MELTING PHENOMENA IN FERROMANGANESE PRODUCTION

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ABSTRACT

The melting phenomena of manganese ore, slag and alloys were studied in an experimental sessile drop furnace. Particles of approximately 20-60mg were placed on graphite substrates and then heated at a constant rate of 5 ℃/min up to 1830 ℃ in a controlled gas atmosphere of Ar or CO. The shape of the particle was photographed with a digital video camera every second. It was observed that the melting behaviour can vary significantly, with some particles exhibiting a large softening/melting range. Selected samples were sectioned and then analysed with EPMA. The implications of the results on understanding industrial furnace operations are discussed.

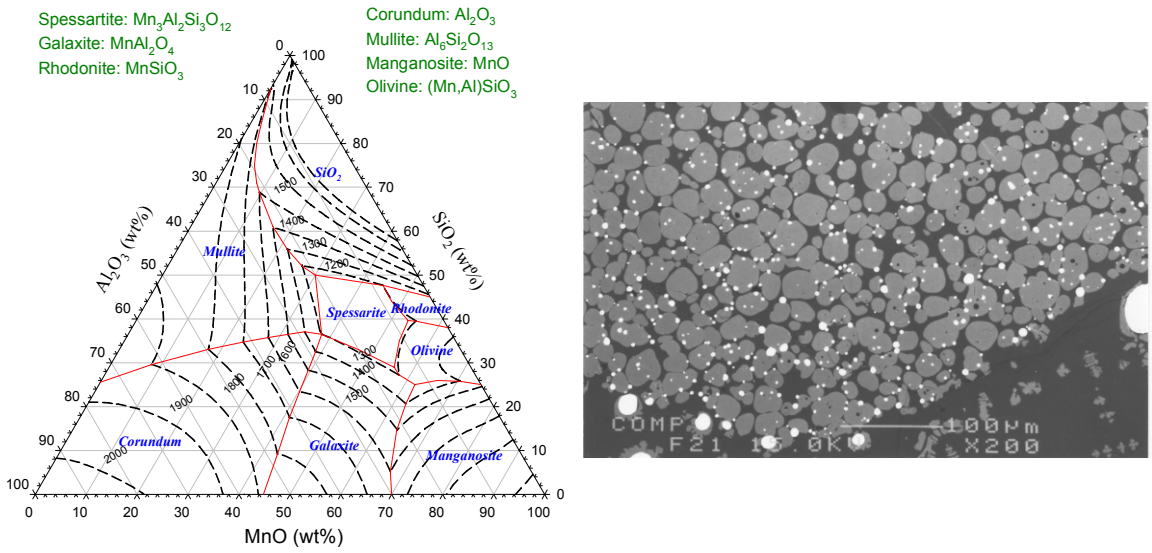
1. INTRODUCTION

The quest to further understand the nature and operation of high temperature industrial processes is often hampered by the inherent nature of the processes being investigated. Several methods have been used to 'freeze' or 'probe' processes during operation, in an attempt to retrieve information that will illuminate the operation of these processes. Furnace excavations have been conducted [1] and [2], but it is not possible to instantly cool a furnace, so there is always a certain degree of uncertainty regarding the results. Likewise, probes into the furnace produce a limited sample, with restrictions in the area to be sampled and the maximum temperature that the probe can be exposed to. However, these methods often provide extremely valuable information which furthers the overall understanding of the process.

This paper discusses the use of a complementary method, where small samples of various raw materials can be combined in a range of configurations and their behaviour can be observed while they are heated within a controlled environment. From this information it is then possible to attempt to understand the behaviour of materials within an industrial furnace.

In the solid state, the higher manganese oxides will be reduced from MnO_2 and Mn_2O_3 to Mn_3O_4 and MnO, when heated in CO gas. At 1100-1200ºC, acid ores like Comilog ore may be presented in the MnO-SiO_2-Al_2O_3 phase diagram, as shown in Figure 1a. As the temperature increases, the first liquid phase in the ore will be present at less than 1300ºC. At this temperature, the ore will contain a solid MnO phase in coexistence with a liquid phase, as shown in Figure 1b. As the temperature continues to increase, the reduction will start and the MnO content decreases. Both the increasing temperature and the lower MnO content will lead to a lower content of solid MnO phase. At a certain degree of reduction, the slag will be completely liquid.

The physical properties of the ore during the heating and reduction will affect the furnace operation. If the semi-molten ore, containing solid MnO phase, is very viscous, the ore will not flow into the coke bed. This work is focusing on the temperatures that will describe the flow characteristics of various ores, which is the temperature where the first liquid phase appears, as well as the temperature where the melting ore behaves like a liquid.



