

Reduction of metallic oxides in liquid slag systems by solid graphite

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Abstract: High global demand for metallic elements such as Fe, Cr, Ti, Mn leads to an intensive technological development of metal recovery. One of the ways is to recover metals from metallurgical slag. The sessile drop method was adopted in order to study the interactions between liquid slag and graphite. Steelmaking slag was used during this research. The slag used included converter slag and slag from chrome steel melting as well as their mixtures with other modifiers. The analysis covered six types of slag in the temperature ranging from 1100°C to 1600°C in the argon atmosphere. In the course of research mass spectrometry and scanning microscope were used. The following were set for the examined samples during the reduction process: liquidus temperature and the nature of interactions (wettability or its lack). It was observed that the volume of slag samples dynamically changed in the course of the reduction of metallic oxides.

Key words: liquid slag, iron oxides reduction, wettability.

1. Introduction:

Enormous energy consumption and greenhouse gases production are one of the major problems connected to metallurgical industry. Iron ore reduction and carburizing iron in high temperatures are the main factors contributing to CO and CO₂ production as well as to high energy consumption. If it is possible to speed up the iron ore reduction in the liquid phase and to successfully carburize iron in low temperatures, such a technology will be extremely valuable in terms of reducing the energy consumption in the blast furnace. It is common knowledge that reduction processes in liquid phases are extremely complex and that their mechanism is not yet fully understood [1].

The blast furnace process uses to a large extent the phenomenon of iron oxides reduction in liquid phases, especially in the primary slag zone and the dripping zone. The currently used blast furnace technologies use mainly coal powder as substitute fuel. Its share continuously increases with every ton of pig iron used. That is why when it comes to reduction, it seems important to understand the interactions between liquid slag phases containing elevated concentration of iron oxides and carbon in various forms. When it comes to metallurgy the reduction process very often takes place in slag which has various concentrations of FeO. In such a case the reducer can be present in the form of: solid carbon, carbon in an iron solution and gas – CO. Slag foaming accompanies the reduction process. It is a characteristic feature of widely used metallurgical processes. It is most common in converter processes, EAF, reduction in liquid phases (SR). It is used in secondary metallurgy, blast furnace processes and alternative iron production methods. In the course of these processes this phenomenon can be desirable or not. Due to the universal character of this reaction authors have been doing a lot of research in order to characterize the specific mechanism and the kinetics of reduction in liquid slag phases as well as to describe slag foaming.

Other optional uses of FeO reduction in liquid phases consist in recycling and utilization of the products of metallurgical processes that contain iron (e.g. dust, mill scale, silt, etc). For some time methods which use these semi products have been in focus and have been widely promoted due to the following factors: a) the use of natural resources as production materials has been decreasing, b) waste reduction by means of diminishing the amount of unused waste, c) indirect energy savings.

Dust and silt recycling in integrated metallurgical plants may be done using one or more methods which involve: sintering, cold agglomeration, insufflation, direct reduction (DR) as well as reduction in liquid phases (SR). The choice of the method depends on several factors such as environmental requirements, energy policies, the situation of the production plant, its recycling strategies as well as the feasibility study of technological and economic aspects [3].

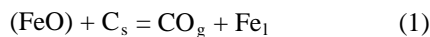
While the probable reduction mechanism in liquid slag phases has been widely accepted by researchers, the specific mechanism controlling the kinetics of the process has still remained unclear [6]. The factors controlling the reduction rate include the following: physical properties of slag phase, phase-to-phase voltage between gas - slag, slag - reducer, slag - metal and slag density. The reduction rate is also influenced by such factors as the type of carbon used and the size of its particles (subdivision surface). Other important issues involve: the influence of the dynamic viscosity rate which dynamically changes in the course of the reduction process, the influence of surface tension of liquid slag as well as the interactions between liquid slag phase and the reducers used (most often carbon reducers) [1-9].

Gas phase in the form of CO, CO₂ is the product of the reduction process. Gas release leads to slag foaming. The authors of this paper [2] conducted research into foaming properties of 6 types of slag in dynamic conditions using an X-ray tube in order to control the behavior of foaming slag and the height of the foam. They enumerated foaming indices for all types of slag. The conclusions drawn show that the behavior of slag foam in dynamic conditions suggests a more complicated system than in the case of static conditions. The behavior of foam is characterized by certain fluctuations, the presence of thin films on gas bubbles which have not been covered by any existing theories or models of slag foaming [2].

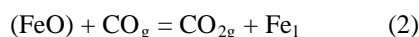
The authors of this paper [4] investigated the kinetics of the reactions taking place on the borders of slag/carbon phase division in the temperature of 1500°C for different carboniferous materials: synthetic graphite, natural graphite and two types of charcoal (active, pyrolytic). Two types of slag were used in the course of this investigation: the first type of slag had an increased iron oxides concentration - 31,52% Fe₂O₃ and C/S - 1,67, the second had an increased concentration of silica - 36,3%SiO₂ and C/S - 1,22 [4].

The sessile drop method was used during this research. The experiment was conducted in a tubular resistance furnace in the argon atmosphere. All carboniferous materials are not wetted by slag number 1 (with a small influence of the time of the process). After some time natural graphite and active carbon (charcoal) show dynamic wettability by slag number 2, which contains an increased amount of silica. Synthetic graphite, however, still seems to be a non-wettable system. The reduction process was predominant in the case of ferruginous slag and it took place in all carboniferous materials. In case of slag number 2 the reduction of silica was the main reaction. It partially proceeded with substantial amounts of unreacted SiO₂ visible in the section. The time was 1800s or longer.

The obtained results show the importance of the chemical composition of slag and carbon materials as far as the reduction process is concerned [4]. Many researchers mention two basic mechanisms of iron oxides reduction in the processes involving liquid state. Direct reduction of liquid iron oxide by means of solid carbon takes place according to the following reaction:



Indirect reduction of iron oxides by intermediate gas phases takes place according to reaction 2 and Boudouard reaction 3 which plays an important role in the kinetics of the reaction:



These reactions require iron oxide diffusion from the slag volume to the subdivision surface, a chemical reaction on the borders of slag/gas division, CO_2 diffusion into the interfacial area and a chemical reaction within the gas/carbon and liquid slag/carbon interfacial areas.

