REDUCTION OF IRON OXIDES WITH CARBON SATURATED LIQUID IRON

Miroslaw Karbowniczek & Piotr Migas
AGH University of Science & Technology, Poland

ABSTRACT

The process of iron oxide reduction from liquid slag, its mechanism and kinetics still has to be investigated and analyzed more thoroughly. There have been several investigations on this topic in the last century, both from thermodynamic and kinetic points of view. Generally, the following reducers have been considered: solid carbon, gaseous carbon monoxide and carbon dissolved in molten iron. Industrially, the most common processes using solid and gaseous carbon reducers are the blast furnace and the EAF process [1]. It seems reasonable to undertake research to describe the mechanism and the kinetics of reduction by carbon diluted in liquid iron and also to analyze the possibilities of using other reducers such as silicon. These reduction mechanisms can be used to reutilize the existing slag heaps and also the slags generated by current production processes. This can have a positive influence on the natural environment and on the recycling of elements such as Fe, Cr and Mn.

The article presents the results of research concerning the reduction of iron oxides by molten silicon present in the iron solution. Experiments were conducted in an induction furnace with 25 kg metallic charges and slags containing practically 100% FeO. The metal bath contained approximately 4% of C and 0.4% of Si. Tests were conducted at different temperatures and times lengths. Results from testing were used to develop a mechanism for the reduction process.

INTRODUCTION

Metallurgical slags are multicomponent phases which are formed directly from the input materials or sometimes modified by the addition of fluxes. In addition, industrial slags´compositions change during the process.

Reduction processes involving metal oxides (Fe, Mn, Zn, Cr, Ti) occur in metallurgical primary processes as well as in the recycling of the industrial wastes generated during these processes. Such is the case for the blast furnace process, refining of pig iron and steel and the recovery of metals from slags [2].

Consequently, detailed knowledge of the reduction mechanisms and their kinetics is extremely significant. Despite the fact that much research has been conducted on these subjects, the phenomena pertaining to FeO reduction in liquid slag phases are not fully defined and clear. It seems essential to thoroughly describe the interaction of liquid slag and metal phases when they coexist in industrial systems; this is very relevant in terms of their optimization and control. Chemical composition, temperature and time are the necessary parameters of such descriptions. [1].

Description of slag metal interactions is very complex, in view of the multiplicity of variables, parameters and the time related changes in industrial processes. Metal, slag and gas compositions are functions of such parameters as time, pressure, surface area, mixing, etc.

In recent years, special attention has been given to the reduction processes of iron oxides in the liquid phase slag. In spite of these efforts, it seems that the phenomena have not been fully understood and the mathematical, physical and chemical descriptions are not clear enough. Mathematical models have to take into account mass and heat transfer in heterogeneous system [3]; this is not easy to achieve.

Iron oxide reduction in a liquid slag phase is used in the production of iron and steel (Midrex, Romelt) and also in the steelworks´ waste utilization, e.g. the utilization of slag, slime, dust from the steelmaking and blast furnace processes [4, 5, 6]. A comprehensive presentation of the phenomena, the ability to influence the mechanism and kinetics of the process as well as the description of the necessary conditions can bring tangible benefits. They may include, for instance, a decrease in energy consumption or an increase in their economic effectiveness. Thanks to such knowledge, it could be possible to optimize already existing metallurgical processes. Also, it might be possible to develop new technology for pig iron and steel production as well as to recover iron from post-production waste.

Laboratory results of the reduction ranges of slag containing iron oxides are presented in this paper. The reduction is conducted by means of oxidation of silicon and other components of the iron solution containing chrome and nickel [6].

METHODOLOGY OF RESEARCH ON THE REDUCTION OF FeO IN SLAG

So far, the research into the system liquid iron – FeO containing slag phase, has been focused on the reduction of FeO by means of a carbon reducer. The latter includes carbon in the form of solid particles as well as that dissolved in the iron melt. The paper presents the results of the analysis of the system: liquid iron – slag, where the iron had a high content of chrome and nickel and the slag was rich in iron oxides. Silicon dissolved in the iron was oxidised by reaction with the iron oxide in slag.

