SOLID PHASE REDUCTION OF IRON AND CHROMIUM IN THE CRYSTAL LATTICE OF FERRIHROMPIKOTIT

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ABSTRACT

The development of reduction process in lumps of rich chrome ore, in which reduced iron and chrome are in the crystal structure of ferrochrome picotite(Mg^{2+},Fe^{2+})·[Fe^{3+},Al^{3+},Cr^{3+}]·O_4, is studied.

Solid phase reduction is made at relatively low temperature and low grade steam coal is used as a reducing agent. The reduction process is distributed along the structure of chrome spinellide of anion vacancies with the excess of electrons. Metal iron and chrome alloy is the prime product of reduction. As a result of the contact with carbon an alloy is carbonated in the surface and is transformed into the highest carbides $(Fe,Cr)_7C_3$. After metal binding of shell into carbides the formation of anion vacancies is slowing down, extraction of iron cations from chrome is beginning firstly from adjacent oxide phase and then from metal particles in the extent of an oxide early formed. Cation vacancies strengthen the structure of spinellide, prevent the formation and distribution of charged anion vacancies. Reduction process is stopped.

The increase of temperature contributes to the silicon reduction, displacement of carbon from carbide phase with the formation of flammable iron and silicon silicide, shell destruction. Destruction of carbide shell makes favorable conditions for vacancies formation. Reduction process of such elements as iron, chrome and silicon is accelerated and goes up to its completion.

***KEY WORDS**: Chrome, chrome ore, solid phase reduction, ion vacancies.*

1. INTRODUCTION

The reduction of iron and chrome from chrome ore by carbon is the basis for technological process of production of carbon ferrochrome. It is carried out in the upper part of ferroalloy furnaces when the components of furnace are charged, that is chrome ore and a reducing agent, are in the solid state, due to which carbothermic reduction of chrome ore metals is the result of solid phase interaction. In spite of a great practical importance and attention to the theory of this process from several generations of researchers the mechanism of reduction can't be explained unambiguously. One can mention difficulty in description of the reduction mechanism due to the fact that the process of reduction is defined by a great number of interrelated stages, which in their turn depend on the properties of reagents and conditions for the processes (the size and pore volume of lumps, temperature, pressure, gas and condensed solutions concentration, gas flow, formation of interstitial compounds, products of reduction, etc.) [1]. Depending on the specific conditions the role of stages can be changed which makes it difficult to state a single mechanism of reduction.

Meanwhile one should mention that actually all types of a mechanism of solid phase reduction is contact, two-stage (adsorptive and autocatalytic or dissociative and adsorptive), oxide-sublimate, gas and carbide, gas solid phase, dissociative and others, a brief view of which can be found in the article [1], they consider only external acts of reduction process with reference to the object under reduction that is the method of reagent delivery to the surface of reacting, the type of the reagent being reacted, determination of direct reduction, etc. It goes without saying that

oxidation processes of the reducing agent and metal reduction are developed on the surface of their contact, and the diagram of reagent delivery to the surface of reacting realized under specific conditions is identified to the mechanism of reduction.

In the Kempirsay chrome ores iron and chrome are in the composition of chemical compounds of an oxide spinel type $(Mg^{2+},Fe^{2+})[Fe^{3+},Al^{3+},Cr^{3+}]_2O_4$ with the cations of magnesium and aluminum, metals which are difficult to reduce [2, 3]. At solid phase reduction in such ores unlike traditional monomethyl iron ore raw materials direct contact between reduced cations and reducing agent plays a subordinate role as their basic weight is separated from the reducing agent by metal compounds which are difficult to reduce. The most important link of a mechanism of solid phase reduction is the processes in crystal structure of complex oxide, determining its transformation into the crystal structure of a metal. In our opinion, it is the core of reduction process without which it is hard to imagine the whole mechanism of reduction.

The objective of the article is an experimental research of the process of solid phase carbothermic reduction of metals in the structure of chrome spinellide.