The authors mention the results obtained by Sarma and his associates, who conducted research into FeO reduction from liquid slag for concentrations below 10% and basicity 1. The reduction took place in the temperature 1300-1500°C and different carbon materials were used. In the course of their research they discovered that when coke was used as a reducer the reaction rate was much faster than in the case of graphite and active carbon. They also suggested a mixed model of controlling the kinetics of the entire reaction. Bafghi and other researchers, who were also interested in slag foaming with the use of graphite as a reducer of iron oxides in the temperature of 1300°C, claim that the reaction rate is affected by the chemical composition of slag. As a rule the overall reduction rate is controlled by different stages in series. For graphite the limiting stages include transportation of mass in liquid phase as well as gas – slag reaction. The gas - carbon reaction does not play any role in the case of this process.

Figure 1 shows wettable systems and non wettable systems as well as border values for each of them.

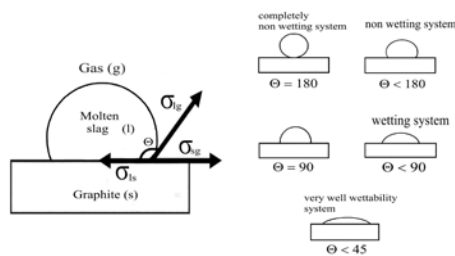


Figure 1. Border values of wetting angles.

Paper number 4 presents wetting angle measurement in case of different carboniferous materials. Figure 2 presents the results of changing in the wetting angle in the function of time.

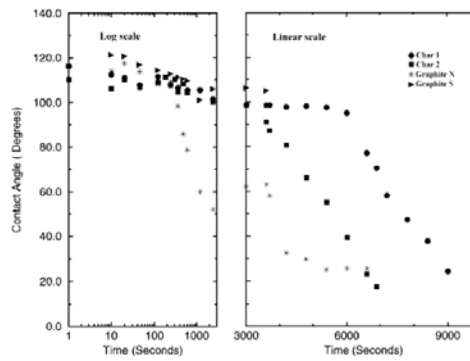


Figure 2. The changes in the wetting angle for slag 2 and various carboniferous materials [4]

Figure 3 shows slag 1 and 2 after approx. 30 minutes of exposure to natural graphite in the temperature of 1500°C

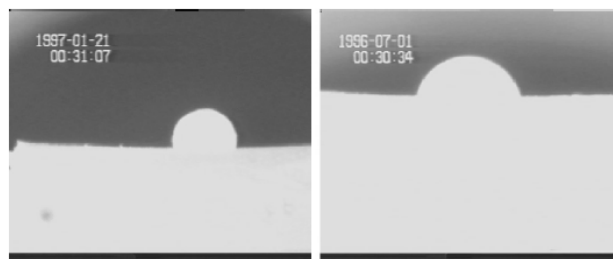


Figure 3. High temperature (1500°C) images of natural graphite with slag 1 (left) and slag 2 (right) after approximately 30 min of contact [4].

The authors [4] have drawn the following conclusions from their research: in case of slag rich in iron oxides all carboniferous materials show a lack of wettability (which does not increase with time). The beginning of dynamic wetting takes place after 3000s for natural graphite, after 7000s for charcoal 1 and after 5000s for charcoal 2. The reaction rate and the measured amount of waste gases CO and CO₂ show substantial differences for different slag – carbon systems.

The wettability characteristics do not depend on the type of carbon materials used. When the iron oxides concentration is low, the reduction of silica in case of slag 2 is the dominant reaction. The overall reaction rates were similar for both types of graphite. As researchers did not expect the wettability to play any significant role at this stage, they measured the reaction rates before the dynamic wetting took place. The results show internal reactivity of carboniferous materials with slag rich in silica. In the temperature of 1500°C the dynamic wetting takes place long after obtaining the steady state of the reduction reaction. The wetting phenomenon is a result of the reaction products settling in the interfacial areas. The results show that the chemical composition of slag and of carboniferous materials plays an important role in the process [4].

The authors [5] conducted research into the possibility of chrome recovery from slag used in stainless steel melting. Chrome could be recovered by means of reduction from liquid phase. Slag containing approx. 2.66% Cr₂O₃ and C/S – 1.35 was subjected to modification of its composition by adding Al₂O₃ and SiO₂. Using a hot thermocouple technique the researchers measured the melting temperature. They observed a decrease in temperature in case of every modification. The results are shown in table 1.

Table 1. Slag weight, basicity, T_{liq} measured using a hot thermocouple technique [5]

Slag	Description	Weight of Mixed Slag (g)				C/S	T_{liq} (°C)
		SA	SiO ₂	Al ₂ O ₃	Total		
SA	No addition	10.0	-	-	10.0	1.35	1444
SB	5% mass SiO ₂	10.0	0.6	-	10.6	1.14	1387
SC	10% mass SiO ₂	10.0	1.2	-	11.2	0.99	1328
SD	15% mass SiO ₂	10.0	2.4	-	12.4	0.78	1292
SE	10% mass Al ₂ O ₃	10.0	-	1.2	11.2	1.35	1299

The rate of chrome recovery for all temperatures is quite slow. It is linked, however, to the addition of the above mentioned fluxes. These fluxes make it easier to obtain liquid slag and to obtain an earlier stage of reduction and as a result they improve chrome recovery index. Furthermore, adding SiO₂ is more effective because of its impact on C/S index [5].

Paper [6] describes research into slag foaming which is a result of FeO and carbon reaction in liquid slag. Carbon was introduced in different forms, such as raw carbon, charcoal (pyrolytic, active) and graphite. Generally speaking, the production rate of gaseous CO from (FeO)-C reaction increases together with a rise in FeO concentration in slag when the concentration ranges from 15 to 45%. The reaction rate measures per unit of external surface area is almost the same as for graphite, active and bituminous carbon - even despite larger internal surface area and higher reactivity of active charcoal (bituminous). The CO diffusion rate can be used to interpret the behavior of slag during foaming. The foam height increases with a rise in FeO concentration in slag in the range from 15 to 25%. With higher FeO concentration the height of foam decreases – even despite higher rate of gas generation. This happens because the influence of decreasing the slag foaming index (when the FeO concentration goes up) is more significant than an increase of gas generation rate. Slag viscosity decreases and slag density increases together with a rise in FeO concentration in slag. Those two factors speed up the process of bubble drainage from foam and as a result affect its height (the foam decreases). When carbon was used, a diffusion of an additional component could be observed. This component came from volatile parts of carbon. The volatile parts, however, did not seem as effective in terms of slag foaming as those produced during CO reaction. It can be the case as gas bubbles generated during the reaction are smaller, which results in a production of more stable foam. What is more, when certain types of carbon (anthracite) were used in the course of research, diffused volatile parts caused carbon disintegration and led to a creation of new, additional reaction surfaces. This led to an increase in CO generation rate, which resulted in higher initial foam. This phenomenon, however, did not increase slag foaming per mass unit of carboniferous materials that were blown in. The influence of different forms and amount of carbon as well as the size of particles should be examined further in order to understand and optimize the foaming process [6]. It was also stated that the mechanism controlling the reduction rate remains to a large extent unclear [6].

