

**COMPARATIVE STUDY OF FEATURES OF PARTIAL SOLIDPHASE METALLING
OF MANGANESE BY THERMAL TREATMENT OF DIFFERENT TYPES
OF MANGANIFEROUS RAW MATERIALS**

S. G. Grischenko

Ukraine, Kiev, CMP Transgeorudmet

ABSTRACT

Summarized are the results of researches of nature of manganese ore substance, features of its composition and structure. Proposed and substantiated with use of modern analysis methods complex is an assumption that natural manganese ore substance belongs to the compounds, suboxidized to stoichiometric composition, but intensively and irregularly hydrated or where there is an appropriate medium, transformed into carbonate and hydrocarbonate compounds.

Possibility of partial solidphase metalling of manganese compounds with emergence at low and moderate temperatures of metal phase as a product of disproportionation of lower suboxide metastable compounds, generated as a result of dehydration of starter hydrated, hydroxide and hydrocarbonate compounds is shown by experiments. Prevention of secondary oxidation is the necessary condition for preservation of the generated metal phase. This is ensured by the timely removal of dehydration – decarbonization reaction product gases (H_2O , CO_2), oxidizing intermediate phases to stable state with oxygen deficiency thus suppressing the disproportionation process.

Shown is the role of solid carbonaceous reducing agent, agglomerated together with ground manganese ore substance in temperature range change and behavior degree of reduction processes.

In the recent years in the sphere of iron metallurgy rather significant changes have taken place in the world connected to the development of so called melting and reduction technologies part of which is aimed at obtaining cast iron without coke or direct reduction [1].

With regard to manganese such technologies have not been developed up to the present moment; what is caused in our opinion by the “traditional” approach to the assessment of reducibility of manganese ore materials as products containing high-stable mineral forms of manganese reduction of which in solid is impossible. But even for these, it would seem, thoroughly studied mineral forms and compounds a set of questions of chemical aspect of reduction processes remains incompletely developed. One has to agree in this context with the propositions of the monograph by M. I. Gasik [2] which has become canonical on the fact that unlike iron yet still inadequate attention is given to the issues of manganese geochemistry and mineralogy.

Difficulties of research of this issue are caused largely by high dispersion ability and hidden crystallinity of the manganese ore substance, absence of generally recognized valid data on its genesis, divisiveness of the existing data on manganese valent state in ore minerals and even on the ultimate composition of the latter, stoichiometric degree of natural and artificial manganese minerals [3, 4]. Even to a lesser degree have been studied the processes proceeding by oxidation-reduction thermal treatment of real manganese ore materials explained as a rule by the majority of the authors on the basis of experiments with “pure” and often specially synthesized artificial chemical agents qualities of which are rather dissimilar from unique structure of natural compounds [5].

Authors of the extensive review study [6] consider extension of fundamental regularities

duced during study of reduction mechanism of simple oxides to the reduction processes of complex mixtures and their compounds to be justifiable. At the same time differential characteristic of the latter – ability to reduce as phases of constant or variable composition with change (in dependence on the process conditions) of both quantitative relation between the products of reduction and qualitative pattern of the process is pointed out in this study. With regard to such complicated multicomponent and multiphase systems as manganese ore substances, loads on their basis, products of reducing thermal treatment, the above given proposition needs substantial concretization.

Authors of the present study conducted theoretical and experimental researches aim of which was to show the nature of manganese ore substance in connection to its genesis, to specify the mechanism of heterophase transformations in the process of thermal treatment of different types of natural manganese compounds at wide range of temperatures and mediums with different oxidation-reduction potential. On the basis of this research new approaches to the assessment of the possibility of partial metalling in solid of specified types of dehydration and decarbonization reactions products of manganese hydrates and carbonates respectively have been proposed [7 - 10].