2. EXPERIMENTAL TECHNIQUE

The process of metal reduction from rich Kempirsay chrome ores is studied. The experiments have been made in encapsulated furnace of resistance with graphite heater using earlier developed techniques to reduce metals from poor and ingrained chrome ores [4, 5]. Due to slow reduction process in a lump of rich ores ore is beaten to the size of 1...3 mm. Thin steam coal ground to 0...0.63 mm is used as a reducing agent. Ore and coal mixture is put into graphite crucible and then into main kiln area, the furnace is encapsulated to create reducing atmosphere, then it is heated and kept at temperature of 1400°C and 1500°C during 60 or 180 minutes. The temperature inside reactor feed is controlled with tungsten-rhenium thermocouple BP5/20. Crucibles with reactor feed and furnace are cooled up to the room temperature. Ore grains are separated from the residues of reducing agent by sizing, then they are poured into plastic materials to produce polished sections. The sections are studied with optic and electronic scanning microscopes JSM-6560LVand JSM-6460LVwith wave and energy-dispersive analyzers. Simultaneously original ore and products of reduction are under X-ray phase analysis using diffraction meter DRON-4.

3. RESULTS OF EXPERIMENTS

In the original ore chrome spinellide is presented by slightly changed initial chrome spinellide that is ferrochrome picotite $(Mg,Fe)(Cr,Fe,Al)_2O_4$ (figure 1). Intermediate layers and impregnation of dead rocks are given primarily in the form of water silicate of a pyroxene group $(Mg, Fe)O{\cdot}SiO_2$. Nickel in the form of complex silicate $(Mg_{1,02}Fe_{0,08}Ni_{0,09})SiO_4$ is found in a silicate phase with the help of X-ray phase analysis.

After hold up time at 1400°C for an hour relatively great reduction process is observed in the form of open shell on the surface of ore grains, tiny metal formations in the form of separate rows are in inner volume of grains which are slightly changed. A darker layer of changed oxide phase enriched with light elements is between outer shell and slightly changed inner part of a grain (figure 1, b). In a grain under thermal treatment in a metal phase on the surface one can observe chrome and iron in the ration which corresponds to their content in original ore grain, and in an oxide phase adjacent to it there are silicon, potassium, calcium which couldn't be observed earlier, the content of magnesium and aluminum is increased, there is no iron but there is a negligible quantity of chrome (figure 2, a). In the metal of rows inside the grain there are two alternating phases of chrome and iron alloy, which is enriched with one metal and impoverished in others and vice versa (figure 2, b; points 3 and 4).

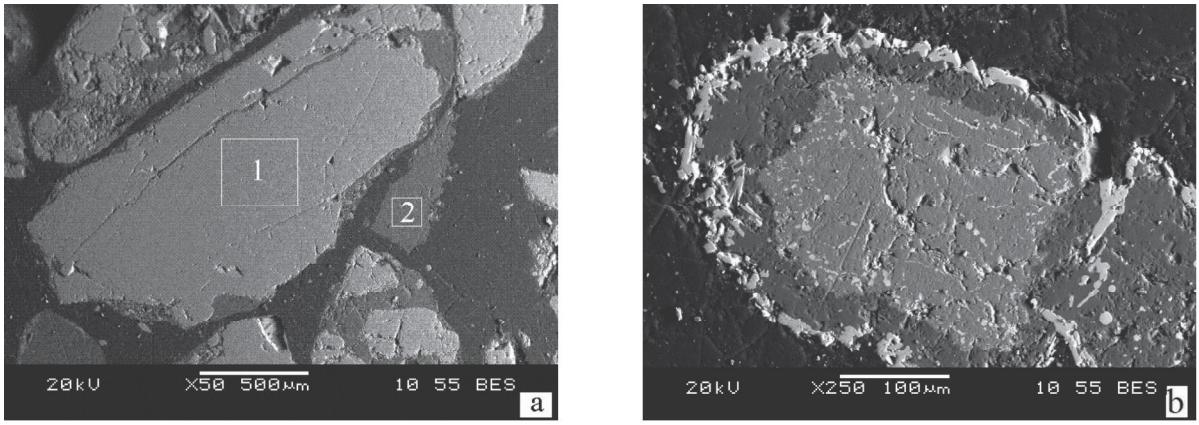


Figure 1: View of chrome spinel grains in the original ore (a) and after reduction burning at 1400°C during the time 1 h (b). Content of elements (at.%) in the spinel grains (1) and in the gangue (2):

	O	Mg	Al	Si	Cr	Fe
1	56.76	9.06	3.98	–	24.89	5.31
2	67.92	19.38	–	10.52	–	2.18

In an adjacent to the rejected metal oxide phase inside the grain there are new formations of magnesium silicate of an enstatite type $MgO \cdot SiO_2$ with the mixture of sodium, potassium, calciumcations (figure 2, b; point 5) and spinel with low content of iron and chrome in comparison with the original one (figure 2, b; point 6).

