SLAG-CARBON REACTIVITY

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ABSTRACT

The kinetics of the carbothermic reduction of oxides from molten slags is affected by the type of carbon material. This effect can be considered as a parameter to select proper carbon material and even to optimize the process conditions. Therefore, design of a practical method to evaluate the potential of carbonaceous materials to reduce slags is of a great interest for metallurgical industries. This has been the motivation of some research work in the last few years at NTNU and SINTEF to develop slag-carbon reactivity test. In this case, three different techniques consisting of thermogravimetery, ASEA induction furnace and sessile drop approach has been applied. These studies were mainly carried out through the reduction of ferromanganese and silicomanganese slags by various solid carbon materials. The details of the applied techniques and their advantages and disadvantages were studied. It is indicated in this work that the sessile drop wettability technique is a proper method for slag-carbon reactivity evaluation. Direct contact between the carbon material and slag droplet is maintained through this technique as well as good heat transfer to the reaction interface. Moreover, sessile drop technique is quite fast and the reduction curve can be extracted through a few experiments. Also, the in-situ observation of the sample during the test, which is a unique benefit, is possible. Sessile drop experiments for the reduction of a typical ferromanganese slag by coke and charcoal is investigated in the present study. It shows that coke is more reactive than charcoal. Based on the literature and the present study, some important points for studying the slag reactivity of carbonaceous materials are also described.

1 INTRODUCTION

Reactivity refers to the rate at which a chemical substance tends to undergo a chemical reaction. Since solid carbon materials such as coal, coke and charcoal are used in many pyrometallurgical processes, the reactivity of carbon to react with specific substances is important. For instance, in high-carbon ferromanganese production in submerged arc furnace, CO_2 reaction with coke particles, Boudouard reaction (1), is very important. This reaction is endothermic and undesirable due to its effects on process energy consumption [1]. In order to characterize the carbon materials via their potential to react with CO_2 gas, *CO_2-reactivity* test is used, where CO_2 gas is reacted with solid carbon under specific conditions.

$$CO_{2\ (g)} + C_{(s)} = 2CO_{(g)} \qquad (1)$$

SiO-reactivity, which is the potential of carbon to react with SiO gas according to the reaction (2), is an important process issue in the production of Silicon and Ferrosilicon [2]. This reaction is essential for these processes to minimise the loss of Si (in the form of SiO gas) and thereby increase the silicon yield. Moreover, as SiO (g) is an energy carrier in the process, it is important to sustain this compound in the process in order to have tolerable energy efficiency. Regarding the importance of CO_2 and SiO reactivities in metallurgical processes, in particular in ferroalloy industry, practical laboratory tests have been widely developed and even standardized to evaluate carbonaceous materials [3-4].

$$SiO_{(g)} + 2C_{(s)} = SiC_{(s)} + CO_{(g)} \qquad (2)$$

In many pyrometallurgical processes, metal oxides are reduced from slags through the carbothermic reduction. It has been observed in many studies that the kinetics of slag reduction can be affected by the type of the carbonaceous materials [5-15]. Therefore, similar to the above carbon-reactivity tests, it is of industrial interest to establish a simple test to determine the reactivity of different slags towards various reductants. In particular, a *slag-carbon reactivity* test can be used to evaluate the potential of carbonaceous materials to react with the main slag components of high-carbon ferromanganese and silicomanganese processes as below:

$$(MnO) + C_{(s)} = Mn + CO_{(g)} \tag{3}$$

$$(SiO_2) + 2C_{(s)} = Si + 2CO_{(g)} \tag{4}$$

In this article, the experimental works done mainly at NTNU/SINTEF for establishing a slag-carbon reactivity test are evaluated. Moreover, the experimental procedure and the obtained results for MnO reduction from a MnO-saturated slag are presented and discussed.

2 APPROACHES TO THE SLAG-CARBON REACTIVITY TEST

The experimental works done at NTNU/SINTEF to develop a test method for slag-carbon reactivity are described as follows.

2.1 Thermogravimetery

The slag-charcoal and slag-coke interactions in CO atmosphere at 1600°C were investigated using thermo-weight experiments [16]. In this case crucibles of the reductants were made from selected large pieces with equal inner diameters. A synthetic slag (34.5%MnO-34.5%SiO_2-8.6%Fe_2O_3-8.6%Al_2O_3-8.6%CaO-5.2%MgO) was prepared and it was filled to the crucibles. The crucibles were put inside an alumina crucible, which were in the thermo-weight. The reduction experiments were carried out with the calcined reductants at 1200°C and 1600°C for 3 hours prior to the experiments. The results showed that charcoal and coke reactivities are equally. For the reductants calcined at 1600°C, equal reaction rates were observed. While, for the reductants calcined at 1200°C, faster weight loss was observed for coke than that for charcoal. This is related to the more remained volatile materials in the coke sample than the charcoal calcined at 1200°C. The most important disadvantage of this method is the difficulty for preparing crucibles from carbonaceous materials.