Researches of peculiarities of the chemical and mineral composition have been performed on the specimens of oxydic manganese ores from Nikopol deposit mainly of monomineralic type with relative subdivision according to the types: pyrolusite (specimen 1), manganite (specimen 2) and psilomelane (specimen 3); carbonate ores of Chiatur, Nikopol and Bolshoy Tokmak deposits (respectively specimen 4–6), as well as on the specimens of foreign raw materials — Obrochishche deposits in Bulgaria (specimen 7, carbonate ore) and Moanda in Gabon (specimen 8, oxydic ore). Chemical composition of the tested specimens 1–8 is given in the table 1.

Table 1: Chemical composition of manganese ore raw materials specimens

№	Mass content of the components											
	Mn	CaO	MgO	SiO ₂	Al ₂ O ₃	Fe _{tot}	BaO	Na ₂ O	K ₂ O	P	S	ignition loss
1	52,9	1,7	2,0	5,6	1,3	2,5	0,1	0,6	1,7	0,13	0,02	12,0
2	41,1	4,2	1,3	16,7	3,5	2,0	0,06	0,5	1,8	0,17	0,05	12,6
3	51,1	2,3	0,9	8,2	3,5	1,5	0,2	0,6	1,5	0,28	0,03	15,9
4	24,5	9,0	1,2	16,0	2,5	1,0	1,1	0,3	0,4	0,18	0,3	23,5
5	26,7	16,7	3,5	11,3	1,7	1,4	0,2	0,2	0,5	0,16	0,1	31,8
6	29,7	12,1	1,6	6,6	2,6	1,4	0,1	0,3	0,5	0,24	0,1	30,8
7	33,7	4,3	3,1	9,9	1,9	1,8	0,6	0,3	0,6	0,13	1,2	29,6
8	51,2	1,1	0,6	2,5	6,1	3,0	0,2	0,4	0,8	0,14	0,1	8,5

Methods of research of the specimens included crystal optic examinations with specification of phase composition with the help of electron-probe test; differential thermal analysis with use of derivatograph MOM 3427/T, usage of the proton magnetic resonance method (PMR) with record of the PMR spectra on the radiometer PJI-2301 at frequency of 16,0 MHz and temperature of 27 °C. Raw materials specimens were subject to heating in different mediums (reducing, oxidizing and neutral medium) in the range of temperatures 300-1300°C with following 30 minutes of exposure and rapid cooling (tempering) for preservation of their microstructure.

Our researches, as well as the studies [11,12], confirmed the presence in the specimens of sufficiently large amount of minerals, containing hydrated components: manganite MnO(OH); (M₂O₃·H₂O); psilomelane (Ba, Mn²⁺...) (O, OH)₆·Mn⁴⁺O₁₆; vernadite MnO₂·nH₂O; cryptomelane

$K_{2-v}Mn_{8-x}(O, OH); \text{ranseit } (Ca, Mn^{2+}) \cdot Mn_4^{4+}O_3 \cdot 3H_2O$ and many others.

It is shown on the basis of the form and width of the PMR spectra and respective thermograms that $Mn(OH)_2$ and probably in small amounts $MnO \cdot OH$ are present in the specimen of pyrolusite type. $MnO \cdot OH$ is the basic compound in the manganite specimen, and in the psilomelane specimen — $Mn(OH)_2$ and $MnO \cdot OH$ in approximately equal amounts. With use of template $[Ca(OH)_2]$ matching technique quantities of OH-groups in the tested specimen have been calculated, what made up expressed as H_2O in the pyrolusite specimen - 6.3 %, in the manganite specimen – 12% and in the psilomelane specimen – 10 %.

Content of hygroscopic loosely bound moisture for these specimens made up respectively 0,6 %, trace and 2 %.

In the same way the composition of hydrate phases in other specimens of manganese ore materials has been researched. For carbonate kinds, in particular, presence of bicarbonate ions HCO_3^- , connected to the manganese and silicium ions was detected.

Hydrated components in ores, being high-reactive, may at the same time be present in the specimens exposed to thermal treatment at low and even moderate temperatures. Not by accident it is said in the study [13] that effective drying with complete moisture removal is ensured by thermal treatment of oxydic and carbonate concentrates at the temperatures of 600-800°C, and for separate types of raw materials — not less than 800°C. In the upper limit of this temperature range decarbonization reactions are basically completed.