Research was conducted in a 25 kg capacity induction furnace. Electric parameters of the induction furnace were: 25 kW power delivered to the coil, intensity 1 kA and frequency 8 kHz. Crucibles (84% Al_2O_3, 16% MgO, Figure 1) were lined with a high alumina ramming material, such as Rodarox mix 17 and others with an acid material such as Silica mix 7 (98-99% SiO_2).

The procedure for the experiments included melting a pig iron charge (4% C, 0.5% Mn, and 0.2% Si) in the crucible, followed by sampling to determine the starting composition and temperature measurement with a PtRh 10 immersion thermocouple. After these steps, 500 g of mill scale (98.2% FeO, 0.9% SiO_2, 0.5% MnO and 0.4% Al_2O_3) was placed on the surface of the metal. A spoon slag sample was taken after melting, 5 minutes after adding the scale. This procedure was repeated until a total of 2000 g of mill scale had been added. A second series of tests included the addition of four portions of 500 g scale every 4 minutes; slag samples were taken every 2 minutes.

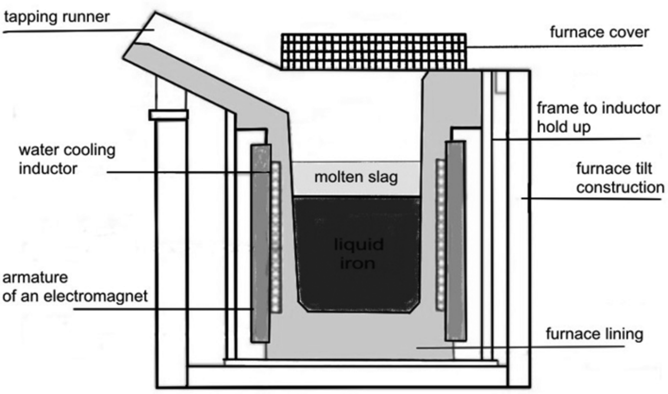


Figure 1: Experimental setup

Such mill scale addition onto the surface of the liquid slag was done in order to oxidize silicon from the iron solution so as to reach its lowest level. Four series of experimental melts were conducted, two for each kind of refractory lining. Test parameters are listed in Table 1.

Table 1: Test Parameters

Test	Samples No.	Time, [min]	Quantity of iron oxide, [g]	Temp., [°C]	Test	Samples No.	Time, [min]	Quantity of iron oxide, [g]	Temp., [°C]
I	1	5	500	1318	II	5	4	500	1296
	2	10	500	-		6	8	500	-
	3	15	500	-		7	12	500	-
	4	20	500	1352		8	16	500	1398
III	9	2	500	1363	IV	17	2	500	1344
	10	4	-	-		18	4	-	-
	11	6	500	-		19	6	500	-
	12	8	-	-		20	8	-	-
	13	10	500	-		21	10	500	-
	14	12				22	12		
	15	14	500			23	14	500	
	16	16		1366		24	16		1326

Tests I and II were conducted with an acid lining while tests III and IV with a high-alumina lining.

ANALYSIS OF RESULTS OF SLAG FeO REDUCTION

Slag compositions for all tests are presented in Table 2.