2.2 ASEA Induction Furnace

In order to develop a simple test method for different reductants and slags with relevance for the production of FeMn and SiMn, the reduction of MnO and SiO_2 was investigated in a graphite crucible in ASEA induction furnace [17, 18]. A graphite holed plate on the top of slag was designed to keep the reductant particles below the surface and prevent them to float at the top. It also reduces the heat losses and let evolved gas escape through the holes.

Monsen et al. [17] tested the reaction of an industrial slag mixed with quartz and iron with carbonaceous materials. A synthetic slag with the composition of 39.2%MnO-10.5%CaO-5.3%MgO-8.4%Al_2O_3-36.2%SiO_2-0.44%S was used with charcoal, metallurgical coke, anthracite, and petrol coke as reductants. Reference experiments without the use of the reductants were also carried out. They showed fairly similar behaviour when the reductants are present or not in the crucible. Based on this observation, they did not recommend testing the slag-reactivity towards different carbon materials in a graphite crucible in an induction furnace. Because the actual reactions are highly endothermic, they are continuously supplied by the graphite crucible inductive energy. The temperature of the crucible is higher than of the carbon particles. Therefore, the observed reduction is mainly due to the reduction by graphite crucible and only to a minor extent by the added reductants.

2.3 Sessile Drop technique

Sessile drop wettability approach is a technique to investigate the contact between a solid substrate and a liquid phase. The carbothermic reduction of metallurgical slags by carbon substrates has been investigated using this method through several studies [5-15]. This method is prefered before thermogravimetery due to the possibility of preparing a more homogeneous substrate, which is more representative of the selected carbon material. Since no crucible is used in this method, it has an advantage over than ASEA induction furnace.

In this study the reduction of a MnO saturated ferromanganese slag by carbonaceous materials is investigated using the sessile drop technique and the obtained results are compared with other studies. In addition, some specific issues and observations that may be important for slag-carbon reactivity are evaluated.

3 REDUCTION OF MANGANESE OXIDE SATURATED SILICATE SLAG BY CARBON

Previous works [10-13] investigated the reduction of MnO from a one-phase liquid slag. In the industrial high-carbon ferromanganese furnace, however, MnO reduction takes mainly place from a two-phase slag, where MnO·MgO solid particles are dispersed in a liquid slag phase. The MnO·MgO particles are dissolved into the liquid slag during the reduction and finally disappear through the MnO reduction [19]. With regard to the fact that MnO reduction in the real furnace takes mostly place from the two-phase slag, a slag saturated with MnO was reacted with carbonaceous materials using the sessile drop method as described below.

3.1 Experimental procedure

In some of the previous experimental works, pressed powders of carbon were reacted with slags [9, 11, 12, 14, 15]. In this study, however, lumps of a polish coke and Eucalyptus charcoal, with the properties shown in Table 1, are reacted with a slag. Small discs with 10 mm diameter and 3 mm height were prepared by cutting their large pieces by a diamond blade with 0.1 mm/min speed.

Table 1: The characteristics of the coke and charcoal used as the substrates [11].

Property (unit)	Polish industrial coke	Eucalyptus charcoal
Fix C (%)	88.88	81.3
Ash (wt%)	9.5	0.43
VM (wt%)	1.32	18.3
Total Porosity (%)	42.9	27.3
Total pore area (cm^2/g)	47200	38600
d 002 (Å)	3.46	3.8
Lc (Å)	21.31	11.5
Approx. fraction amorphous C*	0.22	0.69
S content (ppm)	5600	20
CO_2 react. (10^{-3}/min)	1.63	7.23

Pure oxides of CaO, MgO, Al_2O_3 and SiO_2 with the ratios of $Al_2O_3/SiO_2=0.3$, MgO/CaO=0.5, $(CaO+MgO)/(SiO_2+Al_2O_3)=0.8$ were mixed. The mixture was melted in graphite crucible in air in an induction furnace to produce a uniform slag phase. The obtained slag was then crushed and milled in a tungsten carbide disc mill. The obtained powder was mixed with proper amounts of FeO, MnO and CaS to gain a powder containing 55%MnO-6.43%FeO-16.48%SiO_2-4.95%Al_2O_3-11.44%CaO-5.72%MgO-0.2%S. The reason of the addition of sulphur is that sulphur exists always in the industrial ferromanganese slags and is known to affect the reaction rate [20]. The mixture was then melted in platinum crucible in air at 1550°C for 10 minutes to produce a uniform slag phase. The slag was then casted in copper mould for rapid solidification. Pieces of this slag with 100±1 mg weight were then separated for the reduction experiments.

