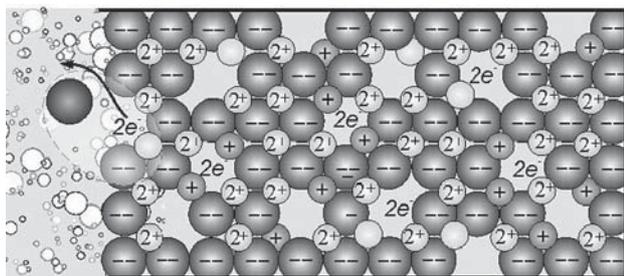


Fig. 3. Pseudoliquid state of oxide at low P_{O_2} and high temperature

F-centres [42] (from German *Farben* — colour), can even be visible as oxides change colour.

The mobility of ions should be consistent with the changing concentration of anionic vacancies. For example, it is a well-known fact that in the case of corundum baking the oxygen diffusion coefficient exceeds the one observed at normal temperature minimum by 10 orders and is close to the oxygen diffusion coefficient observed in liquids [44]. At a low partial pressure of oxygen and a high temperature, the total concentration of anionic vacancies in solid oxides can reach such values that would make mass transfer even more efficient than in a molten oxide [45]. Such state in which the lattice is still stable due to cation bonding and, due to a great number of anionic vacancies, the anionic diffusion rate reaches the one observed in a melt is referred to as pseudoliquid (see Fig. 3) [45, 46]. A pseudoliquid state occurs when at least one anion is missing in the immediate surroundings of each anion. Considering that in closest packing each ion has 12 neighbouring ions, for a pseudoliquid state to occur the anionic sublattice should have approximately 8% of vacant nodes.

Transformation of the Oxide Crystal Lattice into the Metal Lattice

The results of the experiments that looked at the solid-phase reduction of various metals contained in low-grade and complex ores, as well as the analysis and summarization of the findings by other authors accounting for the chemistry and physics of defective crystals and quantum chemistry [39–43] served as the basis for substantiating the metal reduction theory based on electron phenomena [47–53]. The main point of the theory is that the chemical reaction between the deoxidizer and oxide results in deox-

idation anionic vacancies charged with two electrons and appearing on the oxide surface in the oxygen sublattice.

At a high rate of vacancy generation, the vacancies tend to merge together creating an anionic void where they originally occurred, i.e. on the oxide surface. In that void, the vacancy electrons form a metallic bond without forming atoms first. Such scenario, when a metallic shell is formed on the oxide surface, can be observed, for example, in the reduction of iron contained in high-grade ores (Fig. 4, a). With a relatively low concentration of the metallic cations in complex oxides or in low-grade ores, due to the thermal motion of anions the vacancies tend to diffuse in the oxide following the anionic sublattice shared by all the cations in the oxide. Vacancies can also go across the crystal boundaries.

When the cation sublattice contains cations of different metals having different Fermi levels, charged vacancies tend to accumulate in the areas with high concentrations of those cations the Fermi level of which is lower than the chemical potential of “free” electrons in the anionic vacancies. The accumulation of “free” electrons in the anionic void, which occurs when deoxidation and thermal anionic vacancies merge with impurity vacancies, induces a local restructuring of the cationic sublattice resulting in the formation of a metal phase from the cations with the lowest Fermi levels [54–58]. In this case, the metal phase is formed from the cations of a certain type within the initial oxide phase away from the oxide surface (Fig. 4, b).

Because the new phase, after it has just formed, is basically a defect of the initial crystal lattice, it does not create any thermodynamic problems attributed to the elastic strain of the initial phase lattice and interfacial tension, like it happens, for example, in crystal melting [59]. That’s why the growth of the new phase is only governed by the way the relevant cations originating from the neighbouring regions of the oxide phase and charged anionic vacancies resulting from the chemical reaction on the oxide surface flow to its surface. In this case the distribution density and the size of metal particles are dictated by how quickly the vacancies arrive from the surface and the cations arrive from the neighbouring regions of the oxide phase (Fig. 5).