(a) (b)

Figure 1: a) Calculated phase and liquidus relations for the MnO-SiO_2-Al_2O_3 system using the FACT oxide database[3] and b) slag structure of a high MnO slag with solid MnO spheres in coexistence with a liquid phase[4]

2. EXPERIMENTAL DESCRIPTION

2.1 Apparatus

The apparatus is shown in Figure 2. The sessile drop furnace is designed to measure the contact angle of a liquid drop on a 10mm diameter substrate. It is possible to measure the wetting angle of a sessile drop, observe the melting point of substances and investigate the reactivity between different materials.

The sample size is quite small, with a maximum substrate size of 10mm in diameter and a nominal height of 3mm. The substrate is typically machined from a larger sample to the required size, or a fine powder is prepared and pressed into a small graphite crucible. Additionally, it is also possible to machine specific geometries into the substrate, which allows the movement of the molten specimens to be visualised.

The material to be heated must be small enough to sit on top of the substrate without touching the edges when molten, with a typical sample weight varying from 20–60mg. It is also feasible to place several materials within the furnace at one time. All of the heated furnace parts, including the element and heat shields, are constructed of graphite. The furnace is typically heated at 5 to 100°C/min, although up to 1000°C/min is feasible. The maximum temperature is 2400°C. A firewire digital video camera with a telecentric lens was used to record images from the furnace at a resolution of 1280 x 960 with a ½″ CCD sensor. The telecentric lens is able to produce an image from 40 to 3.3mm across the frame, which at maximum magnification is equivalent to 2.5µm per pixel.

2.2 Experimental Method

A typical experiment consists of a substrate, which should remain solid throughout the experiment, and the particle to be investigated, generally an ore. After inserting the sample, the entire furnace was sealed, evacuated and backfilled with the required atmosphere (carbon monoxide or argon). The furnace was then continuously purged with 0.5 Nl/min of gas. The sample was heated at 250°C/min to 950°C, then 30°C/min 1100°C and finally at 5°C/min until the test was stopped.

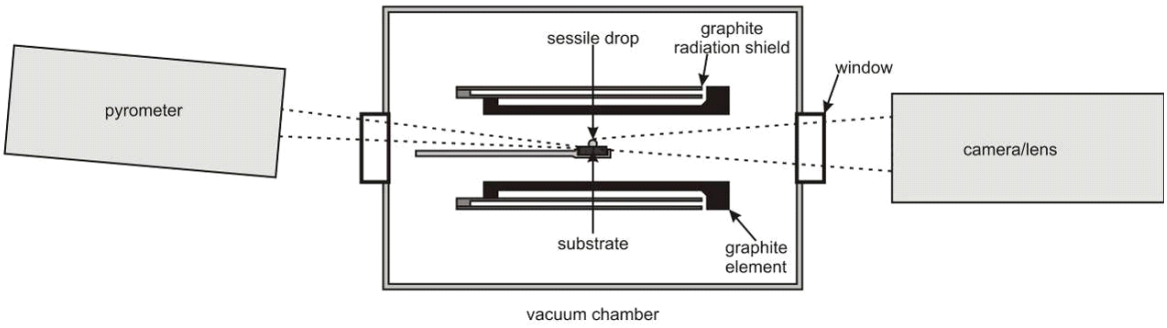


Figure 2: Schematic of sessile drop furnace

2.3 Materials

Industrial materials were used within this investigation, with the exception of some graphite substrates. All industrial materials used were provided by Eramet Norway. Comilog and Asman ore were pre-reduced by heating to 1100°C over 2 hours in 70% CO / 30% CO_2, and then quenched in Ar. The graphite substrates were made from EDM-1 from POCO (a high density graphite with an average grain size of less than 5 micron). Some information on the composition of the materials is provided in the table below.

Table 1: Analysis of materials

Sample	*HC FeMn slag*	*Pre-reduced Comilog Ore*	*Pre-reduced Asman Ore*
MnO(%)	39.3	88.8	74
FeO(%)	0.3	3.4	12.8
SiO_2(%)	23.6	2.5	3.4
Al_2O_3(%)	12.5	5.2	0.7
CaO(%)	16.7	0.1	8.2
MgO(%)	4.4	-	0.9