The blast furnace process and especially the dripping zone are particularly important because the reduction in liquid phases is very intensive there. The possibility of liquid slag to drip in lower parts of the furnace as well as the aeration of those lower parts affect the efficacy of the furnace. The authors [7] conducted an investigation into the interactions between coke and synthetic slag of the blast furnace type in the temperature of 1500°C. They used the sessile drop method during their research. They carried out experiments lasting up to 300min. They observed a reduction of SiO₂

from a mixture of silica and carbon. The reduction began in the temperature of approx. 1400°C in neutral environment and proceeded according to the following reaction:



Combining equations 4 i 5:



The conclusions drawn were as follows: wetting of the slag/coke system improved quickly when the slag basicity decreased within the range of 1 - 1.6; when slag basicity was high coke did not show any wetting properties – even after a long exposure to slag. On the basis of a chemical analysis of the gas produced during slag/coke reaction the researchers showed that the wetting and non wetting behavior of the slag/coke system depends significantly on the kinetics of silica reduction on the subdivision surface of phases as well as on the chemical composition of slag and coke. High content of ashes in coke and a relatively high concentration of silica in coke and in slag are conducive to the kinetics of silica reduction and wetting of the system. As a consequence, a sudden increase in slag/coke wettability was determined by a decrease in slag basicity and an increase in the amount of ash in coke. Wettability of graphite by slag was minor. It was connected to a minimal amount of ash in graphite. The conducted chemical analysis of drops suggests that the chemical composition of slag affects significantly the kinetics of wettability. This is due to the fact that the silica reduction rate is higher for slag samples containing higher silicon concentration. The authors state that dynamic wetting can take place after the reduction conditions become stable and that the reaction products settle in the reaction area. Iron and SiC settling on the surface of slag/coke play an important role when it comes to changes in wetting conditions. The research shows that the slag/coke surface phenomena, which improve wettability, are related to an increase in oxides reduction. These oxides can be reduced by carbon on the border of phase division, such as silica. The research also suggested an influence of settling substances on a decrease in surface tension, and what follows on improving their wettability. The authors concluded that further research is necessary into the casting ability index in relation to slag/coke wettability for different parts of the blast furnace [7].

Researchers [8,9] conducted an experiment using the sessile drop method for two carboniferous materials (metallurgical coke and natural graphite) and for slag from the electric arc furnace process in the temperature of 1550°C. The aim of this research was to improve the understanding of basic rules governing the interaction between slag and carbon in the electric arc furnace process. The following conclusions were drawn: metallurgical coke was highly effective in terms of iron oxide reduction, it had high gas generation rate but low foaming capacities. The researchers had expected that the diffusion of ash components from slag (mainly the diffusion of silica) by means of decreasing the surface tension would significantly affect the slag foaming. Despite this fact, large amounts of produced gas in slag/coke chemical reaction did not stay in the volume of the liquid but it left the reactive system. On the other hand, natural graphite proved to be capable of iron oxides reduction in the entire volume of slag. The reaction, however, proceeded more slowly. Slower rate of gas generation and higher values of surface tension result in better gas retention thanks to stable foaming. The gas generation rate is an important parameter when it comes to characterizing the

carbon/slag relations. It seems inevitable to optimize the best ranges of reaction rates in order to retain gas in the volume of slag so that slag foaming could occur [8,9].

2. Individual research

Research was conducted into the behavior of liquid slag phases on the border of slag/graphite phase division in the course of the reduction process. The changes in liquid slag volume were analyzed. Basic materials used during this research should be treated as waste materials from metallurgical processes. These materials included: BOF slag, mill scale, chrome steel melting slag. Basic slag included: converter slag (BOF) – sample V as well as stainless steel melting slag – sample IV. A mixture on the basis of the above mentioned slag was made for the purpose of this research. Mill scale and pure oxides were added to basic slag - SiO₂ and Al₂O₃. What followed was a synthesis in the liquid phase in a chamber furnace in the temperature of 1450°C in alund crucibles. The following sets of slag were prepared:

Sample I – a mixture of chrome slag + scale + pure SiO₂ + pure Al₂O₃

Sample II – a mixture of chrome slag + converter slag + scale + pure SiO₂ + pure Al₂O₃

Sample III – a mixture of + converter slag + scale + pure SiO₂ + pure Al₂O₃

Sample IV – chrome slag

Sample V – BOF slag

Sample VI – synthetic 4 component slag melted from pure oxide components

After slag was ground in a vibrating mill a spectral analysis of its chemical composition was conducted. The composition of different types of slag was shown in table 2.