Sessile drop wettability technique was used to study the reaction between the synthetic slag and the carbon substrates. A schematic diagram of the experimental set up is shown in Fig. 1. The carbon substrate is located in the graphite sample holder and a slag piece is put on the carbon surface. In this study, the furnace chamber was evacuated initially, and then the furnace was heated up slowly with pure argon (99.9999%Ar) flashing with 0.5 Nl/min flow rate over the sample. The furnace was rapidly heated up to 1500°C with 120°C /min and hold 15, 30 and 60 minutes reaction times, followed with a rapid cooling. The temperature was controlled using a pyrometer focused on the edge of the graphite sample holder. A video camera was used to record images from the sample at 960×1280 pixels. After the experiments, cross sections of the samples (solidified slag droplets on the carbon substrates) were prepared and they were studied by Electron Probe Micro-Analyzer (EPMA).

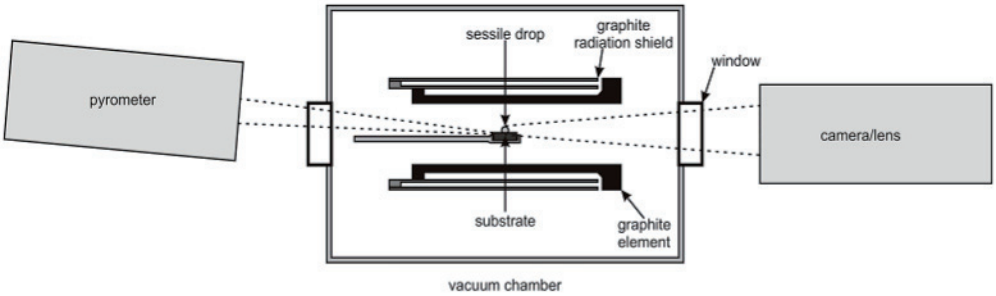


Figure 1: Schematic diagram of the experimental set up.

3.2 Results and discussion

The obtained results of the slag reduction experiments are presented and discussed in the following.

3.2.1 Microscopic observations

Images from the contact area between the slag droplet and carbon substrates within 15 and 30 minutes reduction are shown in Figures 2 and 3. The existence of solid MnO·MgO particles (brighter gray phase) in the slag matrix indicates that MnO is still reduced from a two-phase slag. A few large metal droplets exist at the slag/carbon interface, whereas relatively small metal prills exist in the slag. Figures 2 and 3 show that these metal prills are mainly dispersed in the same region as the MnO·MgO particles are distributed. Moreover, there is a fairly good contact between the metal and MnO·MgO particles (Fig. 3.b). It is found from the microstructures that the extent of the reduction by both coke and charcoal for the samples reacted for 60 minutes is relatively large, because the slag is a single liquid phase for this reaction time (Figures 4 and 5).

