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LIMITATION OF METAL CARBONIZATION RESULTS IN IMPLEMENTATION OF 'ORE-STEEL' PROCESS

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ABSTRACT

Two-stage process of iron and steel metallurgy based; (1) reduction cast iron melting, including non-blast furnace melting of carbonized metals, and (2) oxidizing steel melting has been developed worldwide and is the basis of the industry. Both the first and the second stage of the production is implemented under up-to-date conditions based on construction of large divisions of the metallurgical complex, which is associated with frequent increase of capital costs and prime cost of metal products. Moreover, the second stage (oxidizing steel melting), by nature of the process, is conversely directed to the first one by the reason that together with oxidation of carbon excess, it results in oxidation of all useful reduced metals. As a result, the following goal has been set.

The goal was to study the possibility of limitation of the metal carbonization process at the stage of reduction melting and, hence, achieve the result of direct steel making. The goal shall be achieved by the development of methodology of study of solidphase reduction of iron and accompanying metals directly by solid carbon based on new dissociation-absorption mechanism, which [as opposed to the existing mechanism of iron reduction using hot reducing gas (HRG)] allows more precisely calculate and regulate stoichiometric carbon consumption without formation of its excess.

New approach to the process arrangement has been tested on the laboratory units when processing charge materials made on the basis of iron, manganese and chrome at stoichiometric carbon consumption for reduction of each metal. Results of the experimental studies of solid phase metals reduction within the interval of 600-1200ºC followed by continuous melting of charge materials at 1550-1600ºC have been provided. Samples of metal ingots at specified interval of change in composition of charge materials have been obtained. Chemical compositions of the obtained ingot samples, which correspond to the composition of steels alloyed by manganese and chrome have been provided.

Key words: Ore, Steel, Carbonization, Carbon, Change, Reduction, Stoichiometric carbon.

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INTRODUCTION

Global practice of two-stage metal production (which includes primarily reduction melting of charge materials including recovery of cast iron and other carbonized metals, repeatedly oxidizing melting of cast iron and other carbonized metals including recovery of steel) is developed more intensively and today has reached the world-wide production of more than 1.5 billion tons per year. Also, huge metallurgic complexes are one of the main sources of environmental waste emissions. The humanity faces the global environmental disaster features of which have already been observed today in a number of regions of the earth surface. No tangible results have been reached pursuant to the Kyoto Agreement concluded by the leaders of leading countries of the world. Contradiction between the economy and ecology is observed here. High indicators in the economy and ecology may be reached in parallel only subject to conceptually new contributions to the science and technology.

Procedure for stage-by-stage metal production made on practice is based on the existing theoretical provision recommending the hot reducing gas (HRG) as the universal and necessary reagent for metal reduction. Thereby, reduction melting of iron-ore raw materials is based on the principle of organization of contraflow of charge materials and HRG, at that charge materials include agglomerated ore part and coke where ore load for coke is P_H = 3.3-3.5 t/t. Under shaft furnace conditions, 60-65% of reducing processes are being implemented by interaction of HRG with metal oxides. Within the area of melting the coke carbon is involved in the reactions of direct metal reduction and, as melt is filtered through a layer of coke packed bed, then inevitable carbonization of iron and generation of cast iron melt occur simultaneously. As within the area of fusing of charge materials in the blast furnace the temperature and thermal conditions correspond to the level of temperature conditions also in steelmaking units, the limitation of carbonization process may result in melting of steel instead of cast iron. Such problem may be resolved but it concerns the theoretical basis of metal reduction in general and procedure for organization of processes in particular, where this work is being directed to.

EXPERIMENTAL

Metal carbonization process is directly associated with the carbon involvement in the reactions of reduction and carbide generation of metals. The existing theory considers it as a solid particle, the interaction with the metal oxides of which is restricted by contact and diffusive mechanism, therefore, development of direct reduction of metals by solid carbon is considered only through the gas phase[1]. Exclusively, with CO generation.

However, possibility of implementation of metal reduction through the gas phase is restricted by chemical strength of oxides[2] and reducing potential of CO, therefore, over the last years, we may observe the increased interest in use of solid carbon as a coal and carbon-containing reagents to produce the metals and metallized intermediate products[3-7]. All these new processes at the variety of the process organization are gathered at one final result, i.e. receipt of carbonized intermediate product. Practical actions being taken today on the arrangement for new processes using solid carbon are economically forced events and show the lead of practice before theory. The solid carbon is attractive not only by its mass and accessibility but also by variety of features which have not yet discovered sufficiently. Its unique features are discovered step by step in the various directions of science and technology. New mechanisms of direct reduction of iron by solid carbon and new theoretical provisions[8,9] offered today show that reduction by carbon is implemented not only with generation of CO but significantly with generation of CO_2. The carbon consumption for reduction of iron with generation of CO_2 is 2 times lower than at generation of CO. Therefore, calculation of carbon consumption for iron reduction according to scheme with generation of CO, exclusively, certainly forms the carbon excess which carbonizes the metal. Based on the new mechanism considering gasification of oxygen of charge materials with solid carbon both as CO_2 and as CO, iron carbonization may be excluded or limited and, thus, the steel may be recovered without the stage of cast iron production.