Table 2 Chemical composition of analyzed slag

Sample I		Sample II		Sample III		Sample IV		Sample V		Sample VI	
[%]											
MgO	1.63	MgO	1.80	MgO	2.86	MgO	3.23	MgO	4.74	MgO	1.15
Al ₂ O ₃	12.51	Al ₂ O ₃	11.65	Al ₂ O ₃	13.52	Al ₂ O ₃	6.78	Al ₂ O ₃	0.88	Al ₂ O ₃	13.65
SiO ₂	28.72	SiO ₂	26.63	SiO ₂	26.31	SiO ₂	28.47	SiO ₂	18.85	SiO ₂	59.78
P ₂ O ₅	0.06	P ₂ O ₅	0.15	P ₂ O ₅	0.20	P ₂ O ₅	0.06	P ₂ O ₅	0.50	P ₂ O ₅	-
K ₂ O	0.05	K ₂ O	0.04	K ₂ O	0.15	K ₂ O	0.04	K ₂ O	0.88	K ₂ O	-
CaO	25.42	CaO	30.96	CaO	25.80	CaO	48.90	CaO	50.70	CaO	20.72
TiO ₂	0.76	TiO ₂	0.73	TiO ₂	0.12	TiO ₂	1.29	TiO ₂	0.17	TiO ₂	-
Cr ₂ O ₃	4.83	Cr ₂ O ₃	4.81	Cr ₂ O ₃	0.00	Cr ₂ O ₃	9.64	Cr ₂ O ₃	-	Cr ₂ O ₃	-
MnO	1.11	MnO	1.08	MnO	1.21	MnO	1.59	MnO	2.40	MnO	-
FeO	19.21	FeO	22.02	FeO	29.72	FeO	-	FeO	20.87	FeO	-
B1	0.89	B1	1.16	B1	0.98	B1	1.72	B1	2.69	B1	0.35

Then slag was ground in an agate mortar. Cylindrical shaped samples (3-3mm) were formed. They were placed on graphite plates and inserted one by one into a horizontal pipe furnace. Graphite served as a source for carbon and constituted a reducer. Reduction took place in the argon atmosphere.

The analysis was conducted using high temperature optical microscope EM201, a device produced by Hesse Instruments which is equipped with image analyzer (Figure 4 shows a diagram of the workstation).

1 - halogen lamp 2 - specimen t.c. 3 - furnace with double t.c.
4 - CCD-camera 5 - specimen carriage

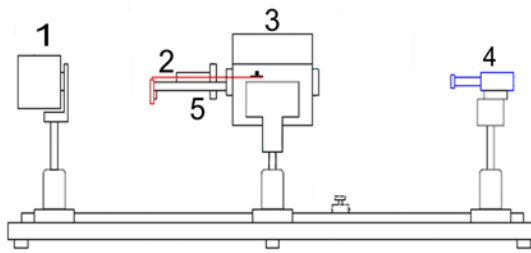


Figure 4. Research equipment: a) a diagram and b) a picture of the measurement workstation

The images of the sample surfaces at the beginning, in the middle and at the end of the reduction process on the graphite plates are shown in figure 5.

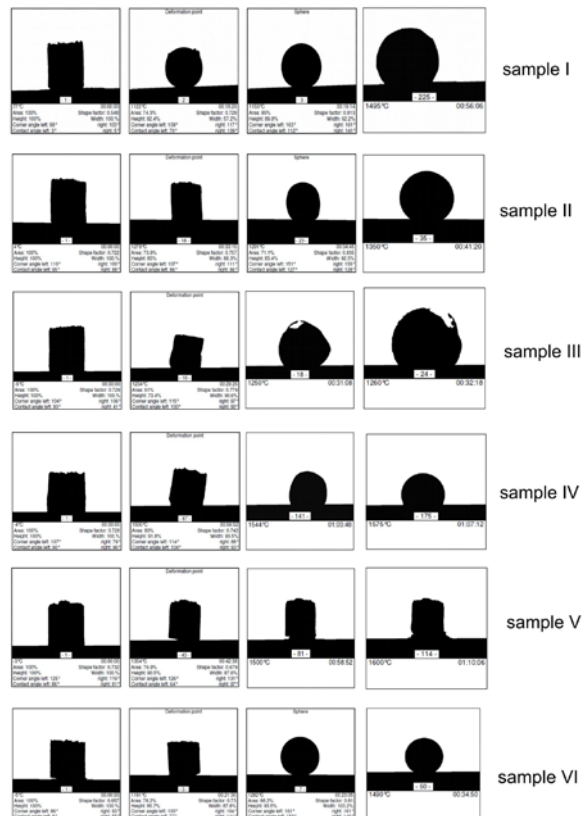


Figure 5. Changes in the slag shape and its state of matter when exposed to graphite

Figure 6 shows samples after they were taken out from the furnace. One can observe differences in shape. Sample V did not go through liquid phase. Sample III underwent intensive foaming. Sample IV attained the liquid state but the diffusion of gas in liquid state did not take place.

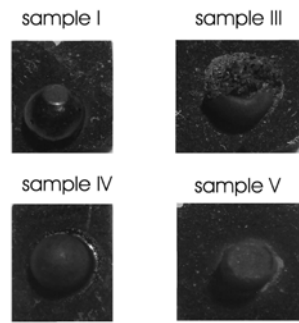


Figure 6. Selected samples on graphite washers

As a result of this experiment the temperature of transition of slag to a liquid state was obtained. These temperatures were presented in table 3.

Table 3. The flow temperature of slag on graphite plates.

Sample I	Sample II	Sample III	Sample IV	Sample V	Sample VI
Flow temp. (obtain spherical surface) [°C]					
1153	1291	1250	1544	-	1282

Slag/graphite wetting angles presented in Fig. 7 increased to over 90° which shows there is no slag/graphite wetting taking place in the first stage after obtaining the liquid state – this is partially supported by data from literature [4,7]. In the case of longer duration of the reduction process the wetting angles change, their values decrease – this suggests a change in a direction of a slag/graphite wetting system.

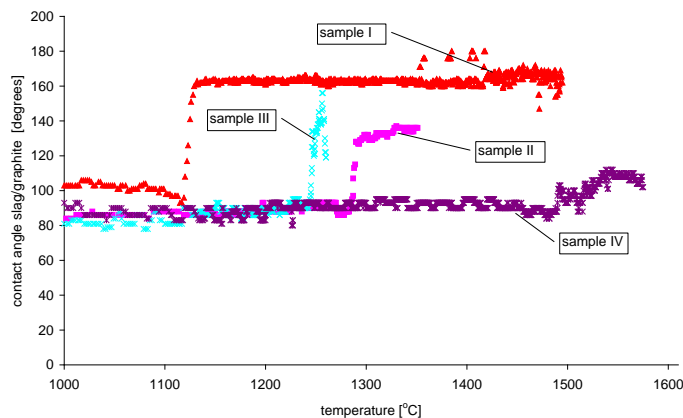


Figure 7 Wetting angles for selected slag samples with graphite

Figure 8 presents a change in the sample areas (their volumes) in the function of temperature. In case of samples I, II, III one can see a change in the surface area of the sample when the temperature increases in the course of the reduction of metallic oxides from the volume of liquid slag. In other two cases (samples IV and V) the surface area (volume) did not change and remained stable. In case of sample IV it might suggest that the degree of reduction was small or reduction did not take place at all in the liquid phase. In case of sample V it can suggest that slag did not liquefy at all.