During reduction of the polyvalent cations $Me^{3+...}Me^{6+}$, the oxide surface may experience a gradual saturation with vacancies, and the cation charge may gradually go down due to the electrons that escaped anions.

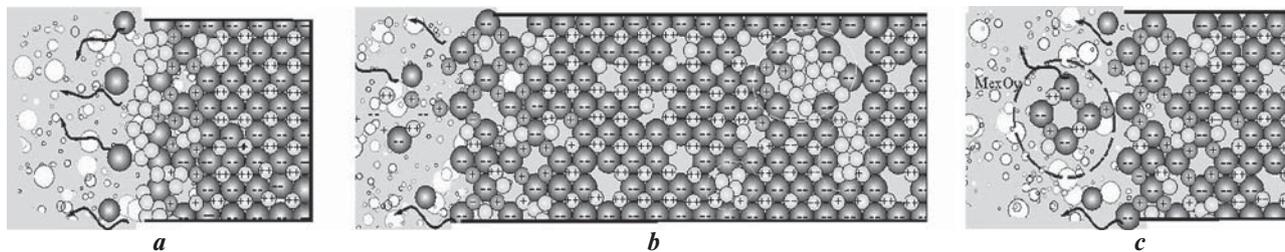


Fig. 4. Possible production of the metallic phase: on the oxide surface (a), in the oxide (b), sublimation of oxide fragments and transfer through the gas phase onto the deoxidizer surface