As will be seen further, exactly the products of low temperature reactions of dehydration-decarbonization, preserved later during cooling in neutral and reducing mediums, potentially promising for the possible solidphase metalling. That is why it is of interest to evaluate the possible degree of manganese metalling in different ore types, e. g. determine the amount of manganese combined into hydrates, hydroxides and hydrocarbonates on the basis of PMR data for these specimens. Calculation data is tabulated in the table 2.

Table 2: Composition of hydrated phases in different types of manganese ores

№ of the specimen	Mass fraction $H_2O(OH)$ according to the data of PMR	Estimated mass fraction of compounds			Content of Mn, mass. %		
		$Mn(OH)_2$	$MnO \cdot OH$	$Mn(HCO_3)_2$	In the hydrate	Total according to the chemical analysis	Part of Mn in hydr. of the tot
1	6,3	33,0	-	-	20,3	52,9	38,4
2	12,0	-	62,1	-	38,8	41,1	94,4
3	10,0	26,2	25,9	-	32,4	51,0	63,5
4	1,6	-	-	14,8	5,2	24,5	21,2
5	1,8	-	-	16,6	5,8	26,6	21,8
6	2,3	-	-	21,2	7,4	29,7	24,9
7	7,6	-	-	70,1	24,6	34,0	72,3
8	3,3	8,6	8,5	-	10,6	51,2	20,3

As it is seen from the data in table 2, ores of manganite and psilomelane types and hydrated and carbonated ore from the Obrochishche deposit are potentially promising for metalling from hydrated phases for 60-90 % of the total amount of manganese contained in the ore. 20 – 40 % of the total amount of manganese contained in the ores can be metallized in solid from the ores of pyrolusite type (among these is the Gabonese ore).

Possible part of metallizing of dehydration products in domestic carbonate ores is relatively small (21—25 %), where however apparently part of the products of decarbonization reaction can be metallized in the same way. Rapid removal (for example by vacuum heat treatment) of the evolved carbon dioxide, for the latter is oxidizer for the lower manganese oxide, is the condition for preservation of manganosite as a product of decarbonization.

Formation of a series of solid solutions from the whole sum of the composing components and then of liquid silicate phase which participates in all following interphase interactions is characteristic feature of phase transformation in the manganese ore substance by heating within the temperature range from 300 to 1400°C. Whereby in case of oxidizing burning decomposition products are presented by distinctly edged crystals of hausmannite and silicate glass cementing them, while manganosite, tephroite, glass, manganous sulphides and separate dispersed beads are the products of reducing roasting. The latter shall be considered as preproducts of decomposition of the solid solution of the lower manganese oxides and other elements, easily decomposable under normal conditions and disproportionating by lowering of temperature into metallic phase and oxide of a higher valency. In terms of thermodynamics behavior of such processes is quite probable, for under conditions of high temperatures protoxide appears to be more stable oxide form in comparison to oxide and at low temperatures, on the contrary, protoxidic compounds are thermodynamically unstable [14].

Firing medium has almost no effect upon the phase composition of the silicate melt; at the same time manganous sulphides and dispersed metallic beads remain in roasted products in reducing atmosphere after cooling.

Main technological task during solidphase metallizing of manganese is thus the preservation of suboxidized dehydration products up to the temperatures of intensive material metallizing. Results of experiments conducted by the authors of the study [15] who observed oxidation of manganese protoxide as a product of low temperature decomposition of crystalline hydrates, even in the atmosphere of helium due to the oxygen evolved during dissociating of manganese superoxide contained in the same specimen indicate the complexity of this.

In order to obtain metallized product during thermal treatment in solid, concentrate of Nikopol oxidyc ore of the pyrolusite type was powdered. Grinding itself, as is well-known, facilitates gaining greater activity by the phases with oxygen deficiency, intensifying their transition into quasi-amorphous metastable state [16, 17]. At the same time during grinding removal of air and adsorbed moisture from the micropores of the manganese ore substance take place what prevents later secondary oxidation of lower manganese and silicium oxides during dehydration of respective compounds and facilitates thereby their metallizing.