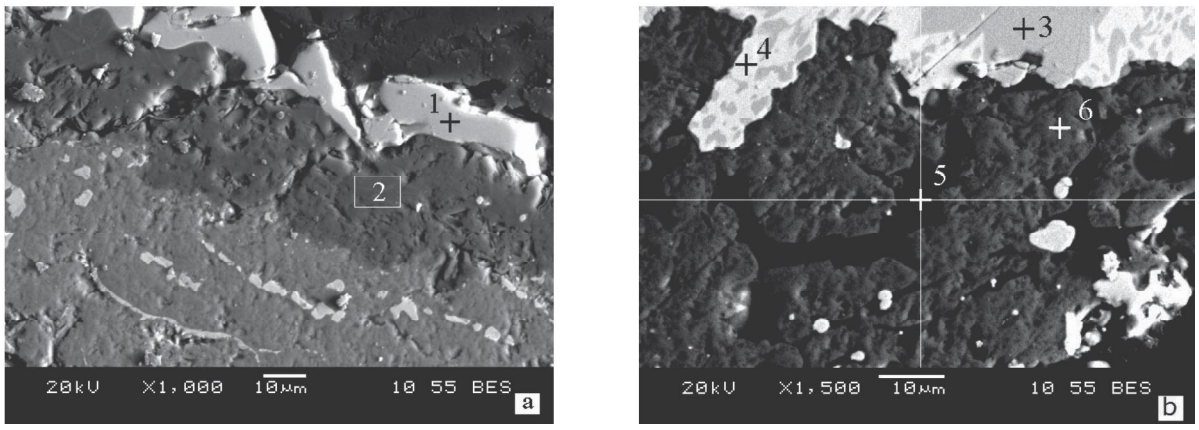


Figure 2: New growth in the chromespinellide grains after reduction burning at 1400°C during 1 hour. Content of elements (at%) in the analysis points:

	O	**Na**	**Mg**	**Al**	**Si**	**K**	**Ca**	**Cr**	**Fe**
1	–	–	–	–	–	–	–	83,07	16,93
2	63,10	–	13,99	6,70	13,70	0,51	0,34	1,65	-
3	–	–	–	–	–	–	–	76.28	23.72
4	–	–	–	–	–	–	–	23.88	76.12
5	62,89	1,11	13,14	2,73	16,17	0,66	2,32	2,10	–
6	56,86	–	11,95	4,84	–	–	–	25,94	0,41

The increase of hold up time at 1400°C up to 3 hours doesn't significantly change the character of reduction products distribution (figure 3, a). However zone distribution of the products of chemical interaction has become more accurate: at the same width of buffer zone between metal shell on the surface and slightly changed core of grain buffer zone has practically been cleared from metal extractions. In metal shell on the surface of grain carbides $(Fe,Cr)_7C_3$ are clearly observed with the help of electron-probe and X-ray diffraction analysis (figure 3, point 1).

In a more plastic and slightly changed oxide phase of a buffer zone one can see magnesium aluminum silicate with the mixture of sodium, potassium, calcium cations, little amount of chrome and iron cations (figure 3, point 2); inside the grain complex spinel is enriched with magnesium and aluminum thanks to the reduction of the amount of chrome and iron cations. In a spinel one can find little concentration of silicon and calcium that couldn't be found earlier (figure 3, point 4). Metal particles in the volume of the grains are enriched with iron (figure 3, point 3).

