SELECTIVE EXTRACTION OF METALS FROM COMPLEX ORES

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ABSTRACT

The depletion of high-quality ore deposits makes it necessary to develop technologies of processing of poor or complex ores such as sideroplezite, titanomagnetites, etc. Processing them in a blast furnace or in well-known alternatives (Corex, Midrex, HYLL, Finemet, ITMk3, etc.) is possible in limited quantities only, and these ores are used only as an addition to the traditional iron-containing raw materials.

The principles of selective reduction and extraction of iron from lean and complex ores without melting have been developed. The iron is reduced directly inside the lattice of complex oxides at a relatively low temperature (1100...1250°C), forming metallic globules. As a result, two products have been obtained: metallic iron and an oxide residue of unreduced metals. E.g., metallic iron and an oxide phase rich in titanium have been obtained from the titanomagnetite ore. The residue can later be used as a high-titania concentrate.

1. INTRODUCTION

Reduction of metals from crystalline oxides is one of the most important processes of metallurgy. The process precedes pig iron and ferroalloys melting and occurs during agglomeration; it is used to obtain metallized briquettes and pellets; it is applied during other ore metallization processes. However, despite the obvious practical significance of solid-phase reactions of reduction, they still form an under-researched area. Thus, the rate of metals reduction observed in practice when reduced from solid oxides by solid carbon at the same temperature is disproportionately higher than the oxidation rate, and does not correspond either to the extremely small contact area of solid materials or the experimentally determined rate of diffusion of the reactants in the solids. Therefrom in 1885 L. Gruner suggested a two-stage scheme of direct reduction, developed in later works by I. Sokolov, A. Baikov, M.A. Pavlov, and others.

According to this scheme, shared by the majority of modern researchers, the kinetic mismatch of reduction is overridden by carbon participation in the gaseous form of carbon monoxide, which is formed by oxidation of solid carbon, interacting directly with the metal oxide. Therefore, the adsorption-catalytic put forward by G.I. Chufarov, complemented by the kinetic theory of diffusion of S.T. Rostovtsev, are commonly used to explain the reduction of metals by solid carbon. In cases where reduction could not be explained by the participation of CO, the role of reactant gas is allotted to various compounds, often exotic, the presence of which in small amounts is possible in certain circumstances. The role of reactant gas may also be assigned to reduced oxides or lower oxides vapors transferring reducible components to the surface of the solid reductant.

However, most of the solid reduction mechanism models, an overview of which can be found in [1-2], to name a few, only consider the acts of reduction process external to the reduced object: a way of delivering reagents to the reaction surface, a type of transferring reagent, an agent directly acting as a reductant, etc. It is therefore assumed that the reducing agent oxidation and metal reduction take place on the surface of a contact, and the scheme of delivering reagents to the reacting surface in certain conditions is identified with the reduction mechanism. This results in an idea of multiple mechanisms of carbothermal reduction, and author even conclude that it is impractical to search for a common approach to the mechanism description [3].

Moreover, the adsorption and catalytic and other reduction schemes are based on the fact that reduction is removing oxygen from the ore. As a result, phrases like “oxide reduction” or “ore reduction” are often used in educational, scientific, and technical literature, and the processes and machines for extracting metal from the ore focused on “eliquation” of metals. The energy costs caused by the need to melt not only the ore components, but also a large amount of ballast additives added to form a slag with the necessary set of properties are therefore significant in smelting processes.

It should also be noted that modern technologies and machines for extracting iron from ore have historically focused on the processing of iron-rich monometallic ores. At the same time, involving the poor (siderite) and complex (particularly titanium) magnetite ores in processing requires significant investments with regard to their treatment, although they may ensure the metallurgical complex operational stability for decades. Even after complicated treatment they can only be used in blast furnaces in limited quantities as an additive to traditional raw materials.

