NEW FINDINGS IN RESEARCH OF SOLID PHASE REACTIONS IN CHROMITE ORE REDUCTION PROCESSES

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ABSTRACT

Reduction interactions in solid phases are widespread and occur in most complex metallurgical processes. Among these processes, reactions between oxides and carbon have a special importance.

The authors conducted experiments for comparison of reduction by different reducing agents of impregnated chromite ores, in which grains of the reducible chromite spinel are isolated from direct contact with the reducing agent by layers of non-ore material. The results of the experiments have revealed that the beginning of reduction is preceded by thermal and impurity order-disorder transformation of the oxide lattice whilst the transformation of the oxide lattice into the metal lattice takes place as a result of removal of oxygen anions from the zone of metal germ nucleation. Since anions are charge carriers, increase of their mobility can be monitored by changes in electrical conductivity of oxides. Respective measurements of electrical resistance of ores of different metals and a number of pure refractory oxides under heating have indicated that the beginning of reduction coincides with the time of drastic (tens of thousands times) increase of conductivity of the oxides. Besides, the temperature of the beginning of carbon-thermal reduction is in line with the Tammann temperature, i.e. the temperature of transition from the predominantly surface diffusion to volume diffusion.

Segregation of metals from the oxide lattice occurs as a result of merging of anion vacancies with defect electrons on defects of the oxide lattice. The transformation of the oxide lattice into the metal lattice requires a certain concentration of anion vacancies and inflow of electrons from the reducing agent to the site of metal segregation. Such inflow has no difficulties due to the mixed anion-electron nature of high-temperature conductivity of oxides. Thus, the reduction is not determined by oxygen diffusion, it is determined by oxygen vacancies diffusion whose speed exceeds the speed of oxygen diffusion by orders of magnitude. This determines that the kinetics of reduction considerably exceeds the kinetics of oxidation at similar temperatures since oxidation proceeds by means of mass transfer of oxygen through the layer of the generated oxide.

1. INTRODUCTION

Reduction interactions in solid phases occur in most complicated metallurgical processes. The pressing need to use ever poorer and complex ores, in particular impregnated chromite ores, requires new technological solutions based on clear understanding of the mechanism of metals reduction from oxides. It is considered that these processes are well studied.

However, the mechanism of reduction of impregnated ores cannot be explained by the widely recognized theories since ore grains cannot react directly with the reducing agent (in particular, with solid carbon) because of the insulating interlayer of the non-ore material. Attempts to substantiate the diffusion mechanism of reduction (oxidation) by diffusion of atoms of the reducing agent, or atoms of oxygen, through the insulating interlayer were undertaken in the 20s to 50s of the twentieth century by G. Tammann, C. Wagner, W. Schottky, G. von Hevesy, J.A. Hedvall, W. Jander, J. Anderson, J.O. Edström, F.D. Richardson, and others. As a result, the theory of order-disorder transformation of lattice was proposed by C. Wagner and W.

Schottky that allows to describe the processes of oxidation rather satisfactorily. However, theories that were plausible for oxidation processes failed to be true for reduction of oxides since reduction processes in most cases run much faster than processes of oxidation and faster than should be expected with the given ratios of diffusion in solid bodies.

The analysis of the recent works has shown that most researchers support the theory of so-called two-stage direct reduction proposed by L. Grüner in 1875. Inconsistent kinetics of reduction by solid carbon in this theory is usually explained by participation of an intermediate gas phase, i.e. carbon monoxide, which is continuously generated in oxidation of carbon and reduces the metal from the oxide. In such cases where it is impossible to explain reduction by the action of carbon monoxide, the role of gaseous reagent is attributed to fumes of oxides or fumes of lower oxides that appear as a result of dissociation of the initial oxide and transfer of the reducible component onto the surface of the solid reducing agent, where the direct reduction happens (Fig.1).

However, the theory of two-stage direct reduction does not explain the mechanism of reduction of impregnated ores and the mechanism of crystal chemistry transformations in the compact ore oxide that is being reduced, as with the presence (or formation as a result of reduction) of the insulating phase on the surface of solid oxide, transformation of the oxide lattice into metal lattice cannot occur without removal of oxygen from the oxide through the enclosing phase.