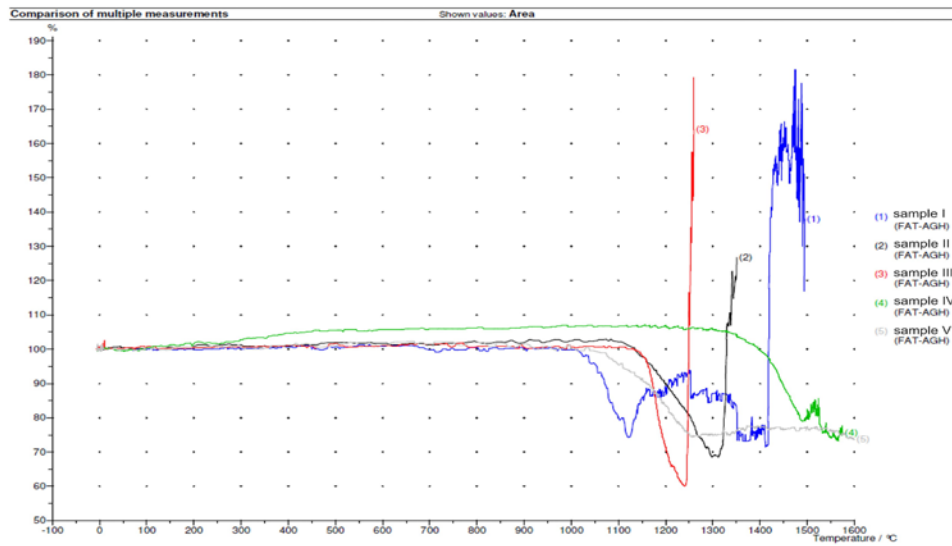


Figure 8 Changes in the surface areas of samples in the function of temperature

In order to verify the possibility of reduction in liquid slag phases samples II and VI were selected for area analysis using a scanning microscope. Samples were submerged in resin and metallographic specimens were prepared. They were dusted with gold in order to analyze them with a microprobe.

3. The results of the conducted analysis

SAMPLES II and VI

Figure 9 shows powdered slag and the area of conducted analysis

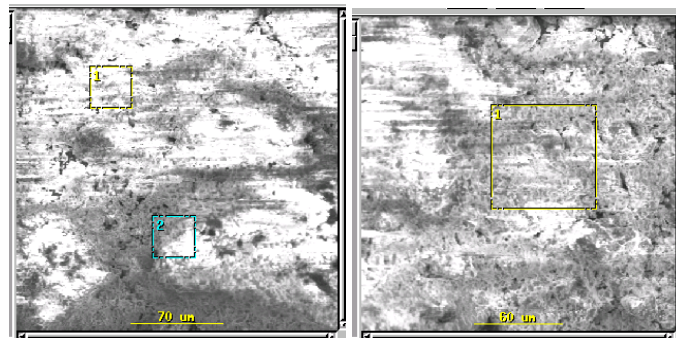


Figure 9. Powdered slag before the experiment (SEM)

Table 4 presents the chemical composition of initial slag analyzed on the basis of slag powder by means of SEM

Table 4. Chemical composition of slag before the experiment (SEM)

Area	Slag chemical composition - "powdered slag"									
	[%]									
	C	O	Mg	Al	Si	Ca	Ti	Cr	Mn	Fe
P1	3.82	31.63	2.51	5.15	11.35	30.98	0.56	1.23	1.39	11.37
P2	4.26	35.71	2.36	6.43	12.67	26.13	0.76	1.14	1.37	9.17
average	4.04	33.67	2.44	5.79	12.01	28.56	0.66	1.19	1.38	10.27
„big” P1	3.41	30.34	2.45	6.59	10.55	29.65	0.74	2.49	2.05	11.73

Figure 10 presents a specimen of the slag drop surface area (sample II) after the reduction process in the temperature range 1291-1350°C.

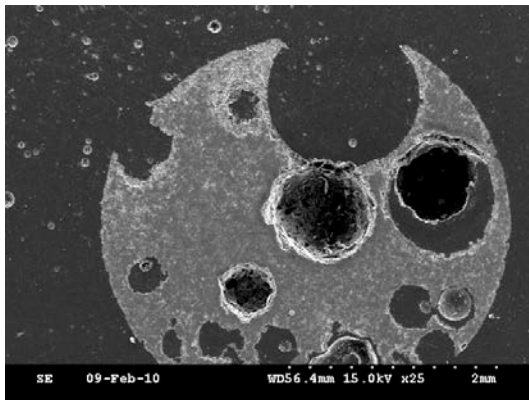


Figure 10 a. Sample nr II

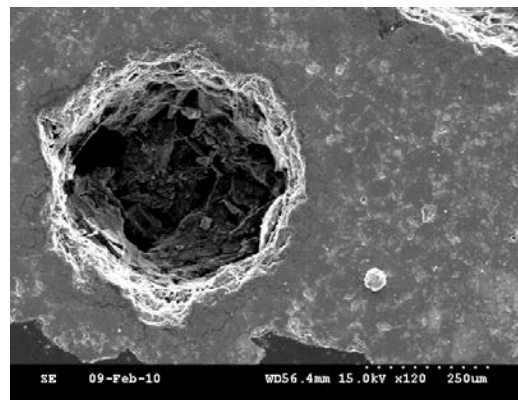


Figure 10 b. Smaller "crater" from sample II

Table 5. The analysis of visible "craters" in the sample volume.