Fundamental studies of the features of solid carbon and provision with the mechanism of its interaction with metal oxides, not at atomic and molecular level (as given in the existing theoretical provision) but at the level of electron and ion exchange between the solid particles, open new possibilities of arrangement for and limitation of the process of metal carbonization. In control of the reduction process, a relevant mechanism of its direct interaction with the metal oxides has not been universally accepted yet. Nevertheless, it may be stated that carbon is not only an active reducing reagent but also an active carbide generating element. Carbide generation is followed by the oxide reduction with the formation and accumulation of metallic phase. Hence, it is obvious that the carbide generation process is conditioned firstly by its occurrence in the system of metallic phase, secondly, by excess of carbon in the system of MeO-C-Me- (CO, CO_2). High-priority process is the reduction of metals by carbon with generation of such gases as CO and CO_2. While developing the process, the share of metallic phase is increased for the account of decrease of the oxide phase. Finally, two phases such as C-Me are left in the system. Then, we may observe generation of new phase-metal carbide Me_3C or carbon solution in the metal. Hence, we may make very important conclusion that the basis of metal carbonization is the carbon excess in the system and it is confined to the moment of completion of metal reduction. As we can see, boundary conditions of the metal carbonization are directly associated with determination of stoichiometric carbon consumption and development of science-based calculation procedure.

RESULTS AND DISCUSSION

Interaction of solid carbon with metal oxides may be based on previously offered dissociation-adsorption mechanism[10,11]. The absorption term in this mechanism is understood not only as a gas flow in a layer but also as a gas phase evolving during the process of dissociation of complex chemical compounds (oxides, carbonates, etc.). Dissociation item itself supposes adsorption and chemical adsorption of the gas phase generating at the surface of solid particles. The initial stage of the mechanism is the dissociation of chemical compounds as phenomenal natural event of complex substances.

New gas phase may be evolved on the surface of solid particles other than through formation of near and far coating, respectively, chemical adsorption and adsorption layers. Oxygen mass transfer from oxides to reducing reagents (irrespective of whether it is gaseous (CO) or solid carbon) is carried out only out of these coating layers. In any case, reaction of interaction of gas CO is implemented to the extent that

$$2\ CO \rightarrow 2\ C + O_2$$

dissociation tension is significantly low than MeO dissociation tension.

$$2\ MeO \rightarrow 2\ Me + O_2$$

Comparative analysis of change in dissociation tensions of the oxides of metal and CO depending on temperature shows the possibility and extent of the course of the reaction of their interaction.

Table 1: Values of dissociation tension of oxides $\lg P_{O_2}$ depending on temperature[12]

Reagents dissociation	**$\lg P_{O_2}$ Temperature, K**			
	1200	**1300**	**1400**	**1500**
$FeO \rightarrow Fe + 0.5O_2$	-16	-14.4	-12.9	-11.6
$CO \rightarrow C + 0.5O_2$	-20.3	-19.6	-18.9	-18.4
$MnO \rightarrow Mn + 0.5O_2$	-30.6	-28.68	-26.73	-24.58

As is clear from the data of the table, the dissociation tension of CO is significantly lower than the dissociation tension of FeO, but much more than the dissociation tension of MnO. Therefore, iron reduction from FeO by carbon oxide is successfully carried out in equilibrium reaction and may be completed by generation of metallic iron.

$$FeO + n\ CO = Fe + CO_2 + (n-1)\ CO$$

Coefficient n shows required excess of CO for the course of the reaction from left to right. The balance of the reaction is characterized by ratio

$$\eta_{CO} = \frac{CO_2}{CO + CO_2}$$

which within 1000-1100 K has a value at the level of η_{CO} = 0.20-0.25. Whereas, the reaction is carried without any change in gas volume, it may be recorded that, $\eta_{CO} = CO_2/(n \cdot CO) = 0.25$ and $n = CO_2/0.25 \cdot CO = 1/0.25 = 4.0$, i.e. only one (1) volume is actually reacted from 4 volumes of CO.