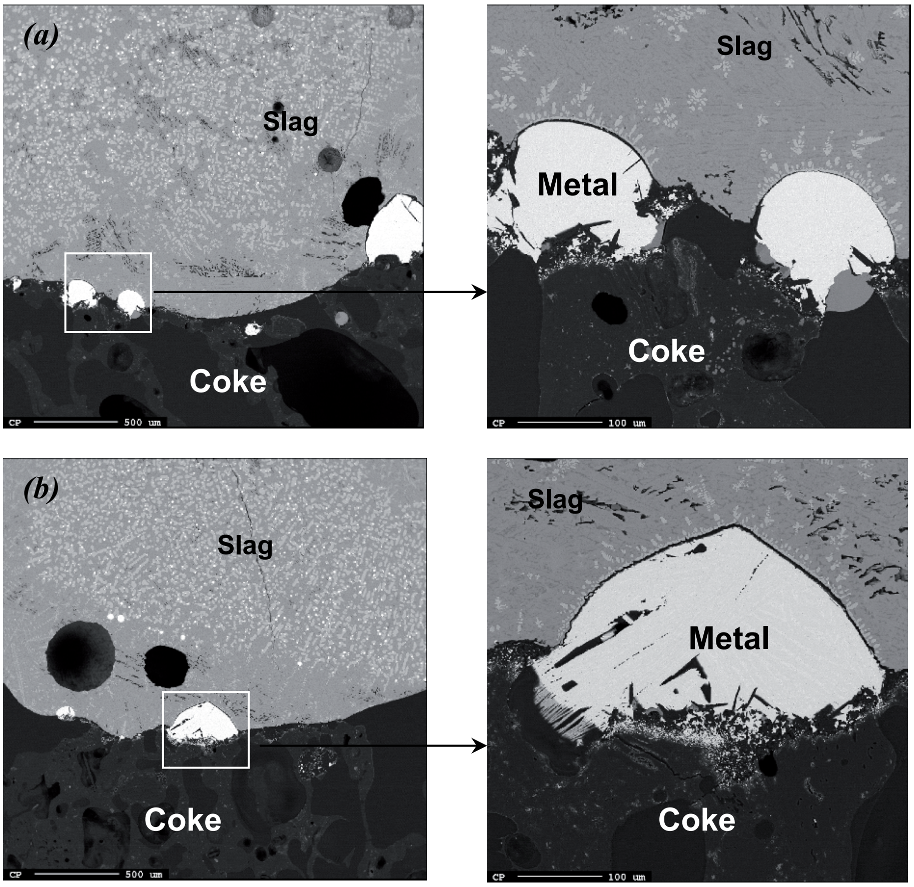
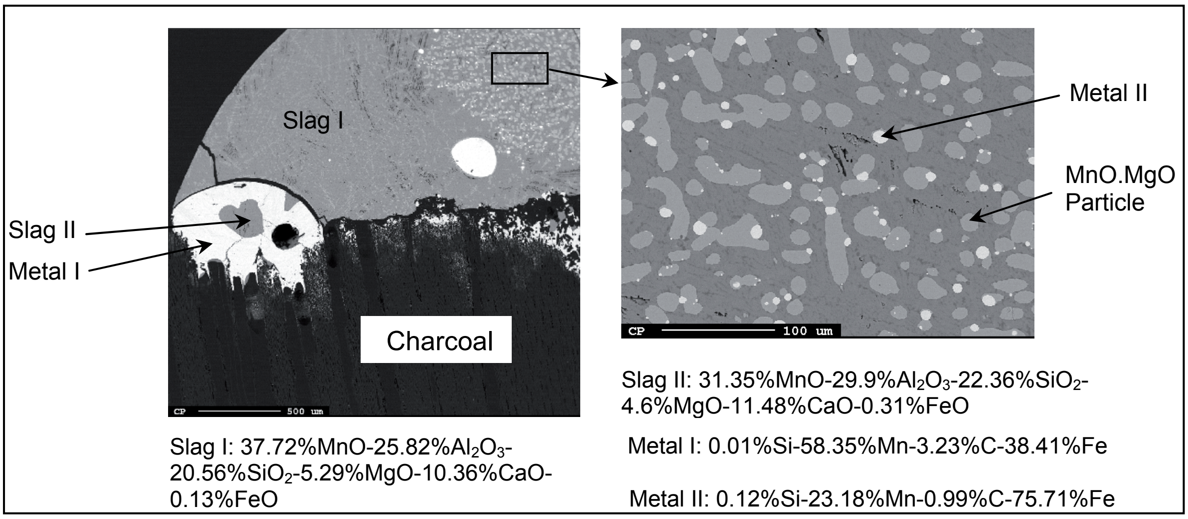


Figure 2: The slag drop/coke substrate reaction area after (a):15, (b): 30 minutes reduction.



Slag II: 31.35%MnO-29.9%Al_2O_3-22.36%SiO_2-4.6%MgO-11.48%CaO-0.31%FeO

Slag I: 37.72%MnO-25.82%Al_2O_3-20.56%SiO_2-5.29%MgO-10.36%CaO-0.13%FeO

Metal I: 0.01%Si-58.35%Mn-3.23%C-38.41%Fe

Metal II: 0.12%Si-23.18%Mn-0.99%C-75.71%Fe

Figure 3: The slag drop reacted with charcoal substrate for 30 minutes, and the measured chemical compositions for the present phases by microprobe.

It is observed that there is always a good contact between the slag and the produced Fe-Mn-C alloy during the reduction as seen in Figures 3 and 4. In particular, the liquid slag penetrated into the liquid metal, and even it led to the trap of slag in the metal. This phenomenon may show that the interfacial tension between the slag and metal is quite low, which is favourable for good mass transfer between the slag and metal.