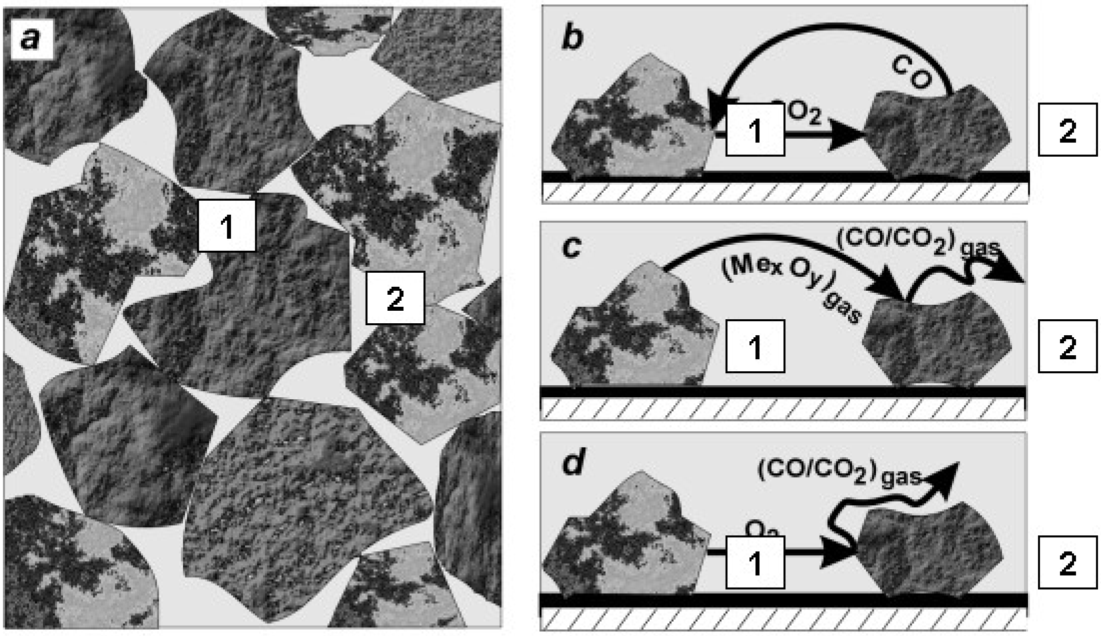

Figure 1. Pattern of solid phase carbon-thermal reduction: *a* - direct reduction by solid carbon, *b* - gasification of the reducing agent, *c* - gasification (evaporation) of oxide, *d* - dissociation of oxide.
1 – ore, 2 – carbon.

2. MAIN PART

2.1 Procedure of Experiments

Samples of two chromite ores differing in quantity and composition of the non-ore material containing ore grains were selected. The selected samples (one from each ore) were divided into several specimens. One specimen (from each ore) was exposed to petrographic and mineralogical analysis and the rest of the ore specimens were exposed to reduction heating. The experiments on solid phase reduction were conducted simultaneously on six specimens of two ore types, with comparison of their reduction by carbon monoxide, solid carbon, and silicon (Fig. 2) [1 and 2]. For this purpose, in three crucibles put one onto another (I - III), two specimens of two different ores were placed. In the first crucible, ore samples were exposed only to CO; in the second crucible, ore specimens were covered by graphite; in the third crucible, ore samples were covered by 75%Si-ferrosilicon powder. Experiments were conducted in a hermetic furnace with a graphite heater. The specimens in the furnace were heated up to 1300°C and kept in that state for 30, 180, and 420 minutes. After exposure, the furnace was switched off, the specimens being chilled together with the furnace, then they were taken out, cut into halves, and polished on the cut side. The polished sides were studied by mineralogical and petrographic methods. Qualitative and quantitative analyses of metal segregations and partially reduced grains of chromite spinel were conducted on X-ray Microanalyzer JEOL Superprobe 733.

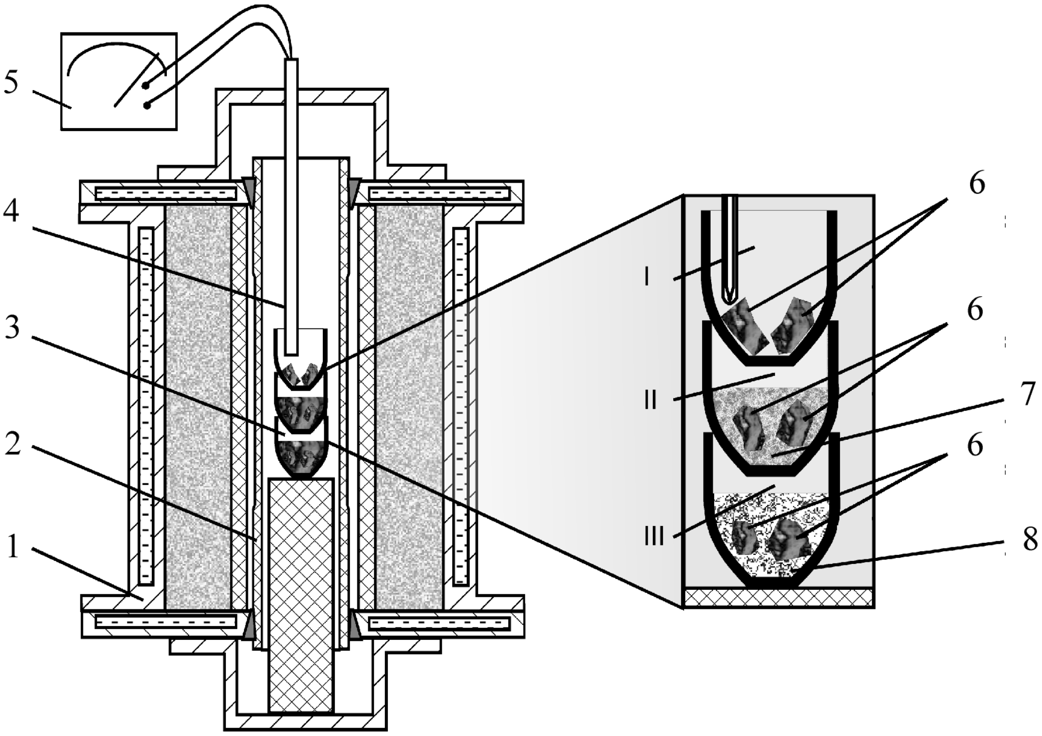

Figure 2. Design of experiment: 1 - electric resistance furnace, 2 - graphite heater, 3 - crucibles with specimens, 4 - thermocouple, 5 - potentiometer, 6 – ore specimens, 7 - graphite, 8 – ferrosilicon.