As to the interaction with MnO, then the dissociation tension of CO is more than the dissociation tension of MnO, therefore, in relation to it there is no sufficient potential and cannot be used as reducing reagent. Metal reduction from more tensile oxide compounds as MnO, Cr_2O_3, SiO_2 may be implemented not by CO but directly by solid carbon.

The argument that the direct reduction of metals by solid carbon is carried only through gas phase is a preconceived idea and cannot be proved by direct experimental or theoretical data. MnO and faster oxides are interacting directly with solid carbon on dissociation-adsorption mechanism[12,13], which discloses the capabilities of solid carbon as universal reagent interacting both with high tensile and with less tensile oxides of metals without mediation of CO. Only depending on tension of the metal oxide, the solid carbon interacts under the principle of gradually phase transformation and forms gaseous product of a different composition of CO and CO_2.

Solid carbon may be used not only for iron reduction but also for alloyed metals as Mn and Cr from their tensile oxide compounds. Manganese, chrome and iron oxides interact with solid carbon according to the principle of phase transformation.

$$MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO \rightarrow Mn$$

$$Cr_2O_3 \rightarrow Cr_3O_4 \rightarrow CrO \rightarrow Cr$$

Each phase of oxides has its individual value of dissociation tension. Maximum dissociation tension corresponds to the highest oxides. While decreasing atomic ratio O/Me, the dissociation tension is decreased. That is why only higher oxides of Mn and Cr may interact with CO, but the reaction balance is changed while decreasing the dissociation tensions of the oxides, for example –

$2\ MnO_2 + mCO = Mn_2O_3 + CO_2 + (m\text{-}1)\ CO$

$3\ Mn_2O_3 + m'CO = 2\ Mn_3O_4 + CO_2 + (m'\text{-}1)\ CO$

$4\ Mn_3O_4 + m''CO = 3\ MnO + CO_2 + (m''\text{-}1)\ CO$

Within this range, the values of coefficient m with change in temperature are gradually increased in the following sequence m = 1.22 at t = 500°C; m′ = 1.55 at t = 800°C; m′′ = 4.00 at t = 1000°C.

Further, as Table 1 shows that the dissociation tension of CO at all temperature levels is higher than the dissociation tension of MnO, i.e. CO not only acquires the oxygen oxide but it may be decomposed itself earlier than MnO. Therefore, CO has no any potential capability to interact with MnO.

Only when metals are reduced directly by solid carbon according to principle of gradual-phase transformation, its oxygen potential is carried at a level higher than 1.0, i.e. at the level of 1.25-1.35 depending on mass ratios of oxide phases and system temperature. Actual oxygen potential of carbon may be determined considering the change in the composition of gas being generated, taking into account the dissociation tension individually by phases. Only in this case, stoichiometric carbon consumption for metals reduction may be determined more accurately, that allows avoiding the carbon excess for metal carbonization.

Passing of the metal carbonization process in the reduction and melting process is a turning point in the arrangement for high technology of the production of qualitative metal. Actual stoichiometric carbon consumption for iron reduction may be determined depending on the temperature and change in the composition of gas (CO_2, CO) on relevant phase transformations.

Proposed new theoretical provisions are approved by the results of experimental studies concerning direct reduction of metals by solid carbon. Table 2 shows the chemical compositions of used components of charge materials.

Table 2: Chemical composition of dispersed components of change materials.

Description	Chemical composition, %												
	Fe	FeO	MnO_2	MnO	Cr_2O_3	MgO	SiO_2	Al_2O_3	CaO	BaO	P	S	C
Manganese concentrate	10.20	13.11	42.55	-	-	0.51	31.2	10.28	1.58	0.30	0.21	0.3	-
Chromite concentrate	10.30	13.24	-	-	52.36	18.35	5.72	7.86	0.64	-	0.020	0.013	-
Rolling mill scale	66.72	32.21	-	0.44	-	-	0.51	-	-	-	0.03	0.017	-
Wood coal	-	-	-	-	-	-	0.48	0.12	-	-	-	0.30	98.0

As per the above methodology, the specific stoichiometric carbon consumption for metal reduction has been calculated for each metal oxide component-iron with reduction ratio $R_{Fe} = 0.98$; manganese $R_{Mn} = 0.75$; chrome $R_{Cr} = 0.80$. The following results have been obtained by the equation.

For iron reduction from 100 grams of rolling mill scale, iron and manganese made of manganese concentrate, iron and chrome made of chromite concentrate, the following values of stoichiometric carbon consumption have been obtained, respectively: (1) $g_{C/Fe} = 14,55$ гр; (2) $g_{C/Mn} = 17,88$ гр; (3) $g_{C/Cr} = 12,75$ гр.