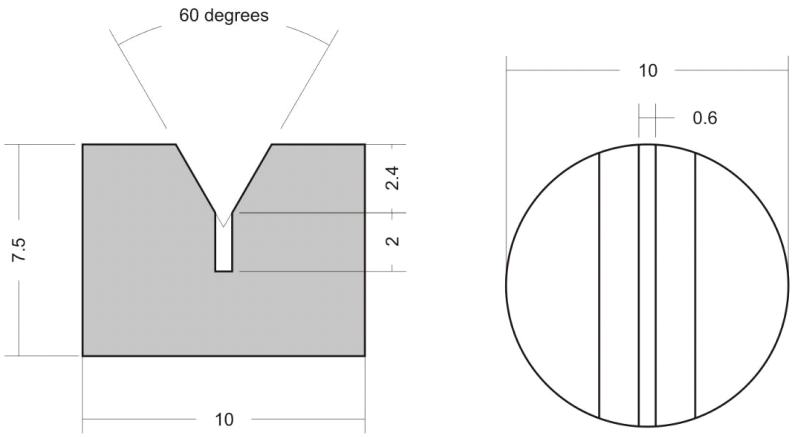


Figure 3: Graphite canyon, side view to the left and top view to the right. All dimensions in mm.

Some experiments were performed in a graphite canyon, to observe how different materials moved/flowed after they were molten. The dimensions of the canyon are given below.

3. RESULTS AND DISCUSSION

The results from some experiments are shown below.

Table 2: Experimental results

No	*Substrate*	*Gas*	*Particle 1*	*MP1(°C) Start*	*MP1(°C) Finish*	*Particle 2*	*MP2(°C) Start*	*MP2(°C) Finish*
1	Graphite	Ar	Comilog	1443	1562			
2	Graphite	Ar	Comilog	1459	1586			
3	Graphite	Ar	Comilog			HCFeMn slag	1232	1234
4	Graphite	Ar	Comilog	1440	1577	Coke particle		
5	Graphite	Ar	Comilog	1390	1443	HCFeMn metal	1210	1281
6	Graphite	Ar	Comilog	1257	stopped	HCFeMn slag	1222	1248
7	Graphite	CO	Comilog	1448	1487			
8	Graphite canyon	CO	Comilog	1346	1489			
9	Graphite canyon	CO	Comilog	1425	1506			
10	Graphite	CO	Asman	1829*	1831*			
11	Graphite	CO	Asman	1384	1471			
12	Graphite canyon	CO	Black Asman	1350	1439			
13	Graphite	CO	Grey+black Asman	1362	1553			
14	Graphite	CO	Black Asman	1443	stopped			
15	Graphite	CO	Black Asman	1438	stopped			
16	Graphite	Ar	HC FeMn metal	1174	1240			
17	Graphite	Ar	HC FeMn metal	1208	1250	HC FeMn slag	1221	1248

* Probably pure MnO (inhomogeneous materials).
"MP1 start" is the temperature at which a liquid is first observed in particle 1.
"MP1 finish" is the temperature at which the droplet formed from particle 1 appears to be completely liquid, with no obvious irregularities on the surface.

Below are some examples of interest for both Comilog and Asman ore.

3.1 Comilog Ore on a graphite substrate in argon

Figure 4 is a series of photographs which shows a simple experiment where 20.4mg of pre-reduced Comilog ore was placed on a disk of graphite in an argon atmosphere. When it reached 1430°C, the sample started to lift up on the right side, possibly due to the formation of a small amount of liquid at the interface between the slag and graphite. This temperature is higher than expected from the phase diagram as discussed previously. The first change in the shape of the particle was at 1443°C, but the shape was irregular, indicating that the particle was not completely molten, but still contained some solid MnO. At 1497°C bubbles started to appear from the interface between the ore and the graphite, indicating reduction of the ore, which became more vigorous as the temperature continued to increase. At 1562°C the droplet appeared smooth on the edges, indicating that there had been sufficient reduction of MnO in the liquid phase for all of the solid MnO to be dissolved. Finally, at 1570°C the reaction with the graphite became so vigorous that the rate of gas evolution was sufficient to throw the liquid from the substrate. As the slag droplet was destroyed during the experiment, no further analysis was possible.