2.2 Results of Experiments

The initial ore contained "aged" cracked grains of complex chromite spinel (Fe, Mg, Ni, Co, Mn, Zn)O·(Fe, Cr, Al, Ti, V)$_2$O$_3$, enclosed in a shell of a hydrated silicate phase of the serpentine-chlorite group (Mg, Fe)$_{4-6}$(Si, Fe, Al)$_4$O$_{10}$(OH)$_8$ (Fig. 3, a). After exposure even for 420 minutes, no traces of interaction of ore grains with carbon monoxide were found, though the transformation of the non-ore phase (Fig. 3, b) was clearly apparent.

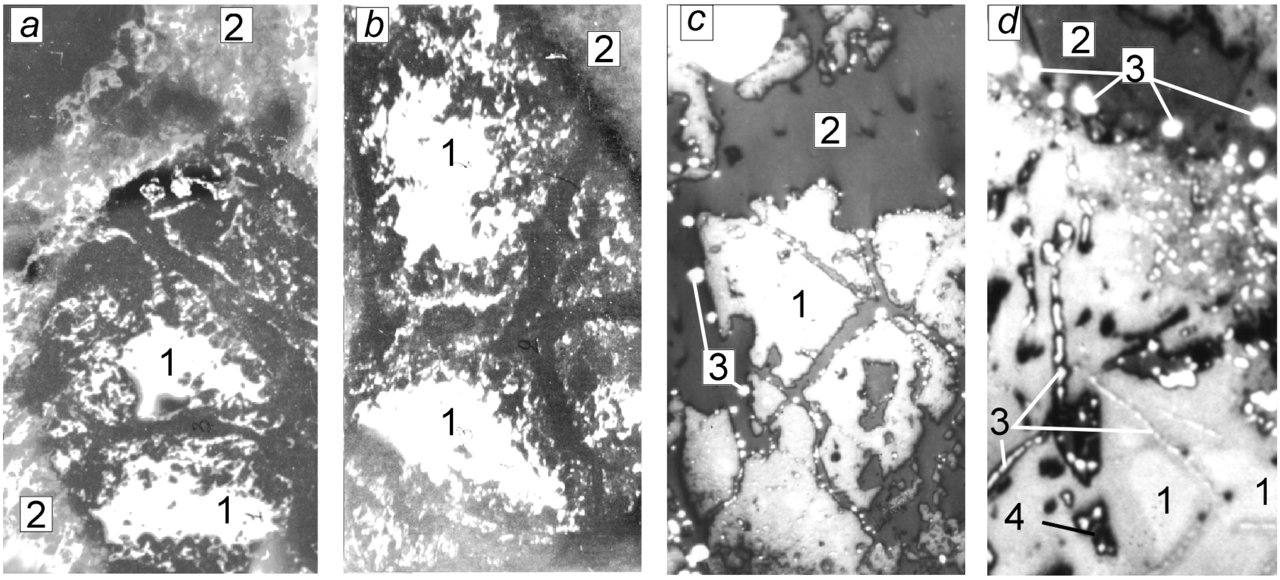

Figure 3. Photomicrographs of ore polished sections, x100 (d – x400). *a* - initial state, *b* - after exposure in CO, *c* and *d* - after exposure in contact with carbon. 1 - grain of spinel, 2 - silicate phase, 3 - metal, 4 - magnesia phase.

The ore grains practically had not changed: their shapes, reflection factor, and nature of secondary changes remained the same. In the non-ore material, dewatering and partial serpentine crystallization disorder happened. At the same time, in the specimens contacted with the solid reducing agents even for 30 minutes, significant changes of ore grains and considerably more drastic changes of the non-ore phase occurred (Fig. 3, c and d). The non-ore phase turned from amorphous fiber mass into a ductile vitreous mass that was easy to polish and interacted with ore grains ("wetting" of grains). In the thin layers between grains, the non-ore material lost crystallization to become cordierite $2MgO\cdot Al_2O_3\cdot 5SiO_2$, enstatite $(Mg,Fe)O\cdot SiO_2$, and glass. Specimens had a clearly expressed zonal structure: in the central part of samples the ore mineral was changed less than on the surface. The transformations in the ore mineral were identified mainly on the borders with the non-ore material. The borders between these components as compared to the initial state lost their separateness and jointing, and became smooth and polished easily. In the ore grains, the products of reduction, i.e. metal particles and magnesia phase (Fe, Mg)O, appeared.

The increase of exposure time up to 420 minutes boosted transformations. The ore pieces lost zonal structure. The quantity of the non-ore phase increased: near the surface of grains the large segregations of this phase occupy a larger area; in the direction of the centre of an ore piece, segregations became smaller and more separate. The new segregations of the non-ore light grey wustite phase include metal particles of different sizes. Spatially, the new segregations of metal and the non-ore phase were confined to cleavage planes and other defects of crystals of chromite spinel. The composition of chromite spinel also changed, colour change of grains in immersion preparations confirms that the grains of chromite spinel acquire a lighter colour: from dark-brownish to red-brownish, in thin layers, to yellow-brownish, and colourless veinlets and spots became apparent. In the non-ore material, the isomeric crystals of spinel $MgO\cdot Al_2O_3$, enstatite, or olivine $(Mg, Fe)O\cdot SiO_2$ became apparent, and the enclosing phase was glass.