It seems reasonable to suggest that the attempts of complex iron ore processing have been not very successful so far because they suggest including a new raw material in the traditional technological processes. This is done, as a rule, basing on the theoretical concepts of iron reduction mechanism that also emerged in relation to the processes of its extraction from rich ores. However, the extraction of iron from complex ores, where it is located in the same crystal lattice as other metals, irreducible in a blast furnace, has its own characteristics, the identification of which will not only provide a rational technological scheme for complex ores processing, but should also help clarify the reduction mechanism in general.

At this point it should be noted that the most important part of the solid phase reduction mechanism, precisely the changes in the crystal lattice of the oxide and its transformation into the crystal lattice of the metal, actually lie outside the scope of research. We are of the opinion, however, that this is the essence of the reduction process, without which is impossible to imagine a reduction mechanism in general. As rightfully put forward in [4], “the mechanism of chemical processes could be understood only on the basis of physical theories that describe the motion of the reacting molecules and electrons, carried out an act of chemical reaction.” The studies [5-15] we conducted in recent years basing on the new features of instrumental research of intermediate reduction products and with regard to the known solid state physics concepts relating to defects in real crystals should largely help close this gap.

2. EXPERIMENTAL

In complex ores iron is located in oxides in a form of chemical compounds or in solid solution with oxides of harder reducible metals: magnesium, chromium, or titanium (figure 1). Ore grains in disseminated ores are also separated by gangue material layers, mainly by silicates of different composition.

In such ores a direct contact of reducing cations with the reducing agent (reductant) during solid state reduction can only play a minor role, since most of reductable cations are separated from the reductant by irreducible metals compounds like silicon, aluminum, and magnesium.

Experiments with different ores show that only in one case no traces of reduction by CO gas were found, namely in chromite ore. At the same time, even in the case of the same ore contact with condensed reductants (carbon or silicon) iron and chromium are reduced fairly quickly. In every other type of ore iron was reduced by each of the tested reductants.

Regardless of the reductant type and aggregation state, allocations of reduced metals are found not only on the surface, but also deep in the ore pieces. At the same time, the condensed products of reductant oxidation (e.g. silicon dioxide) are on the surface of a piece of ore. This indicates that the chemical reaction between the reducing oxide, including reductant oxidation and reduction of metal, is spatially divided: the reducing agent oxidation and its oxidation products formation occur on the contact surface (a reductant contacting with a piece of ore), whereas metal forms pieces and grains. It should be noted that in ingrained ores the reduction process spreads most quickly from the surface deeper in a piece along the veins of silicate phases (figure 2). And the bigger the ramifications of the silicate viens, the faster the reductive process spreads.

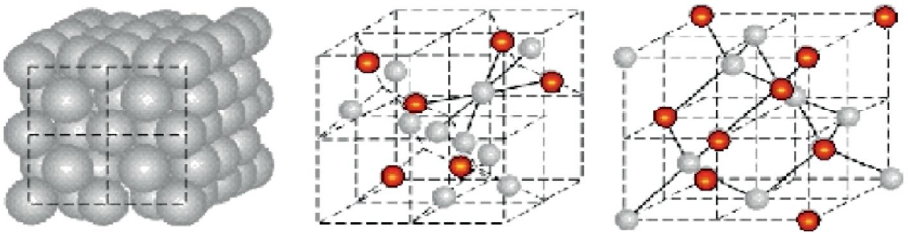
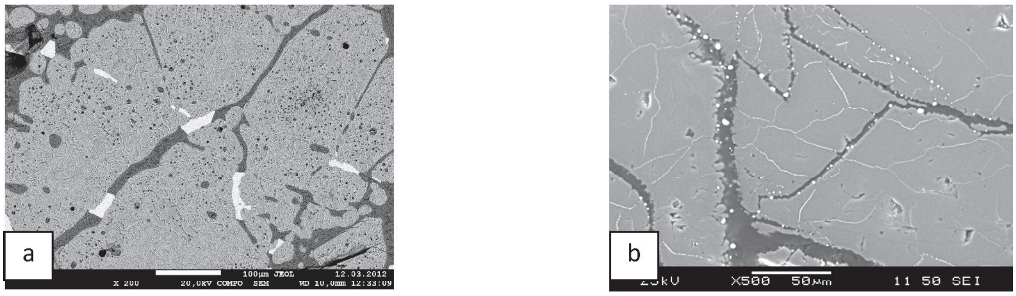