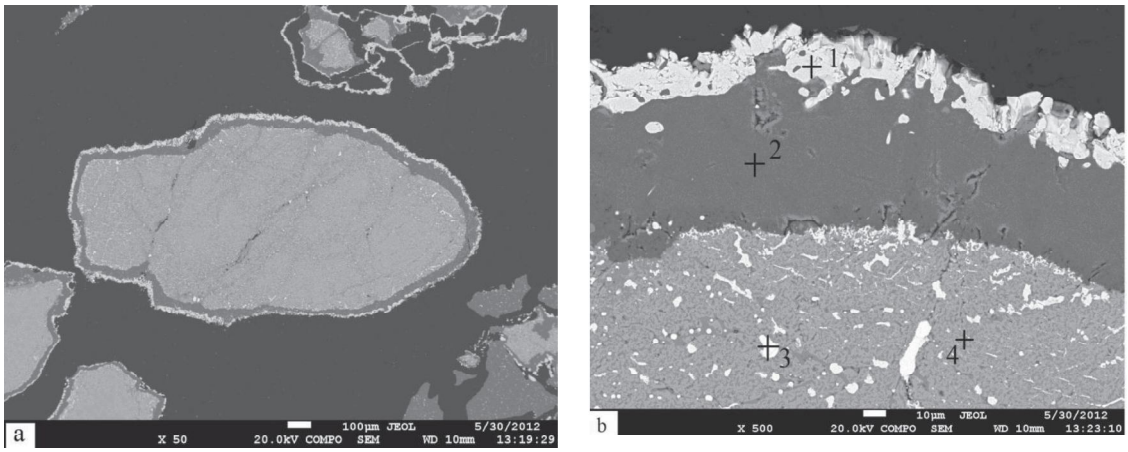


Figure 3: New growth in the chrome spinel grains after reduction burning at 1400°C during 3 hours. Content of elements (at%) in the analysis points:

	C	O	Na	Mg	Al	Si	S	K	Ca	Cr	Fe	Ni
1	44,17	–	–	–	–	–	–	–	–	46,17	9,66	–
2	–	61,63	0,16	9,08	7,91	16,91	0,27	0,10	3,31	0,55	0,08	–
3	–	–	–	–	–	–	–	–	–	45,69	53,83	0,48
4	–	60,48	–	10,7	4,50	0,07	–	–	0,03	20,51	4,14	–

Considerable changes in the character of distribution of the products of interaction and in the phase content are the results of the increase of hold up time temperature up to 1500°C (figure 4). Outer shell of the grains consisting of chrome and iron carbides earlier has almost disappeared.

Its several parts have been kept. Independent sphere-like formations are formed out of shell materials (figure 4, a). Magnesium and aluminum-magnesium spinel have appeared instead of aluminum silicate in a buffer oxide zone (figure 4, b; points 1 and 2). The core of grain is completely metallized, and core metal contains a great amount of silicon apart from chrome and iron (figure 4, c, points 3-5). In the oxide residues there is aluminum and magnesium spinel in the core of former ore grain (figure 4, d; point 6).

New sphere-like formations formed from carbides on the surface of the grain are from chrome, iron and silicon (figure 4, f and g; points 8 and 10). Only in separate microvolumes of these conglomerations one can find carbides (figure 4, g; point 10).