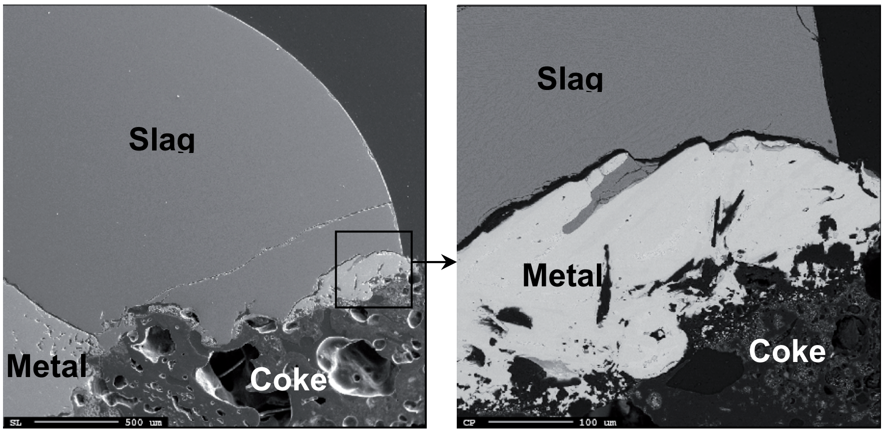


Figure 4: Slag drop reacted with coke substrate for 60 minutes.

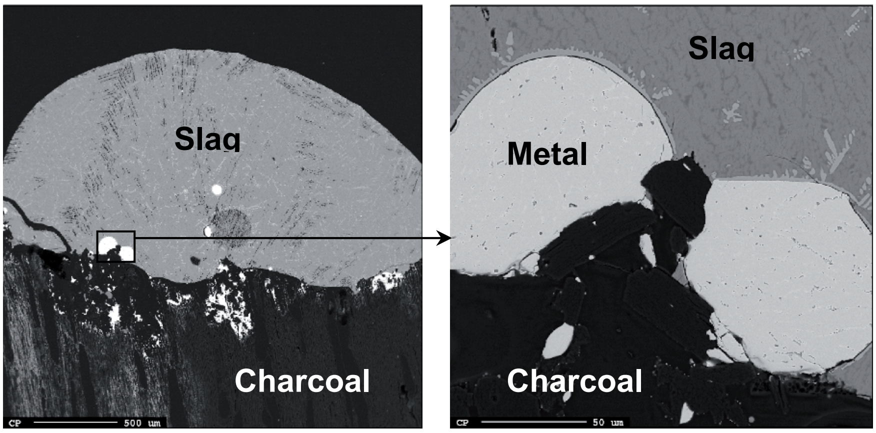


Figure 5: Slag drop reacted with charcoal for 60 minutes.

3.2.2 Slag and metal chemical compositions

The averaged chemical compositions of seven analyzed points in the matrix of the reduced slags by carbonaceous materials are shown in Table 2. As we see the chemical compositions for both coke and charcoal in 15 and 30 minutes are relatively close and they may show the liquidus composition of the slag. Because, as long as solid MnO·MgO phase exists in the slag, the chemical composition of the liquid phase is not significantly changed. MnO is reduced form the liquid phase by carbon and it is simultaneously replaced through the dissolution of MnO·MgO phase. When solid MnO·MgO phase is completely dissolved, reaching the liquidus composition, the chemical composition of the liquid slag is changed with the slag reduction. It is worth noting that the solid MnO·MgO particles contain low amounts of other oxides, for instance 0.8% CaO, 0.4% Al_2O_3 and 0.2 wt% SiO_2. Regarding to very small dissolution of these oxides in MnO·MgO phase, no significant effect of them on the dissolution of the particles is expected. The chemical compositions for the slag reduced in 60 minutes by coke and charcoal in Table 2 are related to the single-phase liquid slags. This means that the measured chemical compositions show the whole slag compositions. Obviously, coke substrate is more reactive than charcoal substrate with around 10% larger reduction extent in one hour.

Table 2: Chemical compositions of the matrix of the reduced slag by coke and charcoal (wt%).

Substrate	Reduction time (min)	Al_2O_3	MnO	SiO_2	MgO	CaO	FeO	Observed slag type
Coke	15	24.49	41.74	19.44	4.15	9.28	0.88	Two-phase slag
	30	26.66	39.55	19.68	4.58	9.22	0.29	Two-phase slag
	60	10.45	33.43	33.31	8.65	14.07	0.07	Single-phase slag
Charcoal	15	25.68	38.42	19.87	4.0	9.87	2.14	Two-phase slag
	30	25.82	37.72	20.57	5.29	10.36	0.13	Two-phase slag
	60	8.13	43.92	28.20	6.62	13.00	0.13	Single-phase slag