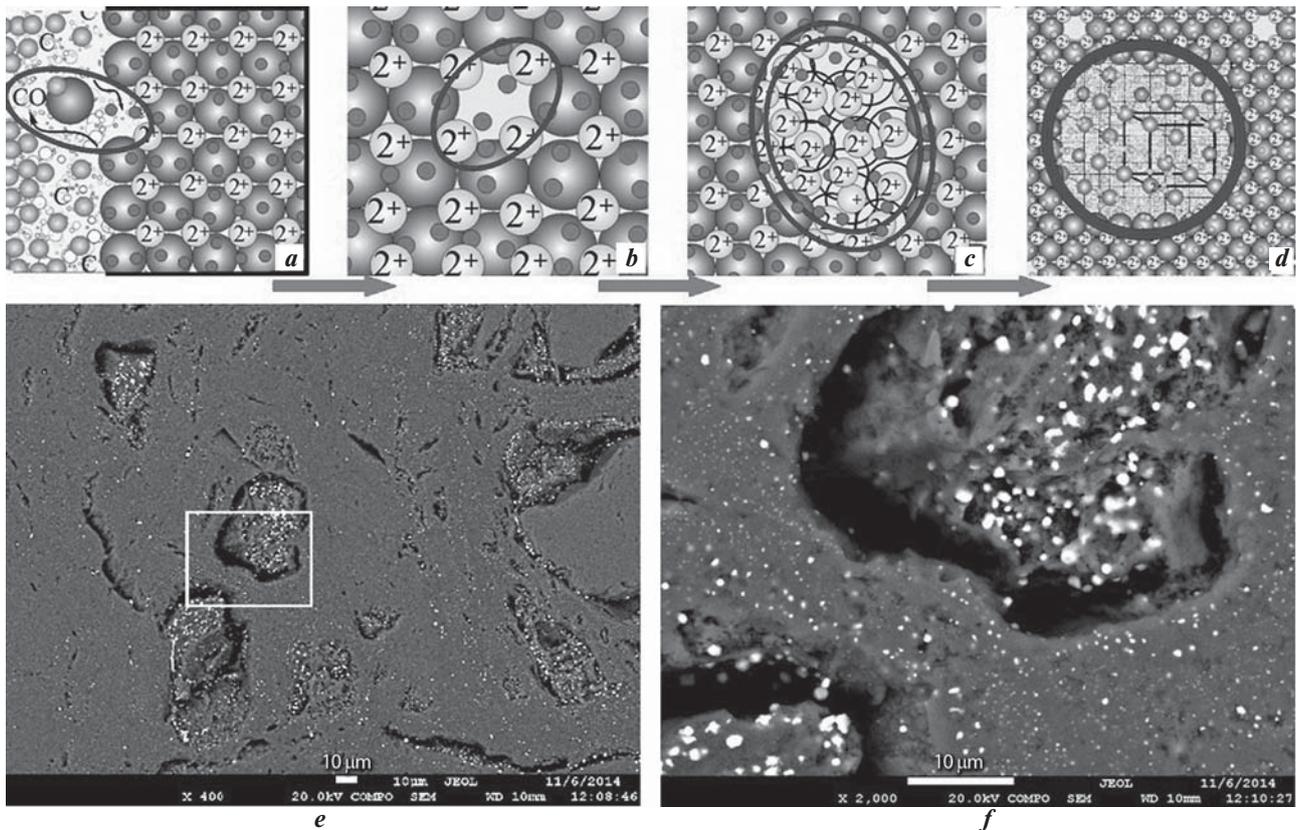


Fig. 5. Successive stages of formation (a–d) and pictures of iron particles (e, f) that precipitated in the oxide phase from the enstatite $(\text{Mg, Fe})\text{SiO}_3$ matrix and the forsterite $2(\text{Mg, Fe})\text{SiO}_4$ crystals having different concentrations of impurity iron cations

As a result, the bond between the cation and anionic nodes gradually becomes weaker. The active thermal motion of ions may cause breaking off of fragments of the lattice which have the same proportion between cations and anions as lower oxides (see Fig. 5, c). Such development is followed by a sublimation of lower oxides of different compositions, which is typical of oxides of such metals as aluminium, silicon, chromium, vanadium, molybdenum and other polyvalent metals [60, 61]. Thus, through condensation of sublimates in the deoxidizing environment, we were able to obtain, divide and thoroughly examine crystals of the following individual oxides: $\text{Al}_2\text{O}_{(3-x)}$, Al_3O_4 , AlO and Al_2O , which were formed by aluminium cations of all possible charges — from 1 to 3 (Fig. 6).

Reduction of Active Metals

As it was mentioned before, solid carbon in the form of coke is commonly used as a deoxidizer not only for iron in pig iron production but also for more active metals — such as chromium, manganese, silicon and oth-

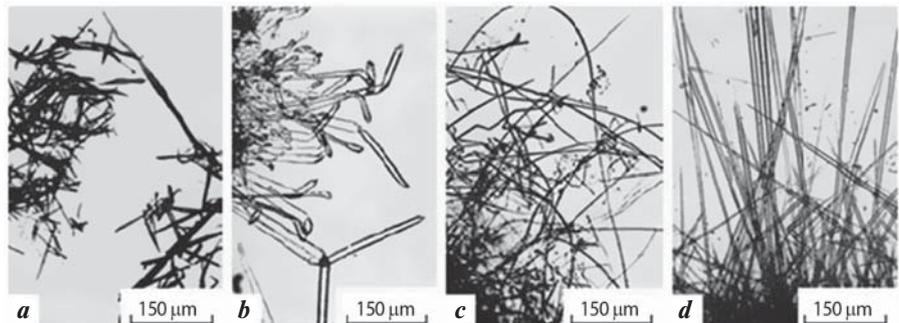


Fig. 6. Sublimate crystals — products of the deoxidizing sublimation of alumina: a — coloured crystals of non-stoichiometric alumina $\text{Al}_2\text{O}_{(3-x)}$; b — transparent idiomorphic crystals of spinel Al_3O_4 ; c — crystal whiskers of AlO ; d — transparent acicular crystals of Al_2O

ers — in the production of ferroalloys. However, the deoxidizing ability of carbon monoxide is rarely sufficient to deoxidize these metals. That's why in this case the so-called soot carbon, which can be the result of either the Boudouard reaction $2\text{CO} = \text{C}_{\text{ads}} + \text{CO}_2$ or the hydrocarbon dissociation reaction similar to $\text{CH}_2 = \text{C}_{\text{ads}} + \text{H}_2$, is considered to play the major role. The resultant atoms of solid carbon are believed to be adsorbed by the oxide surface and react with the oxide molecules following the laws of the adsorption-autocatalytic theory considered above [16–19, 62–65]. And even though the soot carbon reduction has never been observed in a real industrial set-