Figure 1: The complex chromite spinel crystal lattice $(Mg^{2+},Fe^{2+})[Fe^{3+},Al^{3+},Cr^{3+}]O_4$: close packing of anions (a), double-charged cations in the tetra- (b) and triply charged cations (c) in the anion sublattice. Reducible cations of iron and chromium are blackened



a) Titanomagnetite

b) ingrained chromite

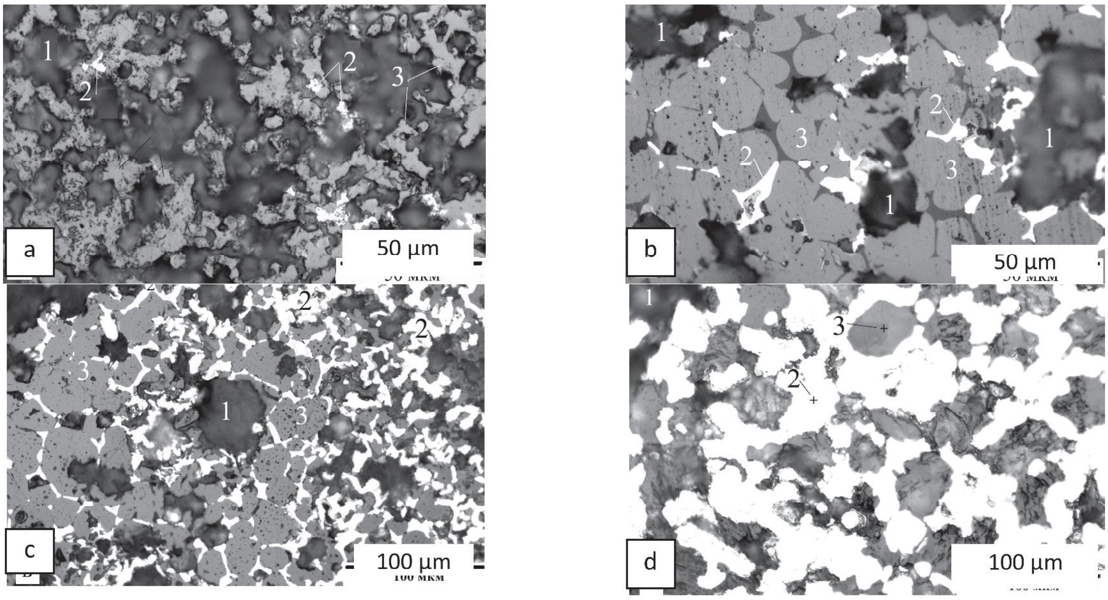
Figure 2: Expansion of the reduction process through the silicate phase veins deep into grains

We should specifically note that the precipitation of the metal phase is not linked to the pores in the ore material. Even in extremely porous lumps like siderite ores, once carbonate is decomposed and carbon dioxide is removed, metal precipitation is by no means associated with pores. Moreover, with the development of the reduction process the size and number of pores are decreased, and the pores disappear as the process is completed (figure 3).

It should also be noted that although all the experiments are carried out at a temperature well below the melting point of iron and oxide phase, the shape of the metal precipitates indicates at their almost unhindered growth. Metal particles in most cases get a round shape (as if melted), and sometimes, in case of a slow reduction, a clear faceted crystal shape that even show traces of growth face on its surface (figure 4). Free crystal growth occurs only inside the oxide phase that forms a crystal, while the surface of the crystal adjacent to the oxide phase not involved in the reduction process experiences resistance and "bypasses" a phase.