If slag is reduced in the single phase area, the chemical composition measurement can be used to evaluate the slag-carbon reactivity. If the slag is reduced from a two-phase to a single-phase, the slag-carbon reactivity can be evaluated through the slag chemical composition measurement. For instance, coke is more reactive than charcoal with regard to the obtained chemical compositions in 60 minutes reduction (Table 2). Since, it is difficult to determine the MnO concentration in the slag by microprobe as long as it is reduced in two phase area; it is not possible to evaluate the slag carbon reactivity through chemical composition measurements. This is obviously observed for the slag reduced by coke and charcoal in short reduction times of 15 and 30 minutes. An alternative way for this reduction stage may be qualitative comparison of the reactivities with regard to the changes in the normalized slag volume, which is the ratio of slag volume (V_s) over the initial slag volume ($V_{s,\,i}$) during reduction. This method has already been used to evaluate the kinetics of MnO reduction from HCFeMn slag by different graphite substrates [20]. The average slope of the $V_s/V_{s,\,i}$ ratio or the slope of the MnO reduction curve within a certain reduction extent can be considered as the slag-carbon reactivity parameter. Figure 6 illustrates the changes in $V_s/V_{s,\,i}$ for both coke and charcoal reduction, indicating higher slag-carbon reactivity for coke substrate. No reason for the different reactivities for coke substrate within the first 30 minutes reduction was found. For both reduction times, however, higher reactivity for coke than charcoal is observed.

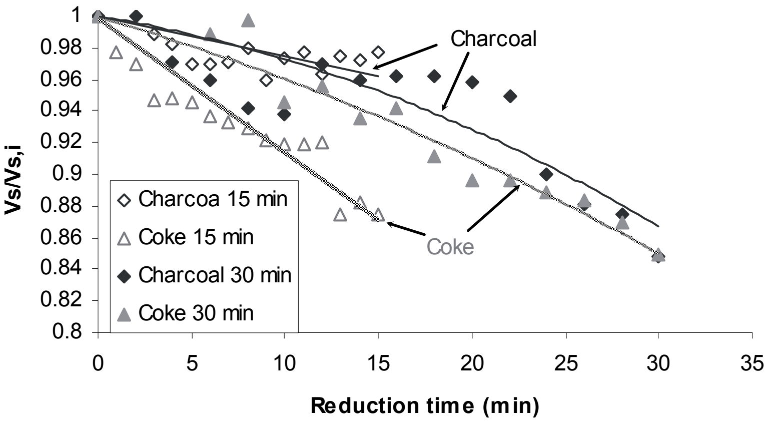


Figure 6: The changes of the normalized volume of slag droplet reduced by carbon substrates at 1500ºC within15 and 30 minutes.

The chemical compositions of the produced metal particles located inside the slag and at the interface of slag/carbon substrate (Figures 2-5) are listed in Table 3. Some metal compositions are also shown in Fig. 3. Much higher Mn and C concentration in the metal at the slag/carbon interface than the metal surrounded by the slag is always observed. It is worth noting that a very thin carbon layer was coated for microprobe sample preparation and the real carbon concentrations are lower than what is presented. The Fe and Si concentrations in the metal dispersed in the slag phase are higher than the metal at the slag/carbon interface. The differences in the chemical composition of the metal phases may indicate the important role of the metal phase in slag reduction mechanism as described in the following.

Table 3: The analysis of metal produced by coke and charcoal in different reaction times (wt%).

Substrate	Reduction time (min)	Metal phase location	Si	Mn	C	Fe
Coke	15	At the slag/carbon interface	0.02	13.59	2.54	83.86
		in slag matrix	0.088	2.11	0.9	96.9
Coke	30	At the slag/carbon interface	0.051	23.28	2.089	74.58
		in slag matrix	0.079	8.75	0.85	90.32
Coke	60	At the slag/carbon interface	0.15	64.8	3.76	31-26
		In the slag matrix	0.13	25.75	1.55	72.56
Charcoal	15	at slag/carbon interface	-	-	-	-
		in slag matrix	0.087	1.94	1.03	96.95
Charcoal	30	at slag/carbon interface	0.006	58.35	3.23	38.41
		in slag matrix	0.12	23.18	0.99	75.71
Charcoal	60	At the slag/carbon interface	0.005	59.0	3.85	37.14
		In the slag matrix	0.13	25.75	1.55	72.56

3.2.3 Mechanism of the reduction

Based on the above observations and the works done before, the possible mechanism of MnO reduction from the slag can be explained. This can help to obtain a better understanding of the parameters affecting the slag-carbon reactivity.

The reduction of FeO from the slag by carbon, reaction (5), is the first reaction in the system through the contact of the slag with the carbon substrates. This reaction leads to the formation of very small iron drops at the slag/carbon interfacial area. The dissolution of solid carbon into the produced iron, reaction (6), is another reaction that takes place simultaneously in the system. The existence of carbon in the metal phase at slag/carbon contact area confirms this carbon dissolution. The formation of Fe-C alloys will then lead to the FeO reduction by the dissolved carbon in the metal through sub-reactions (7) and (8), while a gas phase exists at the slag/metal interfacial area. The mechanism of the carbothermic reduction of FeO from slags has been widely studied in the literature and this mechanism is fairly acceptable [6, 7, 21]. The formation of an initial Fe-C alloy in the system leads to the MnO reduction by the dissolved carbon in the metal (reaction (9)) through sub-reactions (8) and (10), or reaction (11). It has been shown that MnO reduction by Fe can be more dominant [15, 21]. Very low slag/metal interfacial energy in the system, as described in section 3.2.1, provide good mass transfer conditions between the slag and metal phases and this may reinforce the domination of reaction (11).