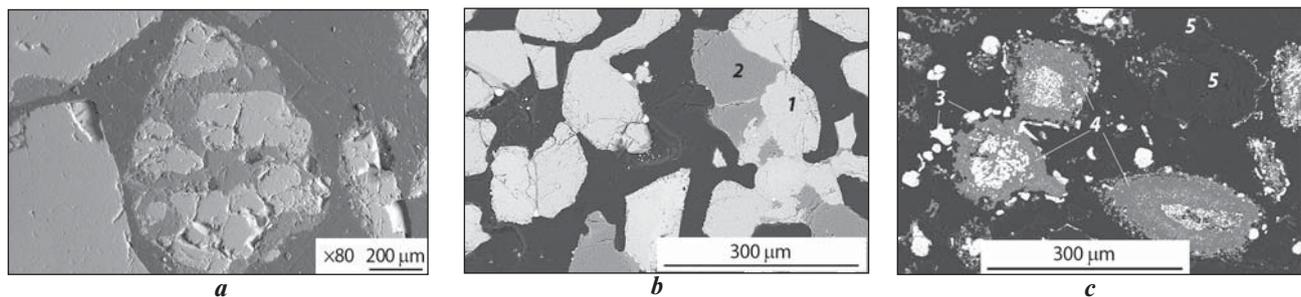


Fig. 7. Transformations in the ore concentrate (a) in the CO atmosphere (b) and the solid carbon mixture (c):
 1 — chromite grains; 2 — carburizing phase; 3 — carbide and silicide conglomerates; 4 — residual chromite in the form of carbon-free ferrochrome inside the remaining spinel $\text{MgO-MgAl}_2\text{O}_4$; 5 — graphite particles in the carbide shell

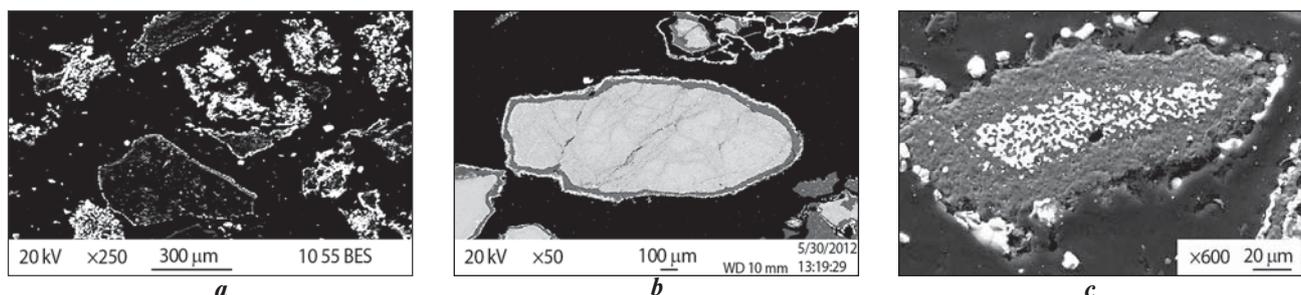


Fig. 8. Carbide shells forming and disintegrating on the surface of carbon (a) and ore concentrate (b) particles and a complete reduction of metals inside the remaining spinel $\text{MgO-MgAl}_2\text{O}_4$ following the disintegration of the shell (c)

ting, such interpretation can be quite possible as there are both carbon monoxides and hydrocarbons present in the furnace gases.

Specially organized laboratory experiments provided consistent proof that solid carbon can be used for the reduction of active metals. Two alumina crucibles with the Kempirsaysk chromite ore concentrate were simultaneously placed in a vertical tube furnace with a graphite heater made with graphite EAF electrodes. In one of the crucibles the ore was mixed with crushed graphite from the heater, while the other crucible only contained the concentrate. The furnace was kept covered, the temperature in the furnace was raised to 1,200...1,400 °C and maintained at that level for 1 to 4 hours.

