

Reductive Smelting of Iron Ore

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Abstract—The carburization of iron is described. Means of preventing carburization by direct reduction of the metal with solid carbon are considered. The interaction between iron, manganese, and chromium oxides and solid carbon is studied in terms of the associated change in dissociation pressure. On that basis, the carburization of iron may be prevented.

Keywords: steel production, carburization, solid carbon, carbide formation, dissociation, reduction

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Iron ore for the production of hot metal not only contains iron but also oxides of manganese, chromium, and vanadium. These metals are alloying elements of steel, and their concentration determines the value of the initial ore. However, in two-stage production of steel—blast-furnace production of hot metal followed by oxidative smelting of the hot metal in the oxygen converter to produce raw steel—the alloying metals cannot be extracted from the ore into the steel. Oxidative smelting to remove carbon leads to unavoidable oxidation of the reduced alloying metals in the iron melt, which enter the slag. The subsequent process depends on the oxidation of the smelter slag.

This slag is mainly discarded in tailings, with undesirable environmental impact. Only vanadium-bearing slag is diverted for processing in the production of ferrovandium slag, since vanadium is very valuable. The reserves of manganese and chromite ore could be processed to ferromanganese and ferrochrome at ferroalloy plants. Only vanadium from the iron ore enters the raw steel, by a roundabout route—as a result of ferrovandium production. Manganese and chromium are lost in the tailings slag. In the reduction and alloying of steel with manganese and chromium, we use ferromanganese and ferrochrome produced at special plants for processing manganese and chromite concentrates. This organization of metallurgical production may be found around the world. However, it is environmentally undesirable. By preventing carburization of the metal, oxidative smelting may be eliminated, and a single-stage metallurgical process may be developed, with the transfer of all the alloying metals from the ore to the final steel.

The carburization of iron may be limited in the reductive roasting of granules by hot reducing gas.

However, the reducing potential of CO and H₂ is insufficient to reduce the strong oxides of the alloying metals. Therefore, solid carbon must be added to the batch in order to reduce the iron and the oxides of the alloying metals. The possibility of complete reduction of all the metals by this means conflicts with the prevailing notion that the reaction of solid carbon with metal oxides is limited by the contact–diffusion mechanism and therefore development of direct metal reduction by solid carbon is only possible through the gas phase, with the formation solely of CO [1].

However, reduction of strong metal oxides by this mechanism is limited by their chemical strength and by the insufficient potential of CO [2]. In recent years, there has been growing interest in the use of solid carbon—coal and carbon-bearing reagents—for the production of metals and reduced intermediate products [3–7]. These new processes, while they differ in organization, yield a carburized intermediate product. The organization of new processes using solid carbon has been driven by economic considerations, and we may say that practice has outrun theory in this area. Solid carbon is appealing not only because of its availability but also because of its diverse properties, which have yet to be fully explored.

The direct reduction of iron by solid carbon results in the formation not only of CO but also of significant quantities of CO₂, as is clear from the proposed mechanisms of the process and theoretical principles [8, 9]. The reduction of iron with the formation of CO₂ consumes half as much carbon as the process with the formation of CO. Therefore, calculation of the carbon consumption on the basis of reduction of iron with the formation solely of CO will create an excess of carbon, which carburizes the metal. On the basis of the new

Table 1. Dissociation pressure ($\log P_{O_2}$) of oxides as a function of the temperature [11]

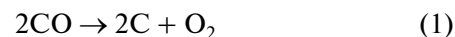
Dissociation process	$\log P_{O_2}$ at temperature, K			
	1200	1300	1400	1500
$FeO \rightarrow Fe + 0.5O_2$	-16	-14.4	-12.9	-11.6
$CO \rightarrow C + 0.5O_2$	-20.3	-19.6	-18.9	-18.4
$MnO \rightarrow Mn + 0.5O_2$	-30.6	-28.68	-26.73	-24.58

mechanism with the formation of both CO_2 and CO , we may eliminate or limit the carburization of the iron. In that case, the production of steel will be possible without hot-metal production.

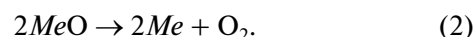
By research on the properties of solid carbon and its reaction with metal oxides at the level not of the atomic–molecular exchange but of electron–ion exchange between solid particles, we may organize and limit the carburization of metals. In controlling the reduction process, this approach to the direct reaction of carbon with metal oxides is not always adopted. Nevertheless, we may say that carbon is not only an active reducing agent but also an active carbide-forming element. Carbide formation follows the reduction of oxides as metallic phase is formed and accumulates. Therefore, it is obvious that carbide formation is due, first, to the appearance of metal and, second, to the appearance of excess carbon in the $MeO-C-Me-(CO, CO_2)$ system. The first step is the reduction of metals by carbon, with the formation of CO and CO_2 . As the process develops, the proportion of metallic phase increases at the expense of the oxides. Eventually, two phases C and Me will remain in the system. Then, a new phase appears: the metal carbide Me_3C or a solution of carbon in metal. Hence, we conclude that the carburization of the metal is associated with excess carbon in the system and occurs when the reduction of the metal is complete. As we see, the limitation of carburization depends on determining the stoichiometric carbon consumption and developing a precise method for its calculation.