3. THEORETICAL ANALYSIS OF RESULTS

Contrary to a popular belief, the nature of reduction is not the removal of oxygen from oxides, but returning lost electrons localized near the oxygen ions in the crystal lattice of oxides to the cations of oxidized metals [16]. Essential for the reduction process is therefore not the MgO + C = Me + CO reaction, but the $Me2^{+} + 2e^{-} = Me^{0}$ reaction, which implies the electrochemical nature of the process, shows that the spatial separation of the reactions of metal reduction and oxidation of the reducing agent is feasible and that the electrical short circuit between the oxidant and reductant by the flow of electrons is possible. This shows the possibility of reducing metals surrounded by oxygen anions, i.e, inside the oxide (and the reduction can occur at a specific point in the oxide volume without transferring reagents to that point). The origin of electrons, whether they are picked out from ore oxygen, borrowed from the carbon or other reductant, or taken from the electric circuit, is generally irrelevant for the process.



1 – pores, 2 – metal (98,67% Fe; 1,43% Mn, analysis at poing 2 pos. d), 3 – oxide phase (90,12% MgO; 6,91% MnO; 3,97% FeO, analysis at point 3 pos. d)

Figure 3: The sequence (a – d) of precipitation of metal phase inside the porous siderite ore: inside ore

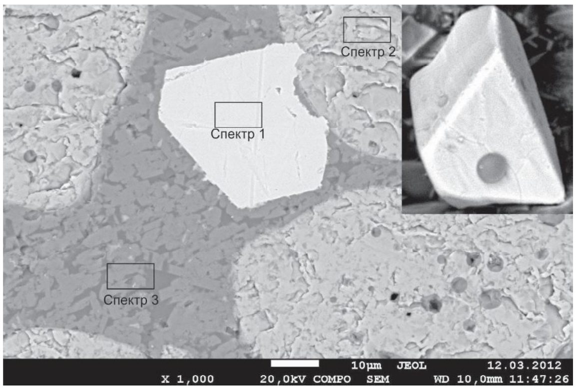


Figure 4: Formation of euhedral crystals of iron during slow reduction

Therefore, to form a metallic phase in the volume of an ore or in a separate ore grain, we do not need to transfer a reducing agent or even cations of metal reduced on the surface, nor do we need to evacuate the reaction product in the form of CO_2. "Extra" electrons that appear here and can be localized by the closest cations are the only necessary condition for the process to result in a metal atom.

Basing thereof, "extra" electrons and oxygen anions moving in the oxide crystal lattice were analyzed to determine the reduction conditions.

Conditions of particle diffusion and electric charge and mass transfer differ for a crystal lattice of an oxide and a metal lattice. This is due to the fact that, unlike metals, an oxide lattice is formed by ions with opposite charges that are arranged in a certain order. In an oxide lattice all electrical charges are compensated both in a general and in any particular volume. In addition, inside the oxide lattice there are no free charge carriers (free electrons), and a large band gap (5 ... 10 eV) makes it practically impossible for free electrons to appear due to thermal excitation, since, according to [17], in the band gap of more than 2 eV the probability of electrons thermal shift to the conduction band is vanishingly small at all available temperatures. Even at a decomposition temperature the number of electrons that could be thrown into the oxides conduction band is much lower than the number of electrons necessary for observed reactions speed [18]. Therefore, the transfer of charge (electrical conductivity) in oxides may be caused solely by ionic displacements.

Movement of cations and anions (diffusion) in the oxide lattice should follow other, more diverse and complex, trajectories compared with the movement of cations in the metal lattice. When analyzing the particles and charges movement conditions, it is therefore necessary to consider not only the size, but also the charge of the particles, as well as the structure of the electric field. With no defects detected in the oxide lattice, diffusion is hampered by densely packed anions and an electric charge of every particle. Even with a large number of cation vacancies (figure 1) the diffusing cation should slip through a narrow window between the anions. The size of such a window is significantly smaller than the size of the cation. The existence of anion vacancies, tjerefore, greatly facilitates anions and cations diffusion.