	Area of analysis near by right edge of bigger "crater"									
	C	O	Mg	Al.	Si	Ca	Ti	Cr	Mn	Fe
	[%]									
P1	48.34	22.86	0.66	2.28	4.10	12.08	0.30	1.57	0.76	7.04
	Area of analysis near by left edge of bigger "crater"									
P1	19.41	23.72	1.86	6.24	10.11	22.81	0.35	3.93	1.44	10.13
P2	59.82	30.82	0.32	0.95	2.29	3.58	0.03	0	0	2.19
	Area of analysis bottom of bigger "crater"									
P1	64.45	31.9	0.02	0.33	0.51	1.83	0	0.07	0.04	0.83
	Area of analysis bottom of smaller "crater"									
P1	52.43	31.86	0.27	-	3.10	8.73	0.00	0.17	0.00	3.44

Carbon concentration in slag (sample II) before the experiment ranged from 3,41-4,26%. After the experiment the analyzed empty "craters" (bubbles) suggest a significant increase in carbon concentration in the analyzed spots. The concentration at the bottom of the crater and at its edges is particularly high and it can be even 10 or 12 times bigger than before the experiment. It can mean that CO or CO₂ was present in this spot during the process. This was probably a gaseous product of the reduction process. In the course of quick cooling and solidification of the liquid, carbon diffusion occurred according to Bell's reaction:



After a theoretical temperature inversion 979K the diffusion of carbon in solid form occurs, but obviously it depends on the composition of carbon oxide, dioxide and pressures. The durability of oxides below this temperature is much smaller than of carbon dioxide. The presence of one of the reduction products may suggest that the reaction took place within the volume of slag. Finding pure iron, another reduction product, proved to be impossible. This can be explained by short duration of the reduction process. Table 6 and 8 present the analysis results obtained by means of using a scanning microscope on the areas of sample cross-sections for the selected parts of the drop. The edges of interfacial slag/gas craters show a decrease in carbon concentration and an increase in the concentration of other elements that are present in slag.

Table 6. Chemical composition for different spots on the surface of the slag drop (sample II)

Left - top side drop	C	O	Mg	Al.	Si	Ca	Ti	Cr	Mn	Fe
4-point Mean	10.60	27.18	2.45	7.58	13.30	28.99	0.24	1.01	0.96	7.71
Right - top side drop	C	O	Mg	Al.	Si	Ca	Ti	Cr	Mn	Fe
2-point Mean	26.46	27.82	1.94	7.22	7.59	18.03	-	5.86	0.98	4.12
Drop center	C	O	Mg	Al.	Si	Ca	Ti	Cr	Mn	Fe
4 point Mean	11.37	23.42	1.93	4.14	11.07	21.96	2.79	2.98	2.65	17.71
Down side drop (graphite)	C	O	Mg	Al.	Si	Ca	Ti	Cr	Mn	Fe
4-point Mean	12.23	28.06	1.76	3.45	14.71	29.89	2.34	0.33	2.76	4.49

Figure 11 presents powdered slag and areas of conducted analyses for sample VI

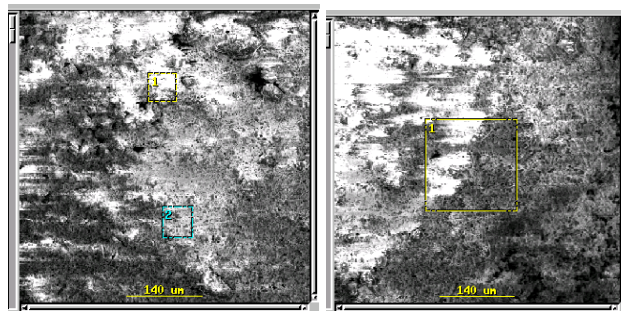


Figure 11. Powdered slag before the experiment (SEM)

Table 7. Chemical composition of slag VI

Area of analysis	Slag chemical composition - "powdered slag" [%]					
	C	O	Mg	Al.	Si	Ca
P1	2.99	42.04	1.57	7.85	30.39	15.16
P2	3.48	44.33	1.49	8.43	28.93	13.33
Mean	3.24	43.19	1.53	8.14	29.66	14.25
Bigger area of analysis						
P1	3.93	43.13	1.38	7.44	29.90	14.22

Figure 12 and b present the specimen of the slag drop surface (sample VI) after the reduction process in the temperature range 1282-1490°C.

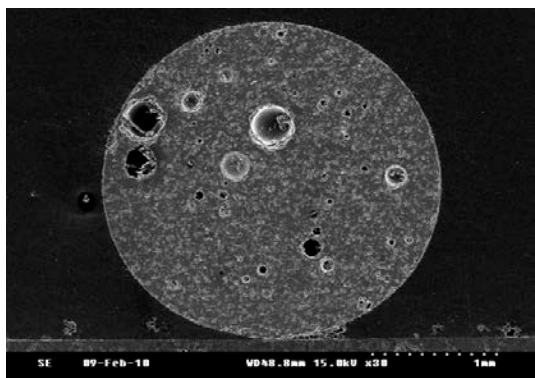


Figure 12 a. Sample nr VI

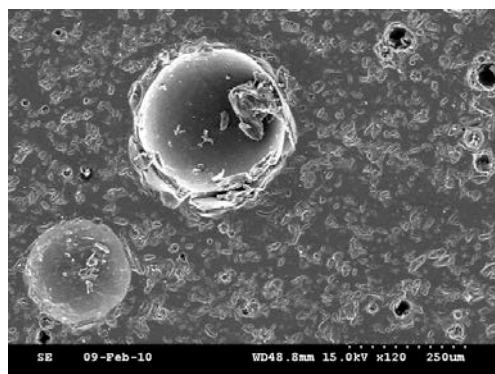


Figure 12 b. Bigger crater from sample VI

Table 8. Chemical composition for different spots on the slag drop surface (sample VI)

Top side of drop	C	O	Mg	Al.	Si	Ca
	[%]					
3-point Mean	8.79	36.18	1.47	8.12	32.37	13.07
Center side of drop	C	O	Mg	Al.	Si	Ca
4-point Mean	8.50	36.43	1.47	8.63	32.05	12.93
Down side of drop (graphite)	C	O	Mg	Al.	Si	Ca
3-point Mean	10.81	34.64	1.31	7.85	32.28	13.11

4. Theoretical analysis of calculation results and experimental research

The authors made theoretical calculations using a thermodynamic database called FactSage. After defining the composition of slag (table 9), which is the same as the composition of samples, the authors analyzed the possibility of slag samples attaining the liquid state. They calculated the value of theoretical initial temperature in which one can notice the first amounts of liquid phase in the volume of the analyzed samples. They also calculated the theoretical value of temperature in which the liquid phase constituted 100% of the sample volume. The above mentioned values of temperature were compared to the actual results obtained in the course of experimental research. Then the researchers calculated the share of solid phase in the sample volume in the temperature equivalent to that of sample melting. In case of theoretical temperatures in which slag would attain the liquid state the researchers assumed that the share of solid particles in the analyzed sample in particular conditions would be equivalent to zero. Furthermore, an analysis of the chemical composition of the solid particles was conducted. It focused on the solid particles present in slag in temperatures equivalent to those in which the sample actually melts.