The reaction of solid carbon with metal oxides may be described by a dissociation and adsorption mechanism [10]. Adsorption here relates not only to the gas flux in the bed but to the gas phase released in the dissociation of complex chemical compounds (oxides, carbonates, etc.). Dissociation implies the adsorption and chemisorption of the gases formed at the surface of the solid particles. The initial stage—dissociation of the chemical compounds—is a phenomenological process involving complex materials. The liberation of gas at the surface of the solid particles may occur through the formation of layers at the surface: the inner layer corresponds to chemisorption and the outer layer to adsorption. The mass transfer of oxygen from the oxides to the reducing agents occurs from these layers, regardless of whether the reducing agent

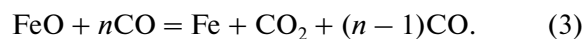
is gaseous CO or solid carbon. In any case, the reaction of CO occurs to the extent that the pressure of dissociation is less for the process



than for



Comparison of the change in dissociation pressure of metal oxides and CO as a function of temperatures shows the limits on their reaction (Table 1). As is evident from Table 1, the dissociation pressure of CO is considerably less than that of FeO but significant greater than that of MnO . Therefore, the reduction of iron from FeO by CO proceeds in an equilibrium reaction and may culminate in the formation of metallic iron



The value of n indicates the excess of CO required for the reaction to proceed from left to right. At equilibrium in Eq. (3)

$$\eta_{CO} = CO_2 / (CO + CO_2). \quad (4)$$

At 1000–1100 K, $\eta_{CO} = 0.20$ – 0.25 . The reaction proceeds without change in gas volume. Therefore, we may write

$$\eta_{CO} = CO_2 / (nCO) = 0.25$$

$$\text{and } n = CO_2 / 0.25CO = 1 / 0.25 = 4.0.$$

Thus, out of four volumes of CO , one will participate in the reaction.

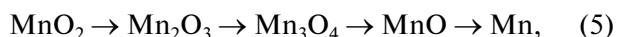
Because the dissociation pressure of CO is greater than that of MnO , Co does not have significant reducing potential with respect to Mn and cannot be used as a reducing agent. The reduction of metals from the strong oxides MnO , Cr_2O_3 , and SiO_2 requires direct reduction by solid carbon, rather than by CO . The a priori assertion that the direct reduction of metals by solid carbon only proceeds through the gas phase cannot be confirmed experimentally or theoretically. Strong oxides such as MnO react directly with solid carbon by a dissociation and adsorption mechanism [11, 12]. That indicates the potential of solid carbon as a universal reagent capable of reacting with metal oxides by means of the fluxes of electrons, ions, and mesons formed on heating, without the intervention of CO . The solid carbon interacts with the metal oxides on the principle of successive phase transfor-

Table 2. Chemical composition (wt %) of batch components

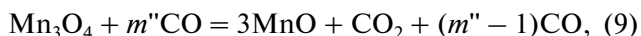
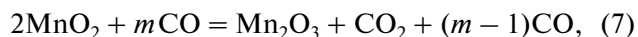
Component	Fe	FeO	MnO ₂	MnO	Cr ₂ O ₃	MgO	SiO ₂	Al ₂ O ₃	CaO	BaO	P	S	C
Manganese concentrate	10.20	13.11	42.55	—	—	0.51	31.2	10.28	1.58	0.30	0.21	0.30	—
Chromite concentrate	10.30	13.24	—	—	52.36	18.35	0.72	7.86	0.6	—	0.02	0.01	—
Rolling scale	66.72	32.21	—	0.44	—	—	0.51	—	—	—	0.03	0.017	—
Charcoal	—	—	—	—	—	—	0.48	0.12	—	—	—	0.30	98.0

mation and forms a gaseous product with different proportions of CO and CO₂, depending on the strength of the metal oxide.