Obtained powder of pyrolusite ore was then pelletized into granules with size of 5 – 8 mm, water solution of industrial lignosulfonates was used as bonding agent during pelletizing. Granules were fired in vacuum furnace with vacuum of 10^{-3} Pa at heating rate of 20 °C/min to the temperature of 1000°C and then cooled without depressurization of the furnace to room temperature.

Analysis of the microstructure of the specimens fired under these conditions has shown characteristic heterogenic association of mineral phases; whereat without melting of mother manganese ore substance in solid metallic phase is formed. The latter is in direct close contact, without intermediate connections, with manganese oxide and silicium dioxide, e. g. Looks like emulsion mixture of oxide and metallic compounds. Such association of minerals is direct evidence, that by removal of hydrate moisture formation of lower oxides with oxygen deficiency, stable at temperatures higher than 800°C and having disproportionated by cooling in vacuum, e.g. oxygen-eliminating, to the mixture of abovementioned products has taken place.

It is possible to intensify the formation of metallic phase by means of thermal treatment of specimens in reducing atmosphere with exposure from 1 to 5 hours at the temperature of 800°C

with further temperature increase up to 1300—1400°C. During heating sampling of the thermally treated raw material was being performed after every 100°C.

Exposure for five hours facilitates after complete dehydration transformation of manganese ore substance into oxides of manganese and silicium with oxygen deficiency. Already during further heating to 1000 °C part of the metallic phase in roasted products amounts to about 5%, increasing with temperature rise over the range 1100—1200°C respectively to 15—20 %, and at temperature of 1300—1400°C — up to 30—35 %.

Formation of metallic phase is at the same time connected to softening of pellets. Already during firing up to 1300°C they lose strength, embrittle, friable from the surface, completely powdering after firing at 1400°C. Microstructural examination of the fired products shows that all mineral components during phase transformation underwent coagulation or granulation. Powder particles have round shape and consist of metallic and slag phases. The latter during firing up to 1400°C is presented mainly by siliceous glass and at 1300°C also by manganosite.

Based upon conducted researches a method of preparation of manganese raw material to melting for production of ferroalloys [18] was developed, it envisages partial metalling of ground and pelletized into granules of the manganese concentrate by means of firing with long exposure at 800—850°C and following temperature rise up to 1100-1200°C.

Aforementioned calculations (table 2) of the possible degree of metalling of the ore substance in solid are partly conditional, since they presuppose the connection of hydroxyl groups with manganese only, while significant part of these groups is also connected to silicium. However this assumption is not of principle in view of the identity of the way of dehydration of silicium and manganese compounds with following disproportionation of nonstoichiometric dehydration products to stable oxide and metal element.

Thus, according to the calculation (table 2) degree of manganese metalling in solid for the specimen of Nikopol oxidic ore of pyrolusite type could amount to 38 %, in fact according to the results of the afore described experiment this value amounted to 30-35 %. Thus, content of hydrate and hydrate and carbonate metastable phases of nonstoichiometric composition in the mother manganese ore substance can be a value characterizing potential possibility of solidphase metalling of the part of manganese contained in ore.

Results of experiments indicate that during solidphase processes with reducing agent as well as without it, metallic phase is half-product of the reactions of stage disproportionation of metal-oxide, metastable under normal conditions phases. Depending on the thermal treatment temperature different generations of metallic phase can form.

Primary generation of metallic phase is recorded in roasted products of the manganese ore substance with reducing agent at the temperature of 800—850°C and is presented by disperse metal beads in mixture with “unstructured” oxidic phase. Microstructure of such products is of emulsion character, characteristic for decomposition of solid solutions.