2.3 Analysis of Experiments Results

It was found that at 1300°C metals from the complex chromite spinel were reduced only if there was a contact of ore with solid reducing agents. It is important that the segregations of metal particles in ore grains enclosed in the shell of the silicate non-ore phase $R_mO_n\cdot SiO_2$ (here R – Mg, Al, Fe) were located inside the ore grains and were confined to the crystallographic planes of the grain. It also should be noted that at the initial stage the metal phase is enriched with iron and incidental (impurity) metals (Ni, Co, V, Ti, etc.), and when the metal phase grows in size, the proportion of metals becomes close to the composition determined by the composition of the chromite spinel $(Fe, Mg, Ni, Co, Mn, Zn)O\cdot(Fe, Cr, Al, Ti, V)_2O_3$. Besides, notwithstanding the decrease of volume during transformation of oxide into metal, in the grains being reduced no porosity was found, and the sizes of ore grains and ore pieces decreased on the whole and the metal particles, as a rule, were enclosed by new formations of the R_mO_n phase. A similar pattern of distribution of metal particles in grains of iron ore and chromite ores, and also accelerated reduction of iron at the initial stage of reduction of chromite ore was repeatedly noted by other researchers as well [3-7].

Considering that during reduction the enclosing silicate phase was in a ductile state, tightly enveloping the ore grains, and was impenetrable for carbon, whilst the participation of carbon monoxide in reduction process is strongly negated by the results of the experiment, we may confidently conclude, that the conventional [8-10] equation of the chemical reaction of solid phase reduction of oxides by carbon with formation of metal follows as

$$Me_xO_{y(solid)} + yC_{(solid)} \rightarrow xMe_{(solid)} + yCO_{\ (gas)} \tag{1}$$

or with formation of carbide as:

$$Me_xO_{y(solid)} + (y+k)C_{(solid)} \rightarrow \chi Me_pC_{k/\chi(\ solid)} + yCO_{(gas)} \tag{1a}$$

does not reflect the essence of the process and place where it happens. It follows from such equations that the interaction of solid reagents is localized in a narrow contact zone between solid phases Me_xO_y and C, and the exclusive role is given to the area of their contact surface which is often referred to as the reaction surface. However, in reaction (1) four phases, i.e. three solid phases (Me_xO_y, C, Me) and one gaseous phase, take part. Four phases can have only one common point, and interactions (1, 1a) therefore should be localized not on the surface of contact of the two initial solid phases (reactants), but at the point of contact of four phases (both reactants and products).

However, it follows from the results of the experiments conducted that not less than six phases, i.e. 5 solid phases (spinel, carbon, silicate phase, metal and a high-magnesium phase remaining after reduction of complex spinel) and 1 gaseous phase, take part in the reaction (Fig. 4, a). Neither five, nor, the more so, six phases can simultaneously contact among themselves. Therefore this interaction should be considered as distributed in space and composed of several successive stages [11-13] that run on different borders and in the volume of different phases. It takes place in the volume of a system that includes as a minimum 7 phase-to-phase borders: two three-phase borders (lines), and five two-phase interfaces (Fig. 4, b). It follows from the above that the widespread opinion of the exclusive role of a surface area of contacting solid phases Me_xO_y - C is wrong.