We may use solid carbon not only to reduce iron but also to reduce the alloying elements Mn and Cr from their strong oxides. Like iron oxides, oxides of manganese and chromium react with the solid carbon on the principle of successive phase transformation



Each phase has its own dissociation pressure. The highest oxide has the greatest dissociation pressure. With decrease in the atomic ratio O/Me, the dissociation pressure declines. Therefore, only the higher Mn and Cr oxides may react with CO. The equilibrium of the reaction changes with decrease in dissociation pressure of the oxides. In the series



we note gradual increase in m with rise in the temperature: $m = 1.22$ at 500°C; $m' = 1.55$ at 800°C; $m'' = 4.00$ at 1000°C. As is evident from Table 1, the dissociation pressure of CO is higher than that of MnO at all temperatures. In other words, CO not only acquires oxygen from the oxide, but is able to dissociate sooner than MnO. Therefore, CO has no potential for reaction with MnO.

In the direct reduction of the metals by solid carbon on the principle of successive phase transformation, its oxygen potential is 1.25–1.35, depending on the proportions of the oxides and the temperature in the system. In determining the actual oxygen potential, the change in composition of the gas formed and the dissociation pressure of the successive phases must be taken into account. In that case, the stoichiometric consumption of solid carbon in the reduction of metals may be determined with sufficient accuracy. On that basis, excess carbon may be eliminated, and so carburization of the iron may be prevented.

Prevention of the carburization of iron in reductive smelting represents a turning point in the organization of steel production. The actual stoichiometric carbon

consumption in the reduction of iron may be determined as a function of the temperature and the gas composition (CO₂, CO) in the corresponding phase transitions. These theoretical principles are confirmed by experiments on the direct reduction of metals by solid carbon. The chemical composition of the batch components is summarized in Table 2.

By the proposed method, we may calculate the stoichiometric carbon consumption for the reduction of metal from each metal-oxide component of the batch: iron with degree of reduction $R_{\text{Fe}} = 0.98$; manganese with $R_{\text{Mn}} = 0.75$; and chromium with $R_{\text{Cr}} = 0.80$. Two types of batch are formulated on the basis of these components and rolling scale:

(1) a mixture of 100 g rolling scale with 5.2, 7.0, or 8.2 g manganese concentrate;

(2) a mixture of 100 g rolling scale with 4.8, 6.0, or 7.15 g chromite concentrate.

Each batch includes a stoichiometric proportion of charcoal calculated for the reduction of the metal (Fe, Mn, and Cr).

The batch components (<1.0 mm fraction) are preliminarily granulated with organic binder. The dried carbon-bearing granules are charged in a sealed refractory cell, which is placed in a smelting furnace. The temperature is raised at 50°C/min to 600°C, when gas liberation begins. Then the temperature is raised at 20°C/min to 1200–1250°C and held at the final temperature for 20–30 min. After gas liberation has ended, the temperature is raised to 1550–1600°C, to ensure complete melting of the system. In smelting the batch with Mn, metal ingots of 70.1, 70.4, and 70.7 g are obtained. In smelting the batch with chromite, metal ingots of 70.6, 70.8, and 71.0 g are obtained. Their chemical analysis is shown in Table 3. As we see, reductive smelting produces metal samples with 0.3–0.5% C. That corresponds to steel. Carburization is limited by the specified stoichiometric carbon consumption.

In comparison with Fe₂O₃ and Mn₂O₃, the oxide Cr₂O₃ is chemically stronger and reacts stably with carbon. Therefore, its direct reduction to metal by carbon is of interest in the carburization of metal. The initial batch sample (<1.0 mm fraction) consists of chromite concentrate (100 g) and a stoichiometric content of charcoal (13.45 g). This mixture is placed in

Table 3. Chemical composition (wt %) of steel samples produced

Batch with	Consumption (g) per 100 g of scale	C	Si	Mn	Cr	S	P
Manganese	5.2	0.36	0.12	1.52	—	0.030	0.020
	7.0	0.381	0.14	2.05	—	0.023	0.018
	8.2	0.248	0.17	2.63	—	0.025	0.016
Chromium	4.8	0.43	0.13	—	1.80	0.020	0.012
	6.0	0.46	0.16	—	2.42	0.02	0.011
	7.15	0.51	0.18	—	2.86	0.018	0.011

a sealed cell (a quartz tube), which is introduced in a Silit furnace. The furnace is heated to 500°C; for 4–5 min, pure argon is blown into the working space of the tube. On heating to 850°C, gas liberation is observed (CO + CO₂). From the quantity and composition of the gas, its content (g) of oxygen from the batch is determined

$$\Delta O_g = 0.714 \times 10^{-2} \vartheta_g (\text{CO} + 2\text{CO}_2). \quad (10)$$

Here ϑ_g is the quantity of gas liberated, dm³.