Emergence of metal of the first generation can be explained by proceeding of dehydration reaction of the respective hydrate, hydrate and oxidic and hydrate and carbonate phases and following disproportionation during cooling of obtained lower nonstoichiometric metallic oxides to stable oxides and metallic phase. Schematically for hydrates this can be presented by the following reactions:



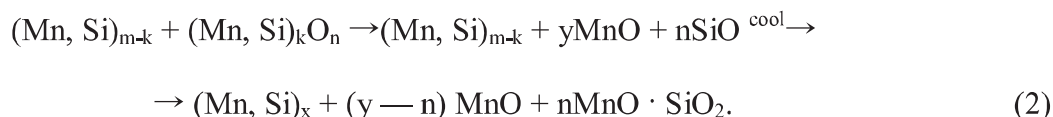
It is noteworthy that, during heating without reducing agent first disperse metal beads were recorded at the temperature of 1100°C on the contrary 800—850°C in experiments with reducing agent.

Thermal temperature rise up to 1000°C with reducing agent intensifies formation of metastable oxides with oxygen deficiency, what leads to emerging in the roasted products of

flocculated metal beads. Oxidic, earlier “unstructured”, mass is devitrified into definite granular manganosite phase with thin silicate threads (figure 1). For the temperature of 1000°C is insufficient for formation of the liquid phase, processes proceed in solid with local participation of liquid and gas phases. That is why initial unequal detrital form of ore grains remains unaltered.

Second generation of metal emerges in the roasted products with reducing agent over the range of temperature from 1100 to 1200°C and is presented by larger metal beads. Beads, as a rule, are associated with silicate tefroite masses and surrounded by thin fringe of new formations of secondary manganosite (figure 2).

Such microstructure indicates fundamental similarity of mechanisms of formation of metal of generations I and II. Intensive slagging is the characteristic feature in the products of this type; it is caused by two reasons: firstly, by melting from the ore of low-melting component [19], secondly, by formation of lower silicium oxides, product of disproportionation of which is the silicium dioxide. Thereby additive reactions between the formed oxides, e. g. processes of silication or slag formation are concomitant. In this case reaction (1) can be supplemented with the following sections:



Participation of lower silicon compounds in the processes of slagging with manganese oxides is shown in our study [20].

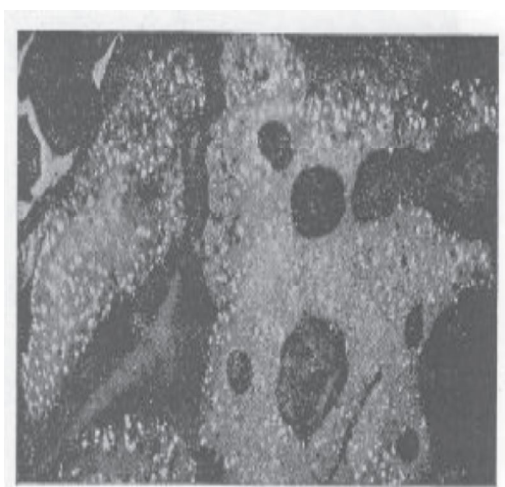


Figure 1: Metal of generation I in mixture with manganosite and thin silicate threads; reflected light, $\times 210$

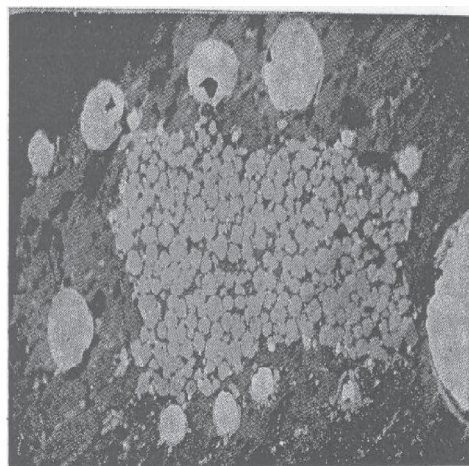


Figure 2: Metal of generation II in contact with silicate; reflected light, $\times 210$

Concurrency of manganese and silicium reduction processes at these relatively moderate temperatures is confirmed by the results of electron-probe test, which determined the presence of silicium in metal beads of generation II.