Two options of charge materials were made from listed components, such as: (1) from mixture of 100 grams of rolling mill scale at various addition of the manganese concentrate – 5.2; 7.0 and 8.2 grams; (2) from mixture of 100 grams of rolling mill scale with additions of chromite concentrate in the following quantities 4.8; 6.0; 7.15 grams. Composition of each option of charge materials was added by stoichiometric quantity of wood coal calculated for reduction of metals (Fe, Mn and Cr).

Prepared dispersed components of charge materials (fractions < 1.0 mm) were preliminarily granulated for organic adhesive. Further, dried carbon-containing granules were dumped in geometric fire-proof cell and set to the melting furnace.

System temperature was increased upto 600°C with a speed of 100°C/min., at which beginning of gas release was observed. Further, the temperature was increased upto 1200-1250°C with a speed of 20°C/min., at which there was equalizing within 20-30 min. Gas release was completed, after that the temperature was increased up to 1550-1600°C until the system is fully melted.

During melting of charge materials with manganese additions, we obtained the ingot metals of 70.1; 70.4; 70.7 grams. During melting of charge materials with chromite additions we obtained the ingot metals with mass of 70.6; 70.8; 71.0 grams, respectively. Their chemical analysis is given in Table 3.

Table 3: Chemical analysis of melted steel samples

S. No.	Blend with additives	Consumption of 1 g per 100 g of scale	Chemical composition (%)					
			C	Si	Mn	Cr	S	P
1	Mn, Manganese concentrate	5.2	0.36	0.12	1.52	-	0.030	0.02
2		7.0	0.381	0.14	2.05	-	0.023	0.018
3		8.2	0.248	0.17	2.63	-	0.025	0.016
4	Cr , Chromite concentrate	4.8	0.43	0.13	-	1.8	0.02	0.012
5		6.0	0.46	0.16	-	2.42	0.02	0.011
6		7.15	0.51	0.18	-	2.86	0.018	0.011

As seen from Table 3, as a result of reduction melting, we have obtained the metal samples where carbon content is within 0.3-0.5%, which corresponds to steel and restricts the metal carbonization by set stoichiometric carbon consumption.

Cr_2O_3 (compared with Fe_2O_3 and Mn_2O_3) has higher chemical strength and stably interacts with carbon. That is why its direct reduction by carbon up to metallic condition is of concern in terms of metal carbonization.

Original sample of dispersed charge materials is made of 100 grams of chromite concentrate and stoichiometric consumption of wood coal 13.45 grams with fraction < 1.0 mm.

Prepared mixture was dumped in a geometric cell made of quartz tube and set in silicon furnace.

The furnace was heated up to 500^{o}C and work space of the reaction tube was being blown off by clean argon during 4-5 mins. When the system was heated upto 850°C, we observed gas release, which consisted of CO_2 and CO. As per quantity and composition of the gas being released, we determined the quantity (g) of gasified oxygen of charge materials according to equation.

$$\Delta O_{\Gamma} = 0{,}714 \cdot 10^{-2} \vartheta_{\Gamma} (CC + 2CC_{2}) \text{, г}$$

where ϑ_{Γ} - quantity of the gas released (dm^3)

The reduction ratio of charge materials has been determined as dimensionless value from ratio of values as per the formula –

$$\Delta R = \Delta O_{г}/O_{ш},$$

where $\Delta O_{г}$ – total quantity of gasified oxygen in the form of CO_2 and CO during the experiment.

Speed of reduction was determined as per the formula –

$$\omega_{ш} = \Delta R/ \Delta\tau \ (min^{-1})$$

where $\Delta\tau$ – duration of the experiment corresponding to change in the reduction ratio $\Delta R = R_{i+1} - R_{i}$.

According to the results of experimental data, we have set the dependences of ratio and speed of metal reduction from chromite concentrate, which are given in Fig. 1, 2.