Table 2: Chemical composition of slags

Samples No.	**Chemical composition of slag, %**							**B1**	**B3**
	FeO	**SiO_2**	**CaO**	**MnO**	**Cr_2O_3**	**Al_2O_3**	**MgO**		
1	59.00	23.51	7.38	4.57	4.89	0.30	0.35	0.314	0.324
2	65.59	19.47	5.73	4.25	4.35	0.19	0.41	0.294	0.312
3	69.35	16.77	6.22	3.62	3.41	0.20	0.43	0.371	0.392
4	69.97	16.23	6.44	3.30	3.44	0.22	0.40	0.397	0.415
5	55.66	28.77	5.69	5.51	3.86	0.24	0.27	0.198	0.206
6	58.89	25.09	7.17	4.78	3.39	0.31	0.36	0.286	0.297
7	65.64	20.85	6.70	3.83	2.44	0.16	0.37	0.321	0.336
8	72.03	20.14	3.29	3.33	0.70	0.08	0.42	0.163	0.183
9	62.09	27.28	2.21	6.89	0	1.17	0.35	0.081	0.090
10	52.41	35.48	1.98	8.38	0.21	1.24	0.30	0.056	0.062
11	73.49	18.72	1.87	4.68	0	0.73	0.50	0.100	0.122
12	69.47	21.02	2.59	5.24	0	1.19	0.49	0.123	0.139
13	77.89	15.01	1.56	4.02	0	0.98	0.55	0.104	0.132
14	76.41	15.99	1.62	4.25	0	1.15	0.57	0.101	0.128
15	83.86	10.02	1.25	3.07	0	1.14	0.66	0.124	0.170
16	81.85	11.79	1.41	3.33	0	1.01	0.62	0.119	0.159
17	55.60	16.06	14.13	3.02	9.59	1.10	0.51	0.880	0.853
18	52.58	16.78	15.64	3.11	10.24	1.15	0.49	0.932	0.899
19	57.17	14.31	12.00	3.20	11.81	1.01	0.50	0.838	0.816
20	53.24	14.70	13.14	3.29	14.18	0.97	0.48	0.894	0.870
21	58.79	13.14	10.81	3.14	12.44	1.12	0.56	0.823	0.798
22	52.16	13.79	13.88	3.20	15.35	1.12	0.50	1.007	0.965
23	64.75	10.20	10.15	2.79	10.83	0.74	0.53	0.995	0.977
24	58.58	11.73	12.07	2.87	13.19	1.01	0.56	1.029	0.991

* $B1 = CaO/SiO_2$; $B3 = (CaO + MgO)/(SiO_2 + Al_2O_3)$

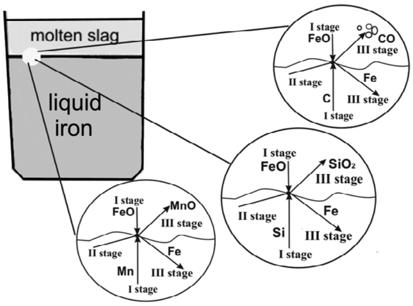
Data in Table 2 show that slags from tests I and II are of the fayalite type; they also contain about 6% CaO, 4% MnO and 3% of Cr_2O_3. Tests in series III led to slags with about 2% CaO and 4% MnO. On the other hand, tests in series IV had slags with 13% CaO, 3% MnO and 12% Cr_2O_3. The content of Al_2O_3 and MgO in all tests remained under 1%.

Based on the chemical composition of the metal bath (Table 3), one can assume that the oxidation of silicon from the metal bath proceeded thanks to the reduction of the iron oxide in slag as a result of the interaction with the metal bath components, mainly silicon, manganese and carbon. Slag foaming was not observed. This may be due to a small quantity of FeO being reduced from the slag or more probably that the viscosity of slag was small. The slags were not tested physically nor chemically; however, fluid slags were observed during all the tests. The metal – slag interface was about 0,0254 m^2 for all tests.

Table 3: Chemical composition of metal during the experimental melts

Samples No.	Chemical composition of metal, %								Quantity of metal, [g]
	C	Mn	Si	P	S	Cr	Ni	Al	
1	4.22	0.152	0.286	0.086	0.017	0.149	0.047	0.0014	19700
4	3.27	0.020	0.025	0.057	0.011	0.041	0.121	0.0024	
5	4.35	0.183	0.388	0.085	0.020	0.104	0.077	0.0017	19700
8	3.67	0.020	0.025	0.046	0.016	0.023	0.077	0.0025	
9	4.01	0.164	0.258	0.222	0.028	0.162	0.090	0.0030	18000
16	3.56	0.025	0.025	0.119	0.003	0.009	0.080	0.0020	
17	4.11	0.177	0.195	0.111	0.025	0.600	0.203	0.0020	17000
24	3.70	0.032	0.061	0.073	0.031	0.208	0.112	0.0020	