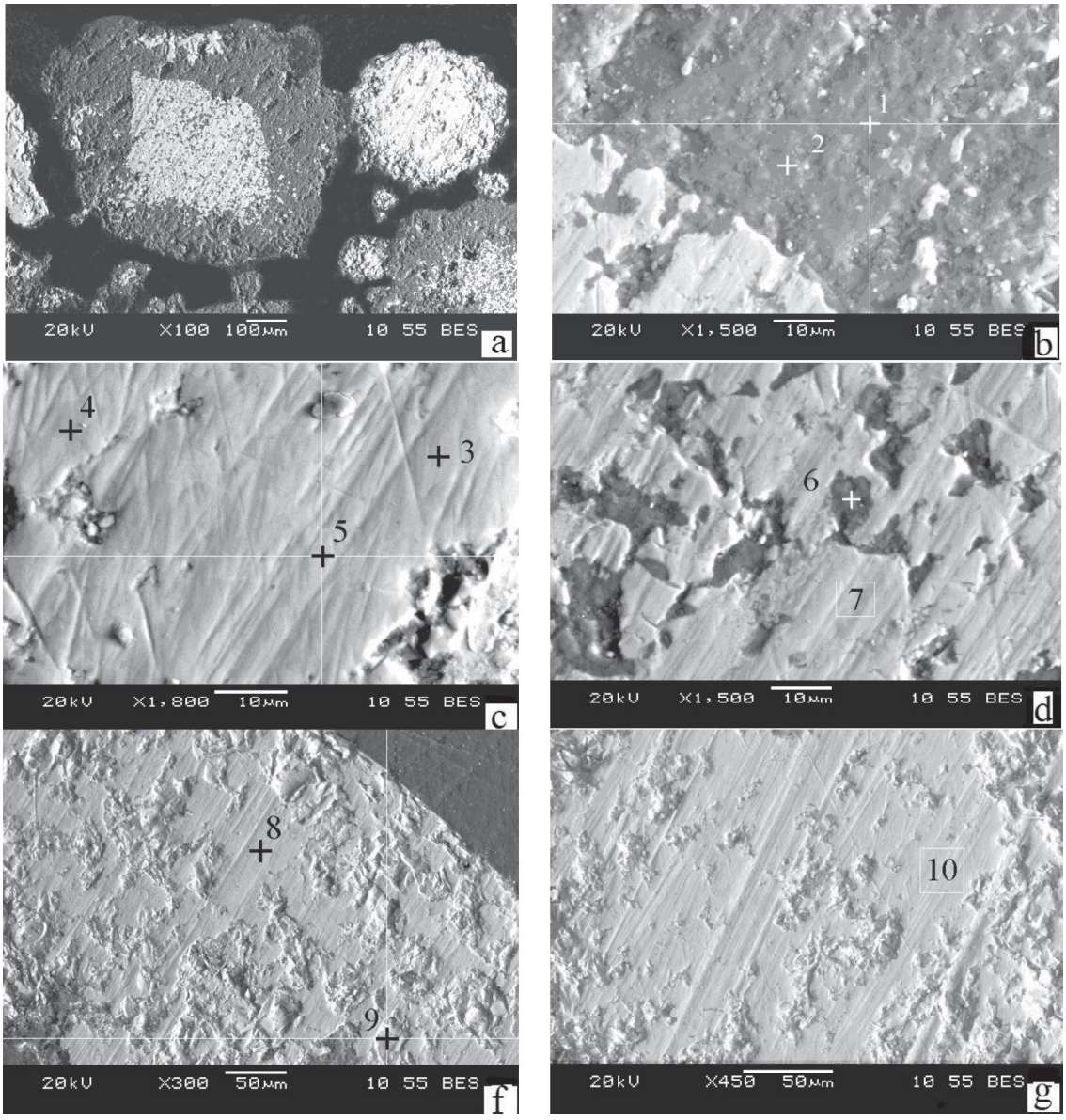


Figure 4: New growth in the chrome spinel grains after reduction burning at the temperature 1500°C during 3 hours. Content of elements (at%) in the analysis points:

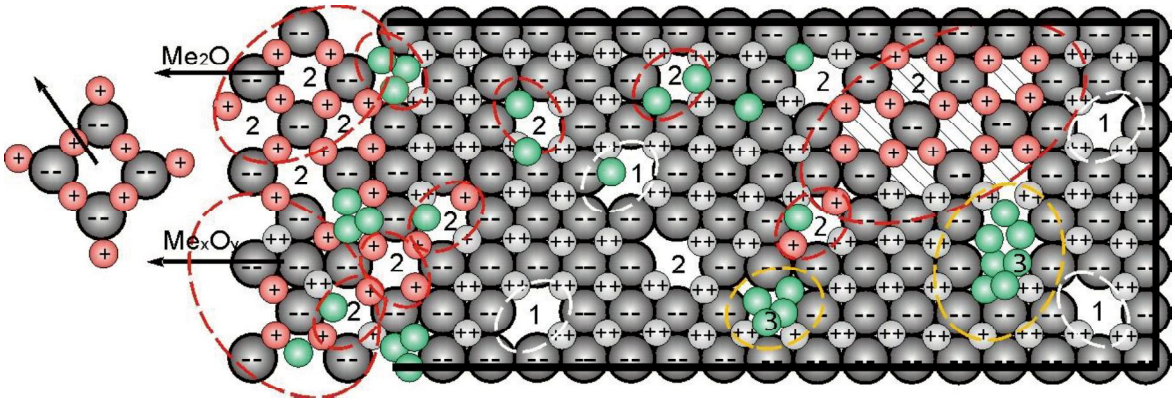
	C	O	Mg	Al	Si	Cr	Fe	Ti	Mn	Ni	
1	–	50.16	48.70	0.76	–	0.39	–	–	–	–	Magnesium
2	–	56.07	31.38	12.08	–	0.30	–	0.16	–	–	Spinal
3	–	–	–	–	8,80	73,42	17,78	–	–	–	Silicide
4	–	–	–	–	2,15	83,53	13,14	–	1,18	–	Silicide
5	–	–	–	–	17,53	62,61	19,86	–	–	–	Silicide
6	–	56,56	22,53	18,74	0,34	1,84	–	–	–	–	Spinal
7	–	–	–	–	3,49	82,41	14,10	–	–	–	Silicide
8	–	–	–	–	15,21	46,86	37,19	–	–	0,74	Silicide
9	49,79		–	–	–	45,37	4,84	–	–	–	Carbide
10	–	–	–	–	8.80	73.42	17.78	–	–	–	Silicide