$$(FeO) + C = Fe + CO_{(g)} \quad (5)$$
$$C_{(s)} = \underline{C} \quad (6)$$
$$(FeO) + CO_{(g)} = Fe + CO_{2\,(g)} \quad (7)$$
$$CO_{2\,(g)} + \underline{C} = 2\,CO_{(g)} \quad (8)$$
$$(MnO) + \underline{C} = \underline{Mn} + CO_{(g)} \quad (9)$$
$$(MnO) + CO_{(g)} = \underline{Mn} + CO_{2\,(g)} \quad (10)$$
$$(MnO) + Fe = \underline{Mn} + (FeO) \quad (11)$$

When Fe-C alloy exists at the slag/carbon interface the activity of the produced Mn (in Fe-Mn-C alloy) is lower than the Mn activity without the existence of Fe. Therefore, faster reduction rates are expected due to the larger driving force for the reaction. However, reduction mechanism can play a more significant role in the slag reduction kinetics. When Fe is present it changes the MnO reduction mechanism through overall reaction (3) to another mechanism through the combination of reactions (11), (7) and (8). This mechanism was proposed many years ago through MnO reduction from slags by Fe-C_{sat} alloy [21]. It is must be emphasized that the dissolved carbon for these reactions is supplied by reaction (6).

The presence of metal prills in the slag can be related to their transfer from the reaction interfaces to the slag through the gas bubbles. These small metal particles react with the slag, and therefore the dissolved carbon concentration decreases as seen in Table 2. The lower carbon concentration in the metal prills may be the reason of higher silicon concentration in them compare to the metal drops at the slag/carbon contact area, as there is an inverse relationship between the concentrations of carbon and silicon in Fe-Mn-C-Si alloys [22].

4 IMPORTANT POINTS REGARDING THE SLAG-CARBON REACTIVITY

Based on the literature and present study on slag reduction by the carbonaceous materials, the following cases are recommended to be considered for slag-carbon reactivity study.

4.1 Initial metal

It has been observed that the existence of an initial metal in the system increases the rate of the slag reduction [12, 20]. Tranell et al. prepared two different slag types from an industrial ferromanganese slag; one containing the “naturally carried-over metal (Fe-Mn prills)” and one without the metallic content [12]. They studied the reduction of both slags as the same method of the present study and they found that the kinetics of the MnO reduction from the slag is significantly dependent on the initial metal phase. In this case the reduction of MnO was significantly faster from the slag containing initial metal for both carbon reductants. It has been observed that when a ferromanganese slag containing FeO, like the prepared slag for the present study, is reduced [15], the rate of the MnO reduction from the slag by the same carbon material is more than the same slag composition devoid of FeO [14]. This is due to the fact that for the former slag a metal phase is formed and maintained at the slag/carbon interfacial area and it plays an important role in the reduction according to the mechanisms explained in section 3.2.3. However, for the slag devoid of FeO, the produced Mn through MnO reduction is simultaneously evaporated due to the high Mn vapour pressure as discussed in the previous publications [11, 13].

As mentioned above, the dissolved carbon the metal phase contributes in the reduction reactions. Therefore, the supply of the dissolved carbon can be an important reaction and even a rate limiting step as previously mentioned [15]. Thus, it might be reasonable to consider another kind of reactivity for the carbonaceous materials, which can be called “metal-carbon reactivity”. This parameter may actually be the dissolution rate of solid carbon material into the liquid metal.

4.2 Gas phase

It has been observed that the kinetics of MnO reduction is affected by the gas phase composition [23] and it even led to suggesting a mechanism in which the kinetics of MnO reduction is controlled by chemical reaction and the transfer of the gaseous product (CO gas) into the ambient gas [23]. Moreover, it has been observed that when sessile drop method is used, the rate of MnO reduction from slags in CO atmosphere is always higher than that in Ar atmospheres [7, 14] for all type of the carbonaceous materials. It has been indicated that this higher reduction rate in sessile drop method is due to the much larger slag/gas contact area than slag/carbon contact area, whereas the reaction rate constant of MnO by solid carbon is much higher than that for the reduction by CO gas. Thus, faster reduction rate in CO gas is due to the geometry of the system [14]. Although CO gas exists in the industrial furnaces; it is recommended that the slag-carbon reactivity test in sessile drop approach be carried out in an inert gas and not in CO atmosphere.