Normal diffusion of ions in stoichiometric oxides caused by thermal motion only contributes to cations or anions mixing (e.g., isotopes), but cannot lead to any ordered motion of single-type ions only, as this would violate the local balance of electric charges. Diffusion mixing, therefore, does not change either the local balance or the volume balance, and cannot be detected by measurement electrical conductivity. Isotopes mixing rate increases with heating; however, it does not affect the electric conductivity of stoichiometric oxides either, since equality of charges is observed in the oxide lattice in general and in any local volume in particular.

For the same reason, in ionic lattice only paired and therefore neutral thermal defects could be formed: interstitial ions and Frenkel vacancies or Schottky divacancies. Movement of ions via thermal divacancies is possible only in the form of a pair of neutral anion-cation complexes and does not lead to the displacement of charges either, cannot cause an outflow of oxygen, and has no effect on the oxide electrical conductivity. Stoichiometric oxides, therefore, are insulators when heated from absolute zero to a certain critical temperature.

Conductivity of stoichiometric oxides arises when impurities of heterovalent cations exist. Cations with lower charge (compared to crystal-forming cations) are electrostatically associated with anion vacancies, and can move in the oxide lattice in the form of a complex neutral defect "vacancy – low charge cation (cations)". Impurity complex defect displacement does not disturb the local charge balance either. However, since the complex charge is not equal to the charge of substituent crystal-forming cations and anions, charges are displaced in a macrovolume, so impurity complex defect displacement can be detected by the change in electrical, or so-called impurity, conductivity.

A similar conductivity mechanism is also typical of nonstoichiometric oxides. Zero balance of charges means that the mass deficit, such as a lack of anions, should not break the balance of charges. This means that an anion cannot just leave the oxide lattice: to compensate the charge it should leave either its own valence electrons or an oxidized reductant electrons in its position. These “extra” electrons are localized at the cation (cations) closest to the vacancy. Thus, in nonstoichiometric oxides there is also a complex “vacancy – differently charge cation (cations),” and such complex movement leads to a charge transfer similar to the impurity conductivity mechanism. Moving a complex (in fact, electrons only) must be counterbalanced by a flow of oxygen anions.

The source of “extra” electrons during the carbothermal reduction (direct or by a two-stage scheme - it is not essential) is the chemical reaction of oxygen withdrawal on the ore piece surface or on grain border. As a result of oxygen removing, in the anion sublattice on the surface of oxides the oxygen vacancy with two electrons is formed, that is a requirement for maintain equal positive and negative charges in the lattice as a whole and in the local volume near the vacancy. Oxide surface become fozy because of anion vacancies, and the "extra" electrons in the anion vacancies under the influence of positive cation charge are shifted and localized at the cations, decreasing their charge.

Difference of intrinsic conductivity of nonstoichiometric oxides from the impurity conductivity of stoichiometric oxides is that in nonstoichiometric oxides differently charged cations are being formed from one and the same chemical element, ie have the same electron affinity. That is why the movement of the complex does not require the physical displacement of the cation - moving of vacancy can be accompanied only by electron hopping from one cation to another. As a result, the mobility of such complex is high and intrinsic conductivity of nonstoichiometric oxides is higher then impurity conductivity at the same concentration of defects.

Nonstoichiometry of oxides caused by a change of oxidative potential of the environment, but there is needed relatively high speed of the oxygen movement in the oxide lattice for changing chemical composition of oxide with changing of potential. Therefore, a simply oxygen partial pressure changing is not enough to remove the oxygen from the lattice, ie, reduction of metal. Also need favorable kinetic conditions, namely sufficient ions mobility, which could be most easily achieved by heating. With temperature increasing, the mobility of the particles increases exponentially, respectively, according to the same law increases the concentration of thermal Schottky and Frenkel defects.