Because the heater and the deoxidizer were made of graphite from graphitized electrodes, there was no risk they might produce volatile hydrocarbons, as during coking and electrode annealing and graphitization the material is subjected to a long (hundreds of hours) high-temperature (up to 3,000 °C) treatment. Because in a closed furnace with a graphite heater all oxygen is bound as carbon monoxide, the ore concentrate in both crucibles is influenced by the CO atmosphere, while in one of the crucibles it is also in contact with solid carbon.

Fig. 7 shows the results of an experiment in which the material was soaked for 1 hour at the temperature of 1,400 °C.

One can see that in the CO atmosphere separate metallic particles of iron formed in the chromite carburizing silicate phase, while chromites did not see any changes. In the concentrate-graphite mixture, iron and chromi-

um saw a complete reduction, and an alloy consisting of carbides and iron and chromium silicides formed on the surface of concentrate particles, while a carbon-free ferrochrome formed inside the particles.

These recent and earlier similar experiments [66–68] indicated that the initial reduction stage sees carbide shells forming on the particle surface in the mixture of solid carbon and ore concentrate. And while on the deoxidizer particles the shell is formed by the higher carbide Me_3C , it is a combination of carbides and silicides that builds a shell on the concentrate particles. Formation of such shells slows down and eventually stops the reduction process. And only if the shells start to melt and disintegrate, the reduction process can resume and come to a completion (**Fig. 8**).

The results of these experiments prove that carbon monoxide only acted as a deoxidizer for iron in the carburizing silicate phase, while it was solid carbon that deoxidized chromium and iron of the chromites. The carbide shells forming on solid reagents indicate not only that oxides transfer to the carbon surface but that there is a counter transfer of carbon to the oxide surface. This mutual counter transfer could be referred to the contact between the solid reagents. But it could hardly be possible that such contact led to the formation of shells that perfectly matched the surface profile of the particles. The entire surface of the particles could only be equally accessible to the counterflows of the matter due to mass transfer through the gas phase, which takes place in the reagent mixture. Consequently, a contactless interaction between solid reagents takes place in the mixture result-

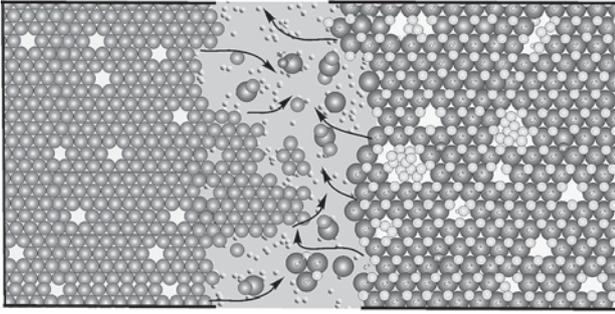


Fig. 9. Electron and mass transfer in the plasma between solid deoxidizer and oxide

ing in a chemical reaction between the deoxidizer and the oxide, charged anionic vacancies formed in the oxide, the latter's diffusion through the oxide phase, and the reduction and separation of metals in the oxide phase.

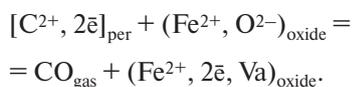
Considering the conditions found in the thin gas gap between the solid reagents (primarily, the temperature), they do not have to be in contact with each other to enable these processes. When the temperature exceeds 1,000 °C, a low-temperature plasma forms at the surface of solid phases, which consists of electrons, ions, molecules and their associations. Plasma is visually detectable as surface glow of hot bodies, which is the result of electron remission.

The impulse to plasma formation is delivered by thermionic emission of electrons from the carbon surface, the quantitative description of which is provided by the Richardson–Dushman equation:

$$I_0 = AT^2 \exp(-\Phi/kT),$$

where A — coefficient determined by the surface state; Φ — electronic work function; k — Boltzmann constant [69–73].