Third generation of metal may be attributed to the temperature range 1250—1350°C; thereby the formed metal beads (figure 3 a) are associated with new formations of manganous sulphide and silicium dioxide (lechatelierite). This indicates complex mixture of metal forming subcompounds, similar to lower oxysulfides.

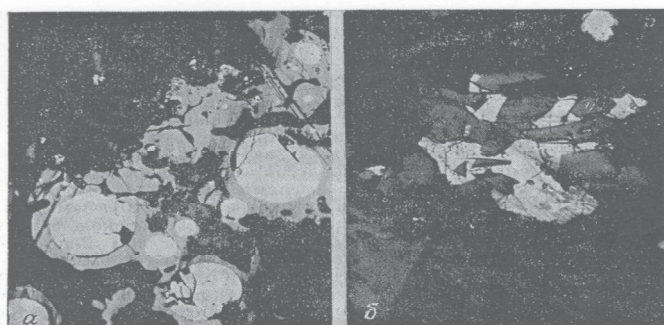


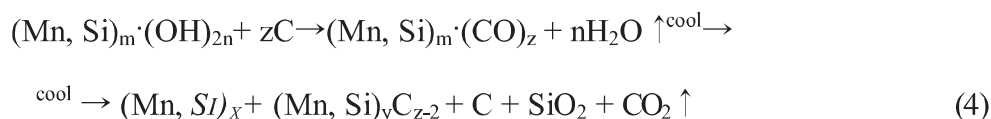
Figure 3: Metal of generations III and IV in contact with manganese and silicium oxysulfide (a) and oxycarbide (b) respectively; reflected light, $\times 210$

Schematically forming of metal of the generation III can be presented by the following reaction:



With temperature rise up to 1400—1500°C with reducing agent gradual disintegration of specimens occurs — at first from the surface only, and then also in bulk with their transformation into powder. Emergence of metal of generation IV under these conditions is associated with participation in reactions of complex oxycarbide compounds, what the stable products of disproportionation are the evidence of. Microstructure of the latter is presented by distinctly confined crystal of hexagonal system, being in contact with metal (figure 3, b) and belonging to oxycarbide compounds of manganese and silicium, as well as graphite and siliceous glass.

Schematically reactions leading to formation of metallic phase from metastable products of dehydration for this stage can be presented in the following way:



Phenomenon of crumbling of hard firing products into powder was recorded above also for processes proceeding without solid reducing agent. The difference here is in intensive participation of gas reducing agent (carbon oxide) in reactions. Composition of end condensation product, presented not only by slagged spherocolloids, but also by thread oxycarbide formations of bizarre form is also an evidence of this. Thus the role of the solid reducing agent in processes of metalling of metastable products of dehydration consists in intensive generation of carbon oxide according to the reaction $\text{C} + \text{CO}_2 = 2\text{CO}$, shifted to the right almost entirely at the temperatures above 1000°C. Thus the necessary reduction potential of the gas phase is ensured; this gas phase preserves the formed suboxides from complete oxidation to stable forms.

Researches did not reveal any fundamental difference in the form and quantity of used reducing agent, with variation of these factors only the intensity of the processes of solidphase metalling is changed. It is known that in comparison with gas coal graphite is more inert, less prone to oxidation and gasification during heating [21]. Slowness of formation of carbon oxide on graphite reduces therefore slightly degree of metalling of manganese ore substance when using graphite in comparison with more reactive gas coal.

Thus, consideration in the present study of mineral composition of manganese ores from the perspective of their genesis allowed to detect belonging of natural manganese ore substance not to

the deeply oxidized materials containing stable superoxides of manganese and silicon, but on the contrary — to the compounds which are oxidized to stoichiometric composition, but intensively and irregularly hydrated or transformed where there is respective medium during the generation process into carbonate and hydrate and carbonate compounds.

By varying conditions of reducing and thermal treatment it is possible to ensure dehydration and decarbonization reactions proceeding with transition of suboxide of manganese ore substance into metallized elements mixture with oxygen deficiency. The latter, being easily decomposable at low and moderate temperatures disproportionate during cooling into metallic and stable oxidic phases.