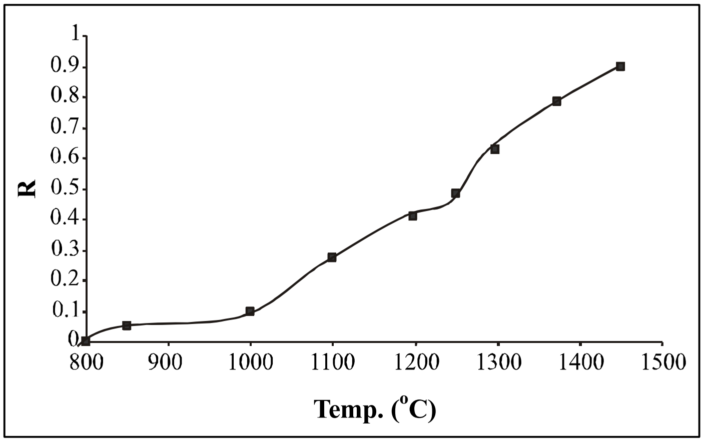

Fig. 1: Change in ratio of reduction of the metals made of chromite ore depending on system temperature

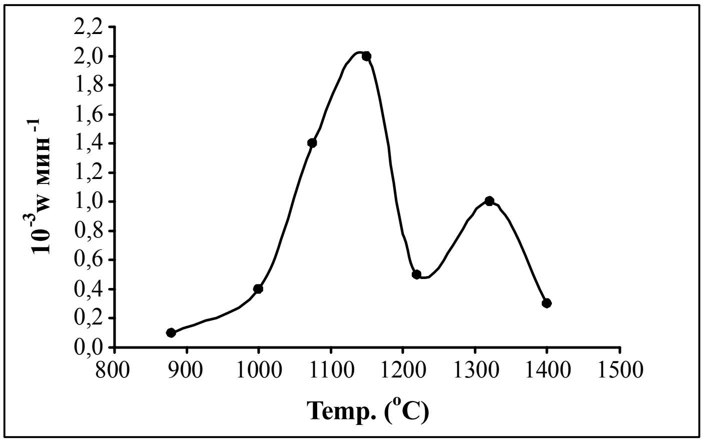

Fig. 2: Dependence of the metal reduction speed on the temperature

As the obtained results show, gas is intensively started to be released at temperature of 850-885°C and keeps on developing with increase of the temperature. Within the range of temperatures of 1000-1100ºC, we have set the increased content of CO_2 in gas up to 7-13% and metal reduction speed up to 0.002 min^{-1}. While time was expiring, the concentration of CO_2 has been decreased furthermore. At 1200°C it was near to zero, while concentration of CO was increased being near to 100%, that proves the decrease up to zero of reduction work of CO. The second maximum of the speed of the chrome reduction at increase of temperature upto 1300ºC has been made due to direct interaction of carbon with lower oxides (CrO). Further decrease of the reduction speed is associated with completion of the metallization process. Along with it, chrome is oxycarbide generating metal, i.e. metallized product simultaneously contains carbide of Cr_3C_2 and CrO, which are usually distributed locally in the volume of metallized product. They may interact by the reactions.

$$2Cr_3C_2 + 4CrO = Cr_7C_3 + CO$$

$$Cr_7C_3 + 3CrO = 10[Cr]+ 3CO$$

The reactions in solid phase system are carried by diffusional transfer, therefore, they require lasting equalizing of the system.

Analysis of metallized intermediate products shows almost full reduction of iron and chrome by 90% and silicon by 5-8%. Chrome carbides in the system may be generated in the presence of insignificant oxide inclusions of CrO. As the analysis of melted metal samples shows (Table 3), during the process of high temperature heating and melting the carbide interaction in the system is carried out under the reaction.

Excess of carbon and lower oxide (CrO), i.e. generation of oxycarbides in the metallized product is intermediate condition of metallized product in the system. Correct and sufficiently accurate calculation of the stoichiometric solid carbon consumption, composition of charge materials, in spite of generation of oxycarbide compounds in the intermediate product at high temperature melting will inevitably lead to the interaction of carbides with oxides and limitation of the carbide generation process.

CONCLUSION

Oxides of iron, manganese and chrome in dispersed carbon-containing charge materials interact with solid carbon on gradually phase transformations. Temperature of the start of reaction has been set at 600ºC for higher oxides of iron and manganese and has being increased while transferring the higher oxides to the lower with consequent and regular change in composition of CO_2 and CO. Metal carbonization is related to accumulation of metallic phase and carbon excess at the stage of completion of the reducing processes. Control of stoichiometric carbon consumption (based on interaction of oxides by solid carbon in accordance with change of tensions of their dissociation by phases) resolves the problem of the metal carbonization.

At higher temperature of reduction and higher dissociation tension of higher oxides of chrome (Cr_2O_3) due to increased concentration of CO_2 the carbon excess may be generated, which results in carbide generation in any individual areas of metallized product during localization of residual portion of lower oxides (CrO). Additional heating and equalizing of oxycarbide metallic system allows the interaction of carbides with residual CrO and, thus, restricts the metal carbonization.

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