4. DISCUSSION OF THE RESULTS

The results of the experiments prove the fact that in spite of widely held belief the essence of reduction is not in oxygen extraction from the crystal structure of an oxide but not return of lost electrons, which are localized near oxygen ions in the crystal structure of oxides, to the cations of oxidized metals [6]. We have already demonstrated the fact that it is not the reaction MeO + C = Me + CO that is the essence of the reduction process but the reaction $Me^{2+} + 2e = Me^{o}$ which assumes electrical and chemical character of the process, allowability of space division of reactions of metal reduction and reducing agent oxidation, the possibility to close electric circuit between the oxidation and reducing agents with the help of electron flow, metal reduction in the environment of oxygen anions that is inside the oxide, provided reduction in the specific point inside the volume takes place without reagents.

Thus, for the metal phase to be in the lump of ore or separate ore grain to the place of its extraction it is necessary to have a reducing agent or even metal cations reduced on the surface as well as to carry the reaction products off in the form of CO_2. A single condition which is necessary for this process is the excess of electrons which can be localized by the cations and it will lead to metal atom appearance.

At carbothermic reduction the source of the excess of electrons is the chemical reaction of oxygen extraction on the surface of lump or ore grain. In the result of oxygen reduction in anion oxide substructure there is oxygen vacancy charged by 2 electrons which is essential for conservation of balance of positive and negative charges in the structure on the whole and in the local area near vacancy. Oxide surface is being opened by anion vacancies and the excess of electrons in anion vacancy moves and is localized by the cations under the influence of cation charge, reducing cation charge up to zero, which is up to metal state. The excess of electrons moves together with anion vacancy and is accumulated in the places of vacancy (flow) disappearance, which is connected with the faults in structure. In the places of vacancies flow cations with zero charge are accumulated which is accompanied by the formation of metal connection as well as metal nucleating grain between them (figure 5).



1 - thermal double (anion + cation) vacancies,
2 - reduction (charged) anion vacancies, 3 – kernel of metal phase

Figure 5: The scheme of metal phase in a crystal lattice of oxides

The place for metal phase separation is determined by the speed of charged vacancies formation and diffusion. At high speed of formation and low speed of diffusion metal phase is separated on the surface. At low speed of formation and high speed of diffusion there are complexes

on the surface, which correspond to the lower oxides, their separation and sublimation as well as to the electron flow in the oxide extent and metal phase separation inside the oxide one.

There is a belief that because of a great change in energy of Gibbs system the prime reduction product of chrome is not a metal but the carbides [1, 2, 12]. In our experiments a metal separating inside the oxide phase doesn't have contact with the reducing agent that is why we can observe extra-low ferrochrome inside the grain. Extraction of iron and chrome from the structure of chrome spinellide enriches spinellide by non-reducible elements such as magnesium, aluminum, and the increase of concentration of silicon, potassium, sodium, calcium and titanium, which couldn't be visible in spinellide due to small concentrations, leads to the buffer shell of complex silicates formed by the cations between metal surface shell and nucleating grain. This contradicts to the statement of the authors [12] of the possibility to dissolve silicon in cgromespinellide by geometric parameters of cations and proves the possibility of replacement of $2Cr^{3+} \rightarrow Mg^{2+} + Si^{4+}$ or $Cr^{3+} + Al^{3+} \rightarrow Mg^{2+} + Si^{4+}$type [3, 9]. Because of such replacement in the structure of spinellide on can observe cationTi^{4+}which is found in spectrum 2 figure 4.

Metal alloy formed on the surface is gradually being enriched by carbon that leads to the formation of carbides in surface metal layer with the increase of hold-up time at 1400°C up to 3 hours. The formation of carbides is followed by further decrease of energy of Gibbs system that is why surface alloy is gradually transformed into carbides. In the result of decrease of chemical potential of iron and chrome in the surface metal layer the transfer of cation residues from oxide phase of buffer zone to this layer starts. This leads to the disturbance of the balance between metal and oxide phases in buffer zone and is accompanied by the dissolution of new metal formations here. The buffer zone is cleared from metal inclusions.