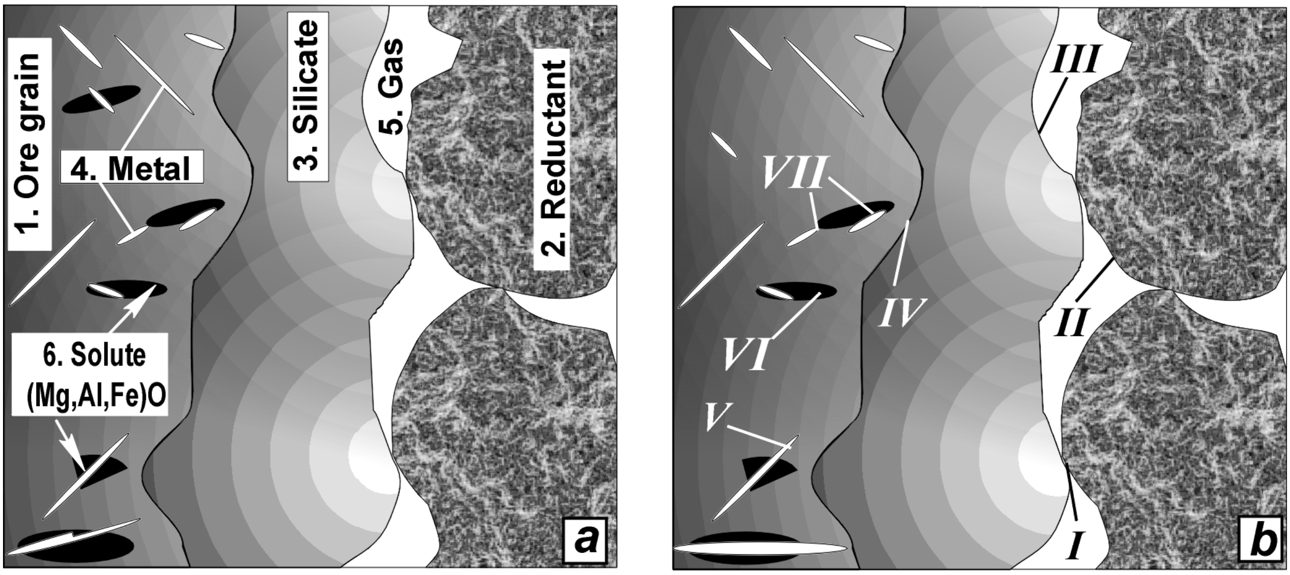

Figure 4. Phases participating in chemical reaction (*a*) and borders of interacting phases (*b*): I - border $R_mO_n{\cdot}SiO_2$ (solid) - C (solid) - gas; II - surface C (solid) - gas; III - surface $R_mO_n{\cdot}SiO_2$ (solid) - gas; IV - surface $R_mO_n{\cdot}SiO_2$ (solid) - Me_xO_y (solid); V - surface Me_xO_y (solid) - Me; VI - surface Me_xO_y (solid) - R_mO_n; VII - border Me_xO_y (solid) - Me - R_mO_n.

Border I. On the line of intersection of the three phases *reducing agent - silicate interlayer - gas*, oxidation of the reducing agent and removal of oxygen from the lattice of oxides of the silicate interlayer take place:

$$C_{(solid)} = C^{2+}_{(solid)} + 2e^- \tag{2}$$

$$C^{2+}_{(solid)} + O^{2-}_{(solid)} = CO_{(gas)} + \square_O \tag{3}$$

or, as overall reaction represented by:

$$C_{(solid)} + O^{2-}_{(solid)} = CO_{(gas)} + \square_O + 2e^- \tag{4}$$

where $\square_O$ is oxygen vacancy.

An important result of interaction at this phase-to-phase border is the formation of oxygen vacancies ($\square_O$) in the lattice of oxides and transition from the reducing agent to the oxides of two "free" ("defect") electrons.

Border II - III. With loss of contact between solid phases, the three-phase border $R_mO_n{\cdot}SiO_2$ (solid) - C (solid) - CO (gas) transforms into two two-phase surfaces C (solid) - gas (II) and $R_mO_n{\cdot}SiO_2$ (solid) - gas (III). Respectively, processes (2-4) are divided into several elementary steps that occur on these two-phase surfaces. On surface II (C $_{(solid)}$ - gas), the role of carbon as the reducing agent apparently contributes to decrease of the partial pressure of oxygen pO_2 in the vicinity of the ore surface:

$$O_{2(gas)} \rightarrow 2O_{(absorbed)} \tag{5}$$

$$2C_{(solid)} \rightarrow 2C^{2+}_{(solid)} + 4e^-_{(absorbed)} \tag{6}$$

$$2O_{(absorbed)} + 4e^{-}_{(\,absorbed)} \rightarrow 2O^{2-}_{(\,absorbed)} \tag{7}$$

$$2O^{2-}_{(\,absorbed)} + 2C^{2+}_{(\,solid)} \rightarrow 2CO_{(absorbed)} \tag{8}$$

$$2CO_{(absorbed)} \rightarrow 2CO_{(gas)} \tag{9}$$

On surface III (ore - gas), with decrease of pO_2, some of the oxygen anions should abandon the surface layer of oxides $R_mO_n{\cdot}SiO_2$ and convert to the gas phase:

$$2O^{2-}_{(solid)} \rightarrow 2O^{2-}_{(adsorbed)} \tag{10}$$

$$2O^{2-}_{(adsorbed)} \rightarrow O_{2(adsorbed)} + 2\square_{O} + 4e^{-} \tag{11}$$

$$O_{2(adsorbed)} \rightarrow O_{2(gas)} \tag{12}$$

Combining reactions (5-12), we have the following reaction:

$$2C_{(solid)} + 2O^{2-}_{(\,solid)} = 2CO_{(gas)} + 2\square_{O} + 4e^{-} \tag{13}$$

Comparison of reactions (4) and (13) testifies that the processes that run separately on surfaces II and III give the same result as direct interaction of the reducing agent with the ore in the presence of contact between them (I). Namely it results in appearance in the ore of oxides of oxygen vacancies and defect electrons. The difference consists only in the genesis of free electrons: in the direct interaction of solid reagents, the electron source is the reducing agent, and with loss of contact these electrons have to come off the oxygen anions during oxygen molecule formation at the oxide surface. Taking into consideration that oxygen has a higher relationship to the electron as compared to the reducing agent, the second way (dissociation) requires more energy and therefore should be hampered.

Border IV. The oxygen vacancies that appeared in the silicate interlayer and free (defect) electrons could remain close to the surface, which would lead to reduction of silicate cations, or they could dissipate in the volume of silicate. As no reduction of the silicate interlayer was found, we should make a conclusion about their sufficiently fast withdrawal from the surface to the depth of silicate. The sites of surface vacancies become occupied by anions that come from the subsurface layers, as a result of which the volume of the silicate becomes saturated with oxygen vacancies. It is unlikely that border IV prevents dissipation of vacancies in the volume of the ore piece. Since the chemical potential of oxygen is
$\mu_0 = \mu^0 + RT\, lnpO_2$,

then with the equal value of pO_2, the chemical potential of oxygen in the silicate phase and in the ore grain depends on the value of μ_0. This value determines the concentration of anion vacancies in contacting oxides $R_mO_n{\cdot}SiO_2$ and Me_xO_y. Under the influence of a difference in chemical potentials, the oxygen from the weaker oxides Me_xO_y of the ore grain passes to the silicate interlayer, and the ore grain becomes saturated with anion vacancies. Thus, the silicate interlayer functions as an oxygen-permeable membrane that conducts anions from relatively easily reducible impregnated oxides to the reducing agent [14, 15]. The anion vacancies and defect electrons move backwards into the ore grain through surface IV.