The surface of any hot body can experience thermionic emission. But in this case the emission from the deoxidizer surface dominates as they are the deoxidizer's peripheral electrons that have weaker bonds with the atomic nucleus. As a result of emission, electron gas occurs at the surface of the solid carbon. The emitted deoxidizer electrons are attracted by more electropositive metal cations and form bonds with the oxide phase cations thus replacing the weaker cation-anion bonds in the oxide and facilitating the removal of the oxygen anion from the oxide lattice following the reaction:



With the gas gap between ions of the solid reagents being small, Coulomb interaction leads to not just separate ions but also fragments of the crystal lattices with not fully compensated charges breaking off the oxide and deoxidizer surfaces (see Fig. 4, *c* and Fig. 9).

Occurrence of such structures of one reagent on the surface of the other reagent leads to carbide formation,

contaminates the reagents' surfaces, impacts the electron-ion exchange rate, and, after solid carbide shells have formed, the reduction halts. When solid shells are destroyed — in particular, through temperature rise — the process resumes.

Electron-Ion Exchange in Blast and Ore Thermal Furnaces

Reduction units originated as and throughout their evolution have been high-temperature machines. Every rise of the fuel combustion temperature would mark a milestone in metallurgy. The accumulated experience of many centuries have turned the blast furnace into one of the most high-temperature thermal units that burns fuel. Even today they keep looking for ways to further raise the temperature in the blast furnace in order to further enhance the unit's performance [6, 20, 21].

It appears that the projected effect of a higher operating temperature makes one overlook the obvious relationship between the operating temperature and the development of reduction processes. In fact, since the very first time humans produced metal reduction has always taken place in plasma — i.e. ionized gas. Flame that occurs when fuel is burning (even just in a camp fire) is basically plasma, even if it is not highly ionized. And any rise in the gas temperature increases the degree of its ionization. The thermal ionization degree of an x gas (i.e. a ratio of the number of ionized molecules to the total number of molecules before ionization in a unit of volume) is determined with the Saha equation [72, 73], the simplified form of which [73] is given below:

$$x^2 / (1 - x^2) = (B/P) T^{2.5} \exp[-(W/kT)],$$

where B — coefficient; P — gas pressure, Pa; T — temperature, K; W — atomic ionization energy; k — Boltzmann constant.

One can see that both the thermionic emission from the surface of hot bodies and the thermal ionization of gases intensify almost equally (exponentially) as the temperature rises, thus contributing to the generation of plasma and intensification of reduction-oxidation reactions.

A truly revolutionary breakthrough in the history of the reduction technology happened when they managed to raise the temperature in the Catalan hearth to ~1,300 °C, i.e. to the level which would melt the carbide shells at the surface of iron ore producing liquid pig iron. As the pig iron would flow down, the ore surface got rid of the shell that would impede reduction. As the oxide surface was free, the reduction process transformed into a kinetic interaction between the reagents' ions in the gas plasma leading to a drastic boost in the process performance [74].

The hearth temperature in modern blast furnaces exceeds 2,000 °C, i.e. approximates $2.5 \cdot 10^3$ K (Fig. 10), whereas in ore thermal furnaces it can even reach

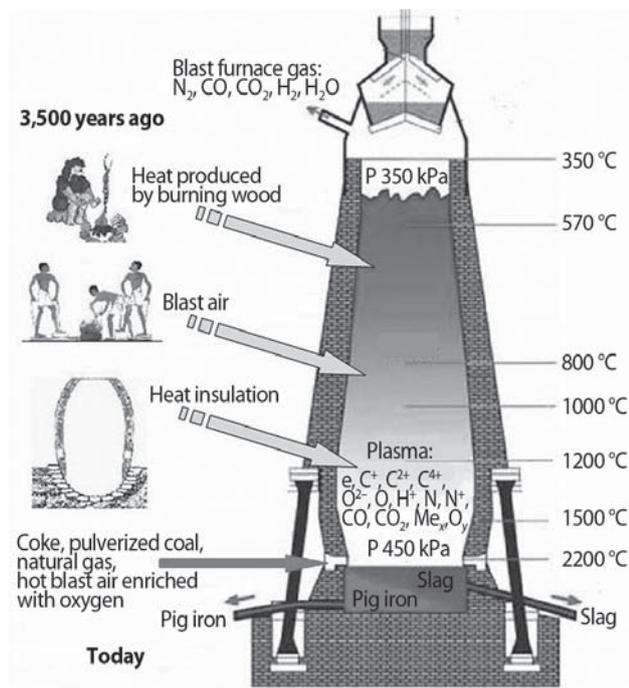


Fig. 10. How the thermal ionization of gases was raised in reduction units over time