When heated to a certain critical temperature, the vacancy concentration reaches a value at which the immediate environment of each ion appears at least one vacancy. So at the close packing with coordination number 12, for the appearance in the immediate environment of each one of the anion of one anion vacancy it should be deficiency of 1/13 or about 8% of the anions in lattice. Exactly this number of anionic vacancies is achieved by doping solid state electrolite materials such as zirconia or β-alumina - oxides of four- or trivalent metal by oxides of one-, two- or triply charged elements. With such a concentration of vacancies solid electrolyte materials are quite stable, although they have a long chains of vacancies - the so-called conduction channels, and are characterized by high speed of the ions - superionic conductivity [19].

When the total concentration of heat, impurities and redox vacancies exceeds critical value the continuous chain of vacancies is forming, similar to conduction channels in laminated and framework structures. At this stage the crystalline oxides passes into a condition in which there is a fairly rigid framework based on cations, but anions like a liquid in sponge or electronic gas in the metal lattice, are able to relative easy moving. This condition can be described as a "pseudo-liquid". Oxides in pseudo-liquid state must have a high conductivity, comparable to the conductivity of superionic conductors.

The difference between high-temperature conductivity of oxides and superionic conductivity of solid electrolytes is in rapid mixing of particles and vacancies due to the increasing of thermal motion of the particles. So the conductivity channels in oxides are short-lived and have a random orientation. In the solid electrolite materials conductivity channels are formed by doping, and therefore stable over a wide temperature range.

The electrical resistance measurements of individual pure oxides and natural ores during heating [6], allowed to set the temperature of its transition into pseudo-liquid state. Heating of oxides with different redox potential of environment and in contact with different impurities confirms the effect of impurities and redox potential on the temperature of appearance of the conductivity and of the transition into the pseudo-liquid state.

It was found that the conductivity onset temperature is almost exactly corresponds to the theoretical Tamman temperature point [(0,5 ... 0,8) Tmelt.] - the temperature of hopping intensification of diffusion [10]. Comparison with published data [20] also showed that at this temperature begins noticeable interaction of oxides with carbon, ie at the same time it is a kinetic temperature of the beginning of metal reduction from its oxide. it was confirmed that this temperature decreases in case of contacting of oxides with carbon or with oxides, formed by cations with lower charges.

Transformation of the oxide lattice into the lattice of metal. From the above follows that when being heated at reducing conditions, the oxide crystal lattice become saturated by anion vacancies, some of which contain "extra" (excessive) electrons [6, 7]. Generator of such (reduction-type) vacancies is a reducing agent, which extracts oxygen out from the oxide lattice. Valence electrons from reductant are going to anion of oxygen and the previously localized at the anion electrons are confined in the oxide lattice by electric field and maintain a zero charge balance. "Extra" electrons are localizes in the nearest environment of vacancies on the cations, in the first order on cations with the highest possible electron affinity.

If all cations in the immediate surround have equal electron affinity and you move jobs, than electrons can migrate easily from one cation to another, accompanying vacancy from place of its appearance to the place of its sink. If, however, an impurity cation with high electron affinity occurs on the path of vacancy, then it captures electron(s) and strong bond between such cation and vacancy is arises. As a result, moving vacancy is lugging off such cation. The effect of "towing" an impurity ion by vacancies is known and even is used in the refining of semiconductor technology [21]. In our experiments, the results of such towing are shown in concentrating of Ni and Co in the metallic nuclei, originally dispersed in a matrix of chrome ore. [11].

In sink places, in the role of which acts oxide crystal lattice defects, vacansies disappears without traces and "extra" electrons, towed by vacancies remain localized on cations. Therefore, the vacancy sink places accumulate cations with gradually decreasing charge up to zero, which ultimately leads to the formation of the metallic nucleus in this volume.