Borders V - VII. The appearance of anion vacancies and free electrons in oxides Me_xO_y does not immediately result in segregation of the metal phase. The removal of one oxygen anion from the oxide lattice is evidently not enough for transformation of the oxide lattice into the metal lattice. Therefore, reduction of oxide can be represented as the following succession of transformations:

$Me_xO_y \rightarrow Me_xO_{(y-1)}\square \rightarrow Me_xO_{(y-2)}\square_2 \rightarrow Me_xO_{(y-3)}\square_3 \rightarrow ....$,

which results in accumulation of anion vacancies and free electrons in the volume of the oxides. However, they distribute in the volume of the oxides non-uniformly - the sites of accumulation ("drains") of the vacancies are spot (incidental cations), linear (dislocations), flat (borders of crystalline blocks), and volumetric (inclusions of another phase) defects of the crystalline structure.

The predominantly ionic nature of the chemical bond in oxides requires fulfilment of the condition of electrical neutrality in each local micro-volume of the crystal. It follows from the above that the anion vacancies and electrons generated under the influence of the reducing agent can move in the oxide lattice in the form of "F-centres" (Farbecenter), i.e. "anionic vacancy - free electrons" complexes [16-18] (Fig. 5, a). Any other combination of atom and electron defects does not fulfil this condition. The accumulation of anion vacancies and free electrons at the sites of "drains" result in formation of the “cavity phase" in the anion sub-lattice. However, the "cavity" of the anion sub-lattice contains cations of metals of the cation sub-lattice. Capturing of the defect electrons by cations causes appearance of a metallic binding and re-building of the cation sub-lattice of the oxide into the lattice of metal (Fig. 5, b). The segregations of the metal phase inside the oxide grain in this case are connected with lattice defects and exposed of them (Fig. 5, c).

Thus, reduction of metals from oxides may be represented as the succession of transformations: *anion vacancy (colouring centre) → double vacancy → triple vacancy → ... → vacancy clusters → the metal germ:*

$Me_xO_y \quad + \square + 2e^- \rightarrow Me_xO_{(y-1)}\square$

$Me_xO_{(y-1)} + \square + 2e^- \rightarrow Me_xO_{(y-2}\square_{)2}$

$Me_xO_{(y-2)}\square_2 + \square + 2e^- \rightarrow Me_xO_{(y-3)}\square_3$

$\alpha Me_xO_{y-n}\square_n + \square + 2e^- \rightarrow \beta Me_{(solid)} + \gamma Me_xO_y,$

and the reaction of reduction of metal on surface VI may be represented as

$$Me^{2+} + \square + 2e^- \rightarrow Me_{(solid)}. \qquad (14)$$

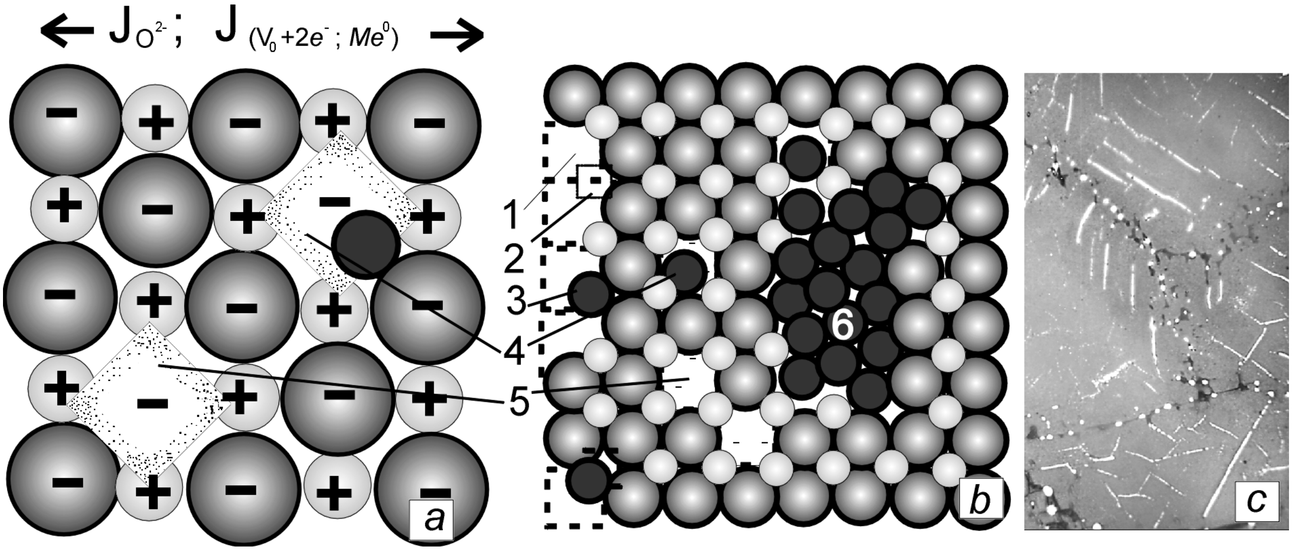

Figure 5. Segregation of metal germ on defects of oxide lattice: *a* and *b* - pattern (1- anion vacancies at the surface, 2 - cation vacancy at the surface, 3 - metallized atom, 4 - "colouring centres - incidental atoms" complexes, 5 - colouring centre, 6 - metal germ; *c* - microphotograph of metal formations in solid phase reduction of impregnated chromite spinel, x200.