4.3 Slag-carbon reactivity vs CO_2-reactivity

Teasdale and Hayes studied the FeO reduction kinetics from iron-saturated slags by graphite, coke, bituminous coal and anthracitic coal-chars using sessile drop technique [6, 7]. They observed that FeO reduction rate is dependent critically on carbon type and faster reduction rates by graphite and coke were observed than by coal-chars. While, the CO_2-reactivities of graphite and coke were significantly lower than coal-chars.

The kinetics of the carbothermic reduction of MnO from slags is not dependent on the CO_2-reactivity of carbon [9, 11-15]. Tranell et al. observed higher reactivity for charcoal than that for coke. Similarly, charcoal was much more CO_2-reactive than the coke [9, 12]. In contrast, in other studies [11, 13-15] and the present study the slag-carbon reactivity is higher for coke than charcoal, while the charcoal is more CO_2-reactive. In short, it is conclude that the slag-carbon reactivity is not correlated by CO_2-reactivity. This may also reveal that the kinetics of slag reduction is not controlled by the Boudouard reaction of solid carbon material.

4.4 Evaluation of the slag-carbon reactivity

Various methods can be used to evaluate the slag-carbon reactivity in sessile drop technique:

i) Contact angle changes:
The changes of the contact angle in sessile drop method can be used to evaluate the slag drop reduction kinetics by carbon substrate. This method can be used when the slag/gas or slag/carbon interfacial tensions are affected by the changes in the slag composition. Moreover, the changes of these interfacial tensions must lead to the changes in the contact angle. For instance, Hayes et al. studied the wetting characteristics and the reaction rates between liquid Fayalite and $PbO\text{-}SiO_2$ melts and carbon and they described the reaction kinetics by a first order relationship as below [24]:

$$\frac{d\theta}{dt} = -k(\theta - \theta_e) \tag{12}$$

Where θ and θ_e are the instantaneous and equilibrium contact angles, respectively. k is the rate constant and t is the reaction time. The surface tension of ferromanganese and silicomanganese slags is not significantly dependent on the slag chemical composition. For example, the surface tension of $CaO\text{-}MnO\text{-}SiO_2$ melt (CaO/SiO_2= 1) is 476 $mNm^{-1}K^{-1}$ for 55% MnO, while it is around 486 $mNm^{-1}K^{-1}$ for 35% MnO [25]. Therefore, the contact angle changes cannot be used to evaluate the slag-carbon reactivity of MnO containing slags, and other alternative methods must be used.

ii) Slag volume changes
The changes of the slag drop volume during the reduction can be used to evaluate the slag-carbon reactivity. This method is applicable as long as the wettability of carbon by the slag is low, the substrate does not have large open porosity and the gas bubble formation and growth in the slag is relatively low. This method was mentioned in section 3.2.2 and has been successfully used [13].

iii) Slag chemical composition

The frequently applied method for slag reduction kinetic studies in sessile drop method has been the determination of the slag chemical composition after certain reduction times [9-12, 14, 15]. In this way the reduction experiments are carried out in different reduction times and the chemical composition of the reduced slag is then determined by the microprobe. This analysis technique is probably the only applicable method, since the sample size is small. Moreover, this technique is prefered due to the fact that it can give more details about the system and the reduction phenomenon, as observed in the present study.

iv) Gas outlet analysis

Since gaseous products such as CO and CO_2 are released through slag reduction reactions by carbon, the kinetics of the reaction in the system can be determined through measuring the amount and composition of the gas outlet from the furnace chamber. The kinetics of FeO reduction from liquid slags by solid carbon materials have been studied using mass spectrometer to analyze the CO and CO_2 concentrations in the outlet gas mixture [5, 6]. It must be emphasized that the furnace components should not be carbonaceous, because they can contribute in the reactions and therefore affect the outlet gas composition.

5 SUMMARY

Slag-carbon reactivity can be considered as a parameter to evaluate the carbonaceous materials for the pyrometallurgical processes. Among the applied practical methods for the slag-carbon reactivity test, sessile drop approach can be considered as a suitable technique. In this method a direct contact between the reactants (small slag drop on carbon substrate) is achieved and the in situ observation of sample is possible. In order to use this method, it is recommended to use carbon powder substrate and inert atmosphere. The slag type and the existence of any initial metal in the slag are two main issues that must be considered, since they affect the reduction mechanism and rate significantly. It is also worth noting that the slag-carbon reactivity should not be compared with the CO_2-reactivity, since no correlation is observed. In general, the slag carbon-reactivity can be evaluated through the changes of the wetting contact angle, the slag droplet volume changes, the slag chemical composition changes or the composition of the gas outlet from the reaction chamber.

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