The degree of reduction of the batch is determined in dimensionless form

$$\Delta R = \Delta O_g / O_b, \quad (11)$$

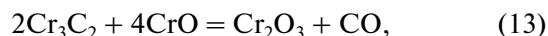
where ΔO_g is the total quantity of oxygen from the batch converted to CO₂ and CO during the experiment; O_b is the initial oxygen content in the batch.

The reduction rate (min⁻¹) is

$$\omega_b = \Delta R / \Delta \tau, \quad (12)$$

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

From the experimental data, we may establish the degree of reduction (Fig. 1a) and rate of reduction (Fig. 1b) of metals from the chromite concentrate. As we see in Fig. 1, intense gas liberation begins at 850–885°C and continues with increase in the temperature. In the range 1000–1100°C, the CO₂ content in the gas rises to 7–13%, while the reduction rate rises to 0.002 min⁻¹. Over time, the CO₂ concentration falls. At 1200°C, it approaches zero, whereas the CO concentration approaches 100%. This corresponds to zero reducing action of the CO. The second peak in the reduction rate of chromium at 1300°C is due to direct reaction of carbon with CrO. The subsequent decrease in the reduction rate is associated with the end of reduction. Chromium forms both oxides and carbides. Therefore, the reduced product includes both Cr₃C₂ and CrO, which are usually distributed within local volumes. They may react



In the solid-phase system, these reactions proceed by diffusional exchange. Therefore, prolonged holding of the system is required. Analysis of the reduced intermediate products shows practically complete reduction of the iron, 90% reduction of the chromium, and 5–8% reduction of silicon. The formation of chromium carbides in the system may occur with a small content of CrO inclusions. Analysis of the smelted samples (Table 3) shows that Eq. (14) is present in the system with high temperature heating and melting.

An excess of carbon and the lower oxide CrO—that is, the formation of oxycarbides in the reduced

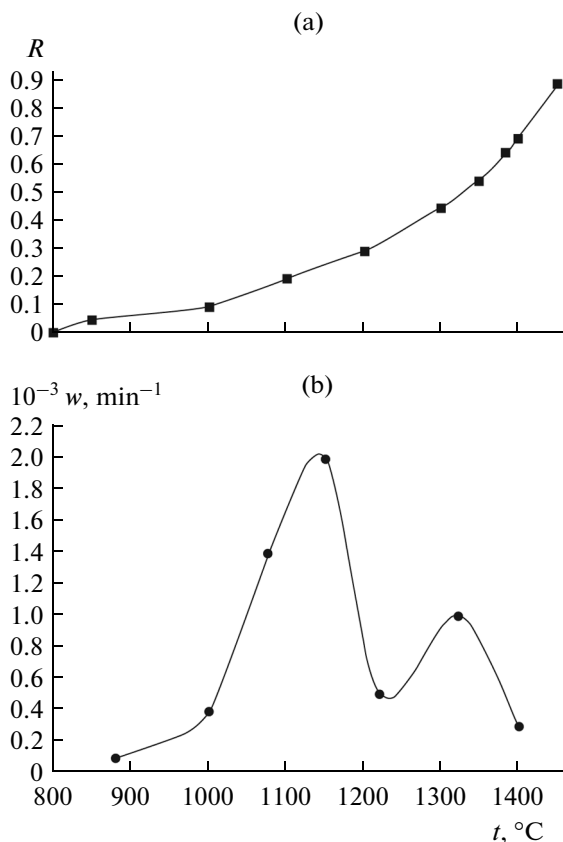


Fig. 1. Degree of reduction (a) and reduction rate (b) of metals from chromite ore as a function of the temperature.

product—may be regarded as an intermediate state. If the stoichiometric consumption of solid carbon and the batch composition are correctly and precisely calculated, despite the formation of oxycarbide compounds in the intermediate product at high-temperatures, the carbides will inevitably react with oxides, and the carbide content will be limited.

CONCLUSIONS

In carbon-bearing batch (consisting of small fractions), iron, manganese, and chromium oxides will actively react with solid carbon on the principle of successive phase transformation. The reaction begins at 600°C for higher oxides of iron and manganese and at high temperatures for lower oxides, with corresponding change in the gas composition ($\text{CO}_2 + \text{CO}$). The carburization of iron is associated with the accumulation of metal phase and excess carbon at the end of reduction. By regulating the stoichiometric carbon consumption, the carburization of iron may be prevented in the reaction of oxides with solid carbon, on the principle of successive phase transformation (in terms of their different dissociation pressures).

At higher temperatures, with higher dissociation pressure of Cr_2O_3 on account of the increased CO_2 content in the gas, excess carbon may appear. That leads to carbide formation in individual zones of the product, with localization of the residual CrO . Additional heating and holding of this system results in reaction of the carbides with CrO ; once again, carburization is limited.

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