Out of the complex spinel lattice, the cations that have the least bonding energy with oxygen in the spinel lattice become metallized first of all. These are incidental cations (Fe^{3+}, Ni, Co, Zn, Ag etc.) unusual for the given lattice, structure-forming iron (Fe^{2+}), and chrome. The removal from the spinel lattice of structure-forming cations entails disintegration of the spinel with formation of metal and high-magnesia phases that form a distribution pattern in the volume of the parent phase of spinel typical for disintegration structures. The interaction of these phases results in appearance of phase-to-phase borders V-VI and border VII.

The transformation of the cation sub-lattice in the anion cavity of oxide into the metal lattice should result in formation of pores around the metal germ since for filling of the anion cavity by the atoms of metal more cations are required than are contained in the cation sub-lattice of the cavity volume. As there are no visible pores around the metal germ (and the volume of pores should be slightly less than the volume of the metal phase), we should conclude that additional metal atoms come to the metal germ. The sources of these atoms can be the surface from which the oxygen anions are removed. If the defect electrons are captured by the surface cation, the neutral vacancy cannot move from the surface to the oxide lattice because the neutral vacancy will break the condition of local electrical neutrality. In this case it is not the vacancy, but the electrically neutral atom of metal that moves into the volume of oxide. The cation vacancy that appears during this process merges with the anion vacancy, which results in formation of the "absolute" cavity near the surface, which entails movement of the oxide surface.

When an electrically neutral atom moves in the oxide lattice that is saturated with anion vacancies, it has advantages over smaller electrically charged cations. The atom cannot exchange places with cations because this would break the condition of electric neutrality. But it can move via vacant octahedral and tetrahedral pores of the anion sub-lattice. As was found earlier [19], cations cannot move in a tightly packed arrangement of anions via empty pores both because of geometrical parameters and their electrical charge. For jumping from one octahedral pore into another in the tightly-packed arrangement of anions (radius R), the cation must squeeze through a narrow (r=0,15R) window between anions 1-3, pass through a tetrahedral pore (r=0,23R) in the centre of a cube, squeeze through one more window in the plane of anions 1, 2, 4, and only after that occupy the vacant site (Fig. 6, a - c). Even if there are anion vacancies, the probability of jumps of cations to the cation vacancy through anion vacancy is insignificant since this is prevented by the electric field. For the same reason, the cation cannot stop at the rather large tetrahedral pore in the centre of a cube as it would appear too close to other cations. The neutral atoms, despite their bigger sizes, can either occupy vacant tetrahedral pores or jump via anion vacancies (Fig. 6, *d*, and *e*). The atoms accompanying the anion vacancies can diffuse to the metal germ inside the oxide. The movement of incidental atoms through vacancies is well known, for example in production of semi-conducting materials [15, 16]. Joining the growing germ or wandering in the oxide lattice of oxide that is loosened by anion vacancies, atoms leave the surface and fill in the anion cavities around the metal germ, giving the "shrinkage" to the surface of crystal.

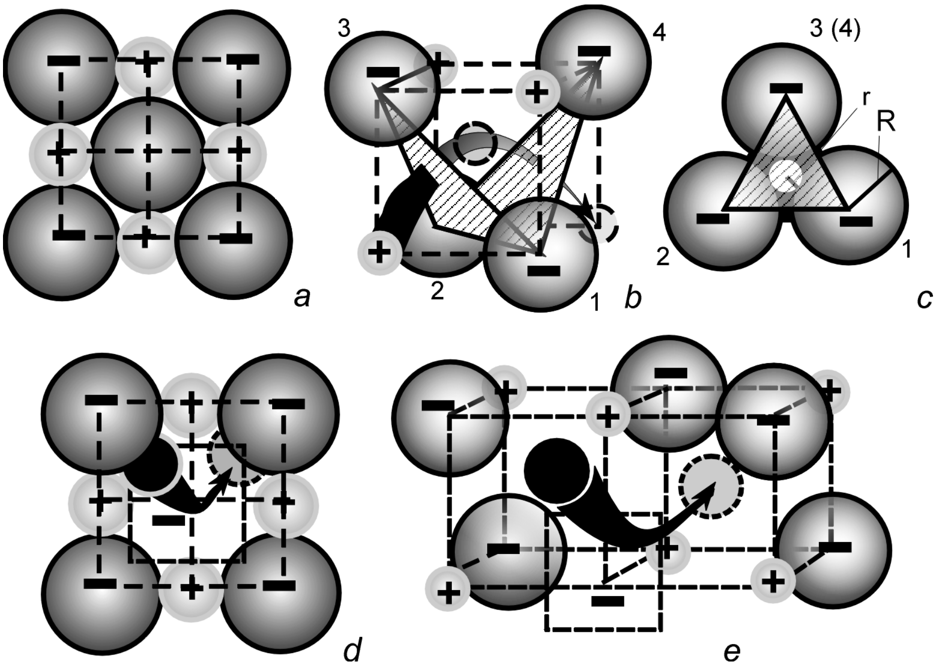

Figure 6. Pattern of movement of cation into the adjacent vacant site in tightly-packed arrangement of anions in the lattice MeO (*a-c*) and movement of atom if there are anion vacancies (*d,e*): *a* - structure of 8MeO; *b* - track of possible jump of cation; *c* - "narrow" window in the plane of anions 1-4; *d* - structure of 8MeO with anion vacancy; *e* - track of movement of atom via vacant pores.