A model for iron oxide reduction with silicon and other elements dissolved in molten iron is shown below (Figure 2).



$$2(\mathrm{FeO}) + [\mathrm{Si}] = 2[\mathrm{Fe}] + (\mathrm{SiO_2}) \quad (1)$$

$$(\mathrm{FeO}) + [\mathrm{C}] = [\mathrm{Fe}] + \{\mathrm{CO}\} \quad (2)$$

$$(\mathrm{FeO}) + \{\mathrm{CO}\} = [\mathrm{Fe}] + \{\mathrm{CO_2}\} \quad (3)$$

$$(\mathrm{FeO}) + [\mathrm{Mn}] = [\mathrm{Fe}] + (\mathrm{MnO}) \quad (4)$$

Figure 2: Model for iron oxide reduction in slag

It was assumed that the process has three stages:

- Transport of the reactants to the reaction sites
- Reaction itself
- Transport of the reaction products as metal and slag.

The factor limiting the rate of the first and third stages is the reactants and products of the reaction; the limiting factor of the reactions is the so called constant rate.

The study of the kinetics of the chemical process occurring is related to the model and mechanisms we have assumed. Process stages take place in succession; this is why the slowest stage has the greatest impact on the rate of the entire process. As it happens with the reduction of FeO in the liquid iron solution by carbon, there are no clear indications to suggest which stage is the limiting one. However, it is most commonly assumed that the slowest stage is the diffusion of FeO in the liquid phase. Mathematically speaking, the description of the diffusion process is represented by Fick's equations. The rate of diffusion depends on the concentration difference and the physicochemical characteristics of the reaction medium. The reaction itself is described by kinetic equations which are functions of the order of reaction and of the interface surface. The study of the rate of iron oxide reduction can refer to the kinetics of the reaction itself or the rate of the entire process of iron oxide reduction in industrial systems [1, 2].

The slag mass in each of the stages was calculated on the basis of its chemical composition. Then it was assumed that the FeO decrease is related to the reduction process involving silicon and other elements such as Mn and C. The constant rates for these processes were calculated using the following formula:

$$\frac{-\,dn_{FeO}}{dt} = k\,A\,C^{m} \tag{5}$$

where n_{FeO} /dt is the FeO mass flow during reduction, k is the reaction rate constant, A is the surface area, C is the concentration and m is the order of the reaction order. Solving the equation leads to the following relation:

$$k = 2{,}303/A * t^{*} \log{(n_o/n)} \tag{6}$$

where t is time, n_0 and n are the initial and final FeO concentrations in slag, respectively.

Results from the calculations are presented in Table 4, while Figures 3, 4 and 5 show the values for the total FeO decrease in slag by the reduction by silicon and other elements. The values refer to all the experimental series and also depict the trend lines for each.

Table 4 and Figure 3 show a larger FeO decrease in test I, a slight FeO decrease in test IV, a practically constant value in test II and a slight decrease in test III.

The data in table 4 and Figure 4 show that in all tests there is a decrease in the rate of FeO loss as far as the reduction in iron solution by silicon is concerned. A similar nature of changes was obtained for test I and II. The FeO loss curves are more gentle in the case of test III and IV. The changes in ΔFeO_{Si} reach similar values of the FeO loss (a plateau) approx. 10-12 minutes later than in the case of test II or IV and they are on a higher level. As far as test III and IV are concerned, the changes in ΔFeO_{Si} happen sooner than for the other tests (I and II). The values of ΔFeO_{Si} are lower. The nature and the extent of changes in the ΔFeO_{Si} values can give evidence to the progress in the reduction of iron oxides and the level of desiliconization of the entire iron. The FeO reduction by silicon is the fastest in case of test III and IV. It is related to the chemical composition of slag. The results show that in the case of test III the slag is almost entirely of the fayalite type with slight admixtures of other components such as FeO and SiO_2.