However, extraction of oxide cations from the structure and formation of cation vacancies lead to the increase of density of anion package [10, 11]. That is why the processes of mass transfer in the structure are becoming slower and are practically stopped, and the increase of hold up time at 1400°C up to 3 hours leads neither to the expansion of buffer zone nor to the increase of the quantity of metal phase in the center of ore grain.

At 1500°C silicon reduction from silicate phase of buffer zone takes place due to iron and chrome carbides. The carbides are transformed into silicide which form sphere like conglomerates at such temperature, releasing the surface of grain for further interaction between reducing agent and oxygen anions. The process of formation of the charged anion vacancies speeds up and in the central part of ore grain metal phase is released. As not only iron and chrome but silicon as well are reduced then in the center of grain there is an alloy of these three elements and small quantity of oxide residues from the initial chrome spinellide is transformed into magnesium and magnesian spinel.

Double-phase particles of metal with different balance of iron and chrome (that is figure 2; points 3 and 4) observed in the samples are the result of spinodal decomposition of ferrochrome at the decrease of temperature [12] and the consequence of periodic reduction reaction behaviour of the elements from complex oxide similar to crystallization of eutectic alloy.

5. CONCLUSIONS

1. Iron and chrome solid phase reduction in the extent of complex oxide is performed selectively with the help of electrochemical process by means of distribution of anion vacancies in the crystal structure, which are formed on the surface of reaction with the reducing agent and connected with the excess of electrons vacancies.

2. Prime products of carbothermal reduction of metals from chrome spinellide are not carbides but metal iron and chrome. Carbides formation is the secondary process of interaction between metals coming on the surface and carbon of the reducing agent.

3. Formation of carbides on the surface of the reducing agent slows down the formation of anion vacancies in the structure due to the extraction of cations ofcarbide-forming metals from the structure, formation of cation vacancies in it, dissolution of formed metal phase which leads to the strengthening of anion substructure and stopping of the reduction process.

4. The reduction of dissolved silicon spinellide in the structure, carbon replacement and formation of iron and chrome silicide contribute to the destruction of carbide shell, restart of the process of formation of anion vacancies and revivification of metals in the whole extent of spinellide.

6. REFERENCES

[1] V.P. Chernobrovin, I.Y., Pashkeev, G.G., Mikhaylov and other. The theoretical basis of the carbon ferrochrome production from the Urals ores. Monograph. South Ural State University 2004. – 346 c.

[2] Grinenko V.I.,Gasik M.I. Chrome Kazakhstan. Metallurgy, 2001. p. 246.

[3] Sazanov V.P. Chrome in the hydrothermal process. Materials of Ural summer mineral school (29 July – 2 august 1997 y.). Yekaterinburg, 1997. pp. 81-86.

[5] V.E.Roshin, N.V. Malkov, A.V. Roshin. Solid phase reduction of chrome from lean ores. Electrometallurgy, vol.1999, № 11. pp. 22-30.

[6] V.E.Roshin. A.V. Roshin. Electrochemical mechanism of pyrometallurgical reduction of ingrained chrome ores. Electrometallurgy, vol.2000, № 6 pp. 38-44.

[7] O.A.Esin. P.V.Geld. Physical chemistry of pyrometallurgical processes. Sverdlovsk, 1962. Part.1. p.671.

[8] V.E.Roshin, A.V. Roshin. Mechanism of chemical interaction and transformation of oxide into metal during solid phase reduction of chromite. Problems and perspectives of development of ferroalloy industry. Aktobe «Nobel», 2003. pp. 416-424.

[9] V.E.Roshin. A.V. Roshin. Physical aspects of solid phase reduction of metals. Electrometallurgy. vol. 2009, №1. pp.13-22.

[10] A.I. Sizyh, V.A. Bulanov. Geochemistry of chrome in rockforming minerals. Materials of Ural summer mineral school (29 July – 2 august 1997 y.). Yekaterinburg, 1997. pp. 87-89.

[11] A.V.Roshin. Diffusion of Anions and Cations in Oxide Cristal Lattices during the Reduction and Oxidation of Metals. Russian Metallurgy (Metally) vol. 2003, №1, pp.1-5.

[12] A.V. Roshin, V. E. Roshin. Electrical Conduction and Lattice Disordering in Oxides upon the Reduction and Oxidation of Metals. Russian Metallurgy (Metally) vol. 2003, №2, pp.97-102.

[13] Gasik M.I., Lyakishev N.P. Metallurgy of chrome.