The specified processes proceed without close contact of metallic oxidic compounds with solid reducing agent, role of the latter under these temperature conditions is limited to maintenance of the definite reducing potential of the gas phase. Timely removal of gaseous products of dehydration – decarbonization (H_2O , CO_2), which are oxidizers for metallic oxidic phases with oxygen deficiency; e. g. stabilizing these phases with suppression of the process of disproportionation is the necessary condition for the processes of the solidphase metalling. Completeness of the process of low temperature metalling is determined by the quantity of hydrated phases in initial substance, temperature and exposure to reducing thermal treatment.

Given mechanism of low temperature solidphase metalling of manganese ore substance seems to be counterintuitive at first sight only. In actual fact diversity of the studied characteristics of chemical and mineralogical transformations of manganese ore substance tallies well with fundamental provisions of the general theory of oxides, their mixtures and compounds reduction.

Firstly, results of the above described researches concern definite forms of manganese ore substance, present in real ores and concentrates, namely hydrated compounds of manganese and silicon of nonstoichiometric composition, being due to the genesis specifics in metastable condition. Beyond all doubt, stable phases of stoichiometric composition are metallized (reduced) in strict compliance with known abstract theorems, what the often resolved in literature results of the reducibility studies, for example, of manganese agglomerations, thermally treated pellets and other materials exposed to stabilizing preliminary heating or melting (slags) is the evidence of.

Secondly, it should be pointed out, that the results obtained in our studies are perfectly explicable. As noted, at high temperatures protoxide turns out to be more stable form of oxides in comparison with oxides and at low temperatures – on the contrary. Thermodynamic easy decomposability is the initial cause of disproportionation of protoxide compounds according to the mechanism $2 \text{MeO} \rightarrow \text{Me} + \text{MeO}_2$. While reactions of dehydration of respective hydrates, hydroxides and hydrocarbonates in real ores are the source of protoxidic forms of metallized elements (Mn_mO , Si_nO) at low temperatures, e. g. when existence of these compounds is unlikely in respect of thermodynamics.

Finally, thirdly, developed considerations do not contradict the known provision of kinetics of oxidation and reducing interactions in complicated heterophase systems. It seems to be useful to mention here the data of the authors of the study [22], who examined the reducibility of manganese ferrite $\text{MnO} \cdot \text{Fe}_2\text{O}_3$. In the mentioned study it was determined that deoxidization on the surface of the crystal lattice $\text{MnO} \cdot \text{Fe}_2\text{O}_3$ leads to emergence of surplus metal ions of iron and manganese which can either diffuse deeper into the lattice, or form metallic phase. During hydrogen reduction at the temperatures of 400—500°C reduction rate (deoxidization) sufficiently exceeds the rate of diffusion and iron and manganese ions form metallic phase. During reduction with solid carbon and at the temperature of about 1000°C reduction rate corresponds approximately with diffusion rate and transformation of the lattice of the ferrite into the protoxide lattice $\text{FeO} - \text{MnO}$ proceeds. In this case metallic phase emerges later, after total disappearance of the initial spinel lattice.

Similar provision, obviously, take place also during disproportionation of the products of low temperature dehydration of the manganese ore substance. Low speed of diffusion of metal ions

in comparison with the speed of other reaction leads to their accumulation with formation of a separate metal phase at low and moderate temperatures, what is convincingly recorded by means of crystal optic method. Emergence of the metal phase at an early stages gives beneficial effect to the whole further proceeding of reduction processes, eliminating difficulties with removal of their metallic products, lowering activity of the latter and facilitating thereby increase of speed and completeness of reduction.

Fundamental provisions on characteristic features of transformation of natural manganese ore substance in the process of reducing and thermal treatment developed in the course of the research can make background for the search of new areas of raw material preparation for ore-thermal melting and improvement of metallurgical properties.

In conclusion the author expresses sincere gratitude towards the experts of UkrNiispetsstal (USSI) – T.F. Raichenko, N.M. Moskaleva and V.V. Sharapova, who participated in the pursuance of the research.

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