Such slag is characterized by the smallest melting temperature and the smallest viscosity in this environment. In the case of test IV the slag contained higher amount of CaO and Cr_2O_3. In such conditions calcium orthosilicates are formed. They diminish the amount of *free* silica, which consequently speeds up the FeO reduction. Chrome oxides in metallurgical slag have a significant impact on its physicochemical characteristics (viscosity in particular). In the case of the tested slag (test IV), the content of Cr_2O_3, which was within the range of 10-12%, significantly reduced the viscosity.

Table 4: The calculated FeO loss and the constant rate during the experimental melts

Samples No.	ΔFeO_{total}, [g]	constant k for ΔFeO_{total}, [g*m-2*s-1]	ΔFeOSi, [g]	constant k for ΔFeO_{Si}, [g*m-2*s-1]	ΔFeO_{other} (including Mn), [g]	constant k for ΔFeO_{other}, [g*m-2*s-1]
1	289.34	0.742542	201.52	0.695153	87.82	0.586330
2	403.98	0.393135	86.33	0.292041	220.36	0.353431
3	569.33	0.277074	42.56	0.163813	292.08	0.247926
4	680.37	0.213642	48.38	0.127058	340.57	0.190976
5	311.63	0.940335	233.69	0.893198	77.94	0.713374
6	354.85	0.480802	107.33	0.382888	247.52	0.451306
7	341.48	0.318438	34.07	0.192620	307.41	0.312700
8	345.10	0.239260	59.01	0.166950	286.09	0.231582
9	282.65	1.848693	229.24	1.780095	53.41	1.302937

10	49.77	0.639902	43.02	0.616027	6.75	0.312746
11	211.71	0.584681	6.41	0.202879	205.30	0.581323
12	37.92	0.297689	24.88	0.263180	13.04	0.210284
13	245.49	0.360505	7.39	0.130986	238.10	0.358504
14	21.66	0.167894	16.00	0.151346	5.66	0.094672
15	203.41	0.248706	5.38	0.098732	258.61	0.259939
16	43.72	0.154670	40.54	0.151577	3.18	0.047377
17	288.50	1.855401	146.64	1.633755	141.86	1.622892
18	15.18	0.445439	3.77	0.217369	11.41	0.398670
19	345.28	0.638083	60.56	0.448029	284.72	0.617028
20	27.54	0.271488	3.36	0.099299	24.17	0.260824
21	378.10	0.388799	24.53	0.209611	353.57	0.384405
22	61.51	0.224862	4.72	0.084756	56.78	0.220500
23	433.89	0.284153	10.83	0.082340	507.38	0.291474
24	65.09	0.170965	14.87	0.110520	50.22	0.160345

Figure 5 presents the changes in the FeO decrease resulting from the reduction by means of elements (Mn and C) dissolved in iron solution other than silicon. A higher loss of FeO was observed for all tests. The reduction of iron oxides proceeds during the entire duration of the tests. In the initial stage silicon plays the leading role in the reduction process. Other elements are less important. In the further stages, when the amount of silicon in the iron solution diminishes, its role becomes smaller and other elements gain importance.

Table 4 shows the calculated rate constant of reactions which can be useful in future research into the iron oxide reduction. They can help construct mathematical models of the process as well as design the industrial technology. As can be seen from the results the constant rate of the reduction reaction diminishes subsequently. It means that the intensity of the process diminishes when the amount of the reducer decreases in the iron solution. It's appear, that if differences of elements concentrations decrease the intensity of diffusion decrease too, what the reason of process rate decrease is. Results and observations from tests show that the controlling stage of process is the diffusion of reagents.