Table 9. The mass share of particular slag components

Sample 1		Sample 2		Sample 3		Sample 4		Sample 5		Sample 6	
[g]											
MgO	1.63	MgO	1.80	MgO	2.86	MgO	3.23	MgO	4.74	MgO	1.15
Al ₂ O ₃	12.51	Al ₂ O ₃	11.65	Al ₂ O ₃	13.52	Al ₂ O ₃	6.78	Al ₂ O ₃	0.88	Al ₂ O ₃	13.65
SiO ₂	28.72	SiO ₂	26.63	SiO ₂	26.31	SiO ₂	28.47	SiO ₂	18.85	SiO ₂	59.78
P ₂ O ₅	0.06	P ₂ O ₅	0.15	P ₂ O ₅	0.20	P ₂ O ₅	0.06	P ₂ O ₅	0.50	P ₂ O ₅	-
K ₂ O	0.05	K ₂ O	0.04	K ₂ O	0.15	K ₂ O	0.04	K ₂ O	0.88	K ₂ O	-
CaO	25.42	CaO	30.96	CaO	25.80	CaO	48.90	CaO	50.70	CaO	20.72
TiO ₂	0.76	TiO ₂	0.73	TiO ₂	0.12	TiO ₂	1.29	TiO ₂	0.17	TiO ₂	-
Cr ₂ O ₃	4.83	Cr ₂ O ₃	4.81	Cr ₂ O ₃	0.00	Cr ₂ O ₃	9.64	Cr ₂ O ₃	-	Cr ₂ O ₃	-
MnO	1.11	MnO	1.08	MnO	1.21	MnO	1.59	MnO	2.40	MnO	-
FeO	19.21	FeO	22.02	FeO	29.72	FeO	-	FeO	20.87	FeO	-
B1	0.89	B1	1.16	B1	0.98	B1	1.72	B1	2.69	B1	0.35

The summary of results obtained using FactStage and temperature values measured in the course of the actual experimental research were presented in table 10.

Table 10. A summary of calculation results and conducted experiments

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample6
T _{theoretical initial} [°C]	1088	1087.6	1119	680	1100.29	1291.3
T ^{theoretical} [°C]	1230	1363	1289	-	-	1291
T ^{actual} [°C]	1153	1291	1250	1544	-	1282
F _{STa} [%]	34.80	5.20	3.90	43.40	-	0.00

where:

T_{theoretical initial} –calculated temperature in which first amounts of liquid phase are to be observed;

T_{theoretical} – calculated temperature in which the liquid phase constitutes the entire amount (the temperature in which the sample melts);

T_{actual} – the actual temperature in which the analyzed samples melted;

F_{STa} % - the percentage share of solid particles in the sample volume, in the actual temperature in which the melting of the sample occurred.

In the case of sample number 4 and 5 due to the presence of solid particles in the volume of the analyzed slag it proved to be impossible to obtain the theoretical value of melting temperature, even in high temperatures. Similarly, in the case of sample number 5 it was not possible to melt the sample. Without a fiducial temperature the calculations of the solid particles share in the sample volume in the actual melting temperature were not made.

Figure 13 presents a chart which is a comparison of the actual and theoretical temperature values in which the slag samples melt. The difference between the values increased with a rise in the theoretical share of solid particles in the slag volume in a temperature equivalent to that of actual sample melting. The share of solid particles in the slag volume was respectively: 77, 71, 49 and 11 for the following samples: 1, 2, 3, 6. The bigger the difference between the temperature values (the actual one and the one calculated using FactSage), the bigger the percentage share of solid particles in the temperature in which the sample melted. As far as sample 1 is concerned, the difference between the theoretical and actual values of temperature was 77 and the fraction of solid phase in the temperature equivalent to the one in which the sample melts was 34.80%. The closest temperature values were obtained for sample 6 (the difference was 11°C). In this case the calculated theoretical share of solid particles in temperature equivalent to that of melting was 0%. As far as sample 4 is concerned, the share of solid particles in the volume of the sample in the actual temperature of sample melting amounted to 43.40%. This seems to explain why the actual melting temperature was the highest for this sample (1544°C).

In certain cases it proved to be impossible to obtain the temperature values for the analyzed chemical compositions of slag (marked as “0” in the chart) – either the theoretical temperature as in the case of sample 4 or both temperature values as in the case of sample 5 could not be obtained.

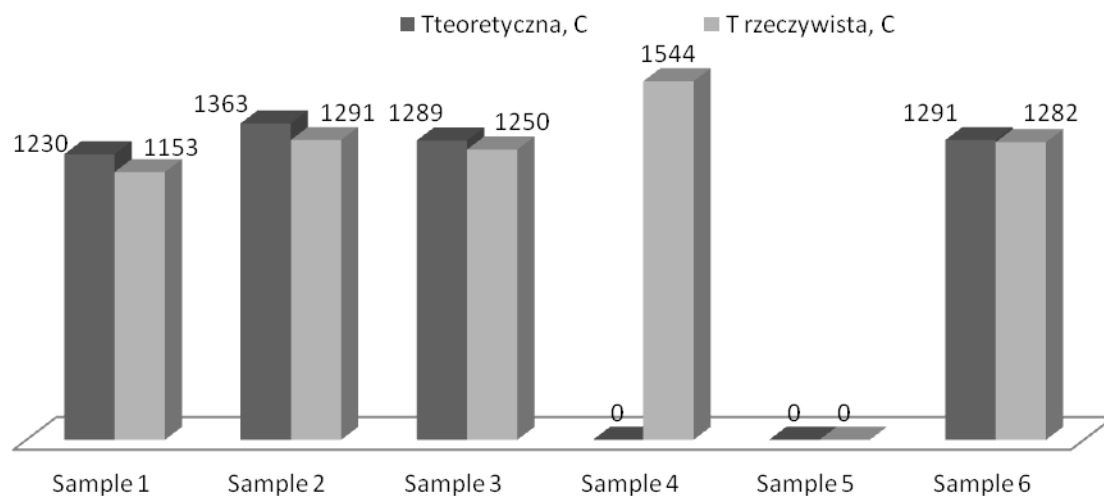


Figure 13. The comparison of the actual and theoretical temperatures

Figure 14 presents in a form of a chart a comparison between the amount of solid particles in the temperature equivalent to the actual melting temperature of the analysed samples and the contents of Al_2O_3 in the sample composition. The values marked as “0” in the chart mean that in these particular cases it was impossible to obtain data concerning the share of solid particles in the sample volume in the actual melting temperature of the sample.