But in sink places cations not only with zero charges could concentrates. It is quite plausible to form clustering structures with cations, which charges is higher then zero, but lower than that in original oxide. Such cluster structures of lower oxides can be formed and exist in the lattice of the initial oxide along with clusters of metal. In addition, in the structure of the initial oxide a large number of scattered anion vacancies, associated with cations having a reduced charge, still could be found at the same time. Therefore, under reducing conditions the ratio of differently charged metal cations continually changing. With that constantly also changes gross-composition of the initial oxide down to the metal, with not necessity for segregation (the formation of the phase interface) of all possible stable phases (daltonides). Thereby, the oxides during metal reduction process should be considered as compounds of variable composition - i.e. berthollides.

If the vacancies, formed on the surface of the ore have time to dissipate in the oxide lattice, then the metal nucleus precipitation take place inside the oxide lattice at a distance from the surface. Scattering condition for vacancies is its high mobility with a relatively low generation rate. It is realized in the case of reduction of metals by mild reducing agent at high temperature. The high concentration of defect complexes at the interaction surface and intensive thermal motion of particles in the oxide lattice can cause in this case, in addition, tear individual fragments off from oxide and its transition from the oxide into the gas phase, ie, sublimation. At that in the gas phase may be found fragments of different structures, the composition of which corresponds to intermediate reduction products. If the rate of vacancy production exceeds the rate of its dissipation in the lattice oxide, they merges in the same places where are they formed, ie on the interaction surface of oxide with reductant. So, in case of intensive reduction the layer of interaction products is forming at the interaction surface, hampering the further reduction process. In such a scenario evolution of the process leads to the frontal growth of reduction products layer, which is most frequently observed in the practice of obtaining ferrous metals.

4. CONCLUSIONS

1. Reduction - the electrochemical process that takes place according to the reaction $Me^{2+} + 2e^{-} = Me$. Its basis is returning of electrons, localized in the crystal lattice of oxides on the oxygen anions to the cations of metal.
2. For reduction is enough to decrease total oxygen concentration in the oxide lattice, at that the place of oxygen extraction from the oxide lattice and the place of formation of the metallic phase may not match. The method of oxigen extraction from the lattice and the origin of the electrons, needed for the reduction has no fundamental importance.
3. Dissemination of the reduction process in the oxide phase volume is going by moving of anion vacancies, the motion of which is accompanied by a shift of "extra" electrons needed to restore the charges of cations. Motion of the vacancies caused by single ion jumps, so it can be done several times faster than diffusion of ions.
4. Anion vacancies involve in moving cations with highest electron affinity. Pair (neutral) thermal vacancies can move neutral atoms without upsetting the balance of the charges.
5. Rate of vacancy displacement and reduction process expansion in the oxide lattice increases with the rising concentration of vacancies. The highest degree of disorder in the ores at reduction temperature have silicate phases, in which along with the thermal and reducing vacancies are abundantly presents impurity vacancies, caused by the presence of cations with lower charge in the lattice of silicate phase. Veins of silicate phases are the distribution channels for the reduction process in ore lumps, which makes ores with veins of silicate phases "easily reducible".
6. Poor and complex ores are more "reducible" in comparison with the rich and monometallic, due to the presence in their structure oxides of hard reducible metals. This oxides does not allow form a massive metal shell on the surface, and promotes the reduction process on residual oxide phases into the volume of ore lump.
7. Precipitation of metal phase inside the solid oxide eliminates contact of metal with a reductant and helps to avoid carburization and pollution of metal by impurities.
8. Different cation to electron affinity allows selective metal reduction and to enrich the oxide phase by less reducible metals, that is, separate ore components without melting.
9. These features of selective reduction of metals in the crystal lattice of complex oxides can be the basis for the development of resources and energy saving technologies of metal selective extraction from poor and complex ores without melting the ore and with utilization of low-grade coal as an energy source and reducing agent

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