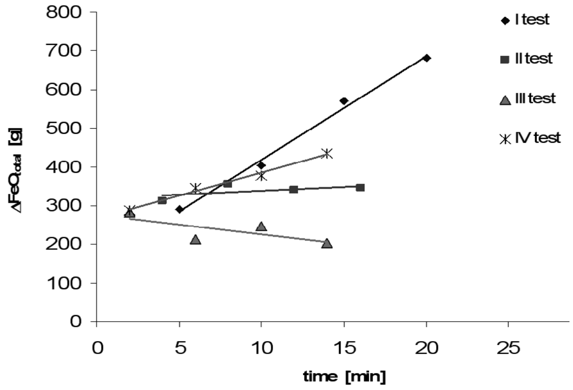


Figure 3: Changes in the total FeO loss during process

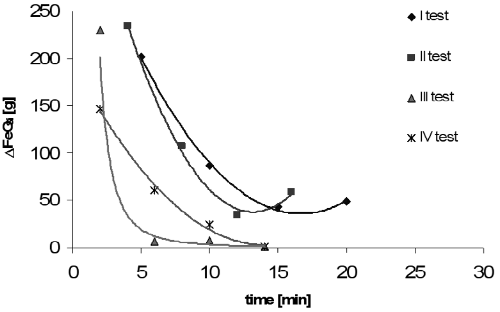


Figure 4: Changes in the FeO loss during reduction process by silicon

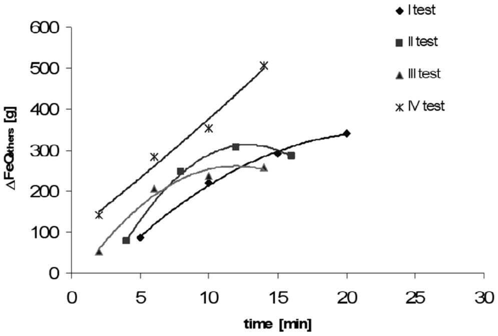


Figure 5: The changes in the FeO loss during reduction process by other elements

CONCLUSIONS

The production of metal, including pig iron and steel, is inseparably linked with the production of slag, a waste material. Some types of slag are used in industries such as construction and in metallurgical processing. However, a significant portion of the slags contain phases such as iron, chrome and managanese oxides; this prevents their direct use. It is necessary to reduce some of these oxides or to add enriching elements in order to use them. In this way it is possible to utilize the slag heaps located near the metallurgical plants and also to utilize slag formed directly during the production.

The technological and economic control of the slag reduction process requires detailed knowledge of the mechanism as well as a thermodynamic and kinetic description of the oxide phase reduction. In the case of the utilization of a metallurgical slag, one needs to pay special attention to the description of the reduction process of iron oxides. Development of an industrial scheme for the use of slags requires proper choice and optimisation of technology. This issue requires a detailed analysis (first in laboratory conditions and then in industrial conditions). The analysis should aim at establishing favourable technological and economic parameters of the process.

The reduction of liquid slag phases containing significant amounts of iron oxides was the centre of the research. The reducers included silicon and other elements of the iron solution. Pig iron was used as an iron solution. In many cases it contained elevated levels of chrome and nickel.

Analysis of test results show that:

- The tests conducted had a unique characteristic, as a carbon reducer was not used. In this way it became possible to study the reduction of iron oxide in liquid slag by reducers dissolved in the liquid iron phase.
- The production process consists of stages. The rate of the process depends on the slowest of the stages. Either diffusion or reduction reaction can be the limiting stage. It depends on the physicochemical characteristics of the liquid slag and metal.
- The iron oxide reduction proceeds during the entire duration of the test. In the initial stage silicon plays the leading role and other elements are of lesser importance. Later, the role of silicon diminishes as its amount in the iron solution decreases. Other elements such as manganese and carbon assume the leading role.
- The rate constant of the reduction diminishes in each of the tests. It means that the intensity of the process decreases when the amount of the reductant diminishes in the molten iron.
- The results achieved and test observations show that the controlling stage of process is the diffusion of reactants in the reaction system.
- Research results and their analysis present this complex set of reactions in a simple way. A more detailed analysis of this phenomenon requires further development of models and additional experimental research.

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