$\sim 10^4$ K. This is the temperature range in which gas molecules reach a significant thermal ionization degree [72]. Besides, all reduction units offer a good environment for the thermionic emission from the surface of liquid and solid metal, hot burden (especially coke), as well as lime and fluxed sinter, which contain easily ionizable calcium. In the bulk of the burden, as well as in pellets and briquettes, which are used in the production of direct-reduced iron [75–78], because the gap between the solid reagents' surfaces is very small, the emitted electrons bridge the gas gap ensuring an electron-ion exchange between the reagents.

Hence, modern blast and ore thermal furnaces are, in terms of the reduction processes that take place in them, plasma units having extremely powerful thermal plasma generators in the form of oxygen tuyeres in blast furnaces and electric arcs in ferroalloy furnaces. High gas pressure in the furnaces increases the concentration of particles in plasma leading to a higher frequency of collision between ions, atoms and molecules and more intense reactions between them. As the plasma rises in the furnace shaft, it cools down, which results in more intense recombination processes and reduction-oxidation reactions in the gas phase.

The electron reduction mechanism described above provides a common ground for explaining all the known instances of deoxidizing of any metals using any deoxidizers in any conditions, even the production of aluminium through electrolysis [79]. And there is no need to involve any supporting theories, such as sequential reduction, adsorption-catalytic theory, diffusion-kinetic theory or others.

Conclusions

1. The basic theses of the current reduction theory are based on atomic-molecular views and define reduction as an exchange of oxygen atoms between oxide molecules and deoxidizer. Such theses are in contradiction with the current knowledge about the structure of solid bodies as there are no molecules or atoms in either oxides or metals.

2. Reduction is not about the removal of oxygen atoms but rather about building metallic bonds between the cations of the oxide crystal lattice through the sharing of “extra” electrons. What produces “extra” electrons is the physical and chemical processes that take place in plasma, as well as at the oxide and deoxidizer surfaces which are not washed with plasma.

3. Plasma in reduction units is the result of the thermal ionization of gases and the thermionic emission from the surface of the metal and burden materials, which predominantly include a solid deoxidizer and lime.

4. “Extra” electrons in oxides appear and co-exist with anionic vacancies simply resultant from the extraction of oxygen from the oxide lattice induced by the deoxidizer and (or) the temperature. In a deoxidizing environment, the anionic sublattice, common for the cations of all metals, is a solution of anionic vacancies and “extra” electrons.

5. Anionic vacancies merge together and metals separate in the oxide where there are groups of cations the Fermi energy of which is below the chemical potential of “extra” electrons. When extracting metals from high-grade and single-mineral ores, vacancies merge together and metallic phases occur at the oxide surface. In this case a metallic (carbide) shell is formed at the oxide surface impeding the reduction process. Reduction resumes after such shells are destroyed (when they melt and flow away).

6. The metallic phase forms in the oxide skipping the atom production stage, i.e. as a result of metallic bonds occurring between the closest cations of the oxide in an anionic void. The latter occurs when anionic vacancies merge together. There is enough energy in the anionic void to support nucleation.

7. In a deoxidizing environment, a metallic nucleus of any size cannot dissolve in the oxide. It is stable because the metallic bond can only become an ionic bond if there is additional oxygen supplied.

8. The reduction process enters the oxide very fast. This happens not due to atomic or ionic diffusion, but rather due to the motion of vacancies and electrons through the anionic sublattice shared by all the cations. During reduction of polyvalent cations, weaker bonds between partially reduced cations can cause sublimation of the lattice's fragments that have the same composition as the lower oxides of changing compositions.

9. The electron mechanism of oxide-to-metal transformation encompasses particular reduction patterns typical of various metals independent of the properties of oxides, deoxidizer or the process conditions. This is why this mechanism can fairly be considered as providing a universal description of the reduction process.

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