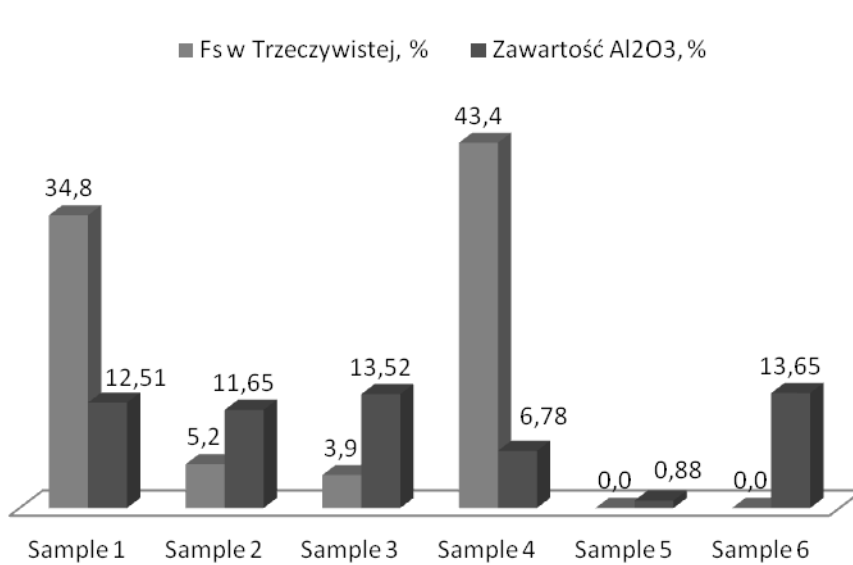


Figure 14. The amount of solid particles and Al_2O_3

On the basis of the data presented in figure 8 and tables 9 and 10 one can notice that an increase in Al_2O_3 in the acid slag composition makes it possible to decrease the actual melting temperature of the sample. What decreases is the difference between the theoretical and actual melting temperature values. Among others, this is manifested by a decrease in the share of the solid phase fraction in the temperature equivalent to that of actual melting of any particular slag. As far as slag number 3 (basicity of 0.98 and Al_2O_3 content of 13.52g) is concerned, the difference between the theoretical and actual temperatures was $49\text{ }^\circ\text{C}$ and the share of solid phase in the temperature equivalent to that of

actual melting amounted to 3.9. In the case of slag sample number 6 (basicity of 0.35, Al_2O_3 content of 13.65g) the difference between the temperature values was 9 and the share of solid phase in the temperature equivalent to that of actual melting was 0.0.

Using the thermodynamic calculations made thanks to FactSage it was possible not only to calculate the amount but also the possible mineralogical form of the solid particles present in slag in temperatures equivalent to those of actual melting. In the case of sample 1 the solid particles were as follows: CaSiO_3 , $\text{CaAl}_2\text{Si}_2\text{O}_8$, $\text{Ca}_2\text{Al}_2\text{SiO}_7$, CaTiO_3 ; sample 2: $\text{Ca}_2\text{Al}_2\text{SiO}_7$; próbki 4: Ca_2SiO_4 , Cr_3C_2 , $\text{Ca}_2\text{Ti}_2\text{O}_5$.

5. Conclusions

The conducted analysis focused on the behavior and the interactions of slag exposed to solid graphite in the course of the reduction process of metallic oxides in ionic liquid. The following conclusions can be drawn from the obtained analysis results:

1. Despite the lack of wetting phenomenon between slag and graphite the reduction process takes place with different intensity. This fact is supported by the changes in the sample volumes resulting from the diffusion of gaseous products such as CO, CO₂. The gas diffusion (and slag foaming) affects the volume of the liquid drops.
2. Carbon concentration on the surface of the crater (bubble) and on its edges is 10 to 12 times bigger than the initial concentration in slag
3. A transitional period (sample I and VI) could be observed for the changes in the sample volume after the temperature of liquid state had been reached. The sample surface did not get bigger. Only when the temperature increased did the sample volume change intensively. The incubation period shows that the slag solution needs to reach a certain temperature in order for the reduction to take place. It can also suggest that the physical properties, such as viscosity, surface tension change.
4. Basic slag: converter slag (sample V) and stainless steel melting slag (sample IV) have higher melting temperature. In case of sample IV it is the result of Cr₂O₃ presence in slag, in case of sample V it is because of CaO.
5. Thanks to the modification of slag's chemical composition it was possible to obtain lower melting temperatures for samples I, II, III. These samples contained BOF and stainless steel melting slag. During the experiment the reduction of metallic oxides took place in each of the samples, which was in fact the aim of the experiment. The volume of samples I and III doubled from the moment it liquefied to the end of the experiment. This may suggest that slag has very good foaming properties or that the reduction process was extremely intensive.
6. The difference between the theoretical and actual temperature values increased with a rise in the theoretical share of solid particles in the slag volume in the temperature equivalent to that of actual melting. The bigger the share of solid particles in the sample volume, the bigger the melting temperature. Furthermore, the difference between the theoretical and actual temperature values obtained in the experiment increased, too.
7. The increase in Al_2O_3 contents in the acid slag composition (basicity lower than 1) fosters a decrease in the actual melting temperature of the sample. What is more, the difference between the theoretical and actual

melting temperature decreases, too. This is manifested by a diminished share of solid phase fraction in the temperature equivalent to that of actual slag melting.

8. Further research is expected to focus on the influence of selected factors on the efficiency and kinetics of the reduction process of liquid slag and the possibility of recovering certain elements - Fe, Cr, Ti and Mn.

Acknowledgements

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