The proposed model of segregation of a new phase inside an impregnated ore grain is realizable if dispersion of anion vacancies and defect electrons in the oxide lattice runs at a high speed. As the result, the vacancies and the atoms accumulate not near to the surface, but on defects of the lattice where the formation of a new phase is more preferable. Thus, segregation of a new phase on the lattice defects of the parent oxide phase takes place in the result of "slow" reduction, when the speed of removal of "colouring centres" from the oxide surface exceeds the speed of their formation under the influence of the reducing agent.

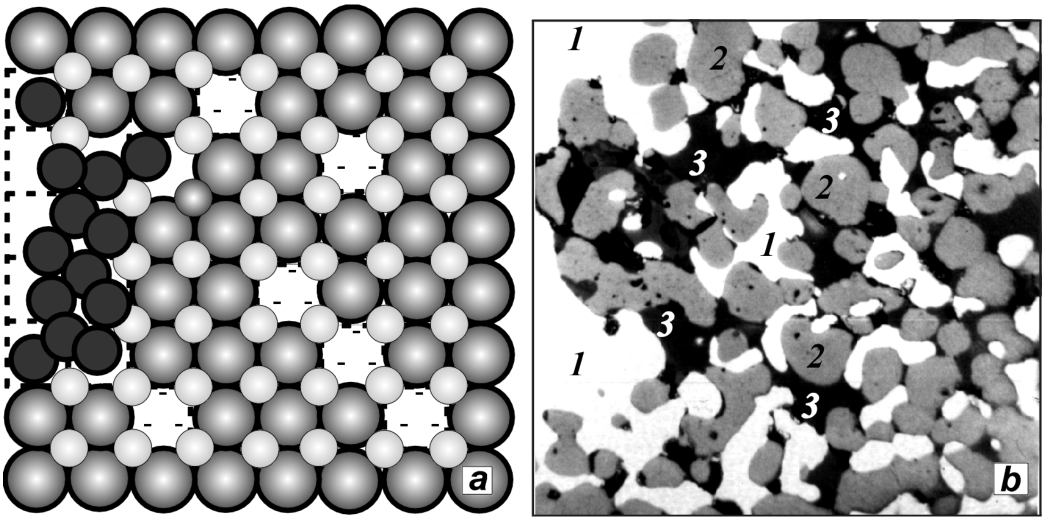

Figure 7. Segregation of iron during the "fast" reduction of siderite ore: *a* -pattern, *b* - microphotograph, x100. (1 - iron, 2 - wustite, 3 - the high-magnesia phase).

In reduction of thermodynamically unstable oxides or in the case of use of strong reducing agents that are capable of generating anion vacancies with a high speed at relatively low temperatures when the mobility of vacancies is not yet high, the generated anion vacancies (and, consequently, the defect electrons) have no time to disperse into the volume. Accumulation of vacancies (F-centres) near to the surface and the capturing of electrons by the surface cations results in segregation of the metal phase on the surface of the oxide that is being reduced. In this case essentially nothing changes in the mechanism of removal of oxygen, movement of vacancies (F-centres), and atoms, but segregation of a new phase begins from the surface of each grain, and frontal growth happens. As an example, Fig. 7 shows a pattern of "fast" reduction and distribution of products of reduction (iron and high-magnesia phase) of sideroplesite $(Fe_{0,74}Mg_{0,24}Mn_{0,02})CO_3$ by carbon monoxide at temperatures below 1000°C.

3. CONCLUSION

Segregation of a metal phase inside the ore grains enclosed in the silicate shell, which is impenetrable for carbon, strongly testifies that the solid phase reduction of metals from oxides occurs by way of removal of oxygen anions from the reduced oxide. The oxygen ions are removed by the reducing agent from the surface of an ore piece and from the non-reducible silicate phase, too. The anion vacancies and "defect" electrons generated on the surface disperse in the oxide lattice in the form of negatively charged anion vacancies - "F-centres". The merging of "F-centres" results in formation of an anion "cavity" and metallization of the cations contained therein. Depending on the correlation of the speed of formation "F-centres" and speed of their dispersal in the volume of oxide, the segregation of a new metal phase can occur either on the surface of a crystal ("fast" reduction), or in its volume on oxide lattice defects ("slow" reduction). In the processes of "slow" reduction, the essential role is played by the diffusion of atoms (including atoms of incidental metal) that accompanies the movement of "F-centres".

The location of the chemical reaction between oxide and reducing agent and the place of segregation of the reaction product (metal) can be spatially parted and even separated by an interlayer of non-reducible oxides. The surface of contact of solid reagents (oxide and reducing agent) does not have a fundamental importance because some stages of the chemical reaction occur on other surfaces, on lines of contact of three phases, and even at the points of contact of four interacting phases.

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