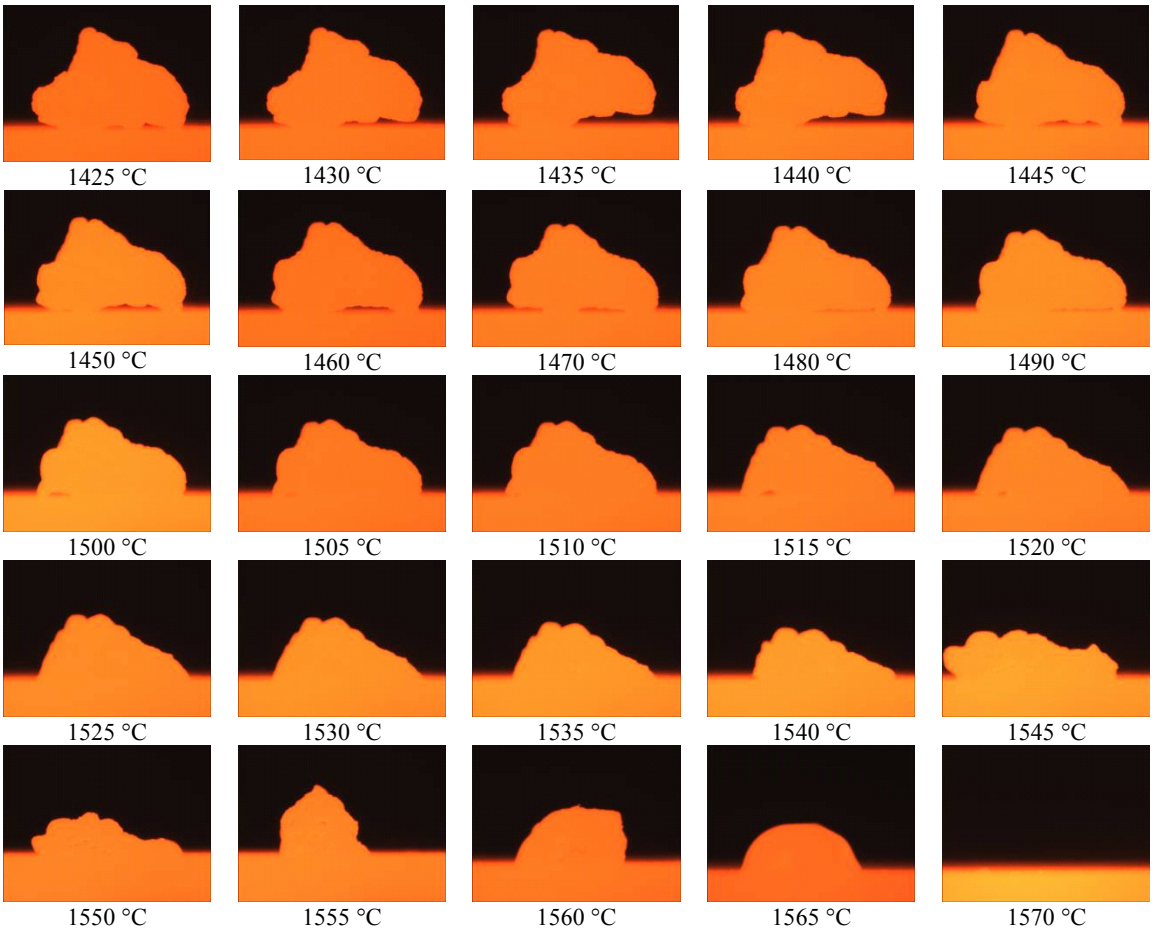


Figure 4: Experiment 1. Comilog ore on a graphite substrate in argon. The sample started to melt at 1443 ℃ and appeared completely molten at 1562 ℃. The individual temperatures are labelled below each photograph. The heating rate was 5 ℃/min. The reaction with graphite was so vigorous at the end of the experiment that the droplet 'exploded', with no slag remaining on the substrate

3.2 Comilog ore in a graphite 'canyon' in a CO atmosphere

Figure 5 shows the flow behaviour of Comilog ore as it melts in a 'canyon'. The dimensions of the graphite canyon are given in Figure 3. The Comilog ore started to melt at 1425°C, and appeared completely molten at 1506°C. As soon as the droplet was molten, small particles were seen to fall from the bottom of the suspended droplet of ore, which was most likely small metal prills reduced from the ore. These prills were very small, indicating that there was little attraction between the slag and metal. The experiment was stopped at 1600 °C, when only a small piece of molten ore remained. The final slag composition was 41%MnO, 28%Al_2O_3 and 26% SiO_2, with some other minor elements, as analysed in a microprobe. This experiment indicated that when metal is formed within a slag droplet, it is most likely to fall to the base of the furnace. The surface tension of the molten ore is sufficiently high to maintain a small slag droplet suspended in a gap 0.6mm wide, with most of the liquid remaining in a cavity a few millimetres wide for most of the experiment. This observation is in accordance with furnace excavations, where the majority of the metal is found in the bottom of the furnace, while slag is also found in the coke bed [2]. This is also in accordance to the previous results from pilot scale experiments where it was found that most of the MnO reduction occurs at the top of the coke bed [4]. The surface tensions and the viscosity keep the slag on top of the coke bed until it is heated and reduced close to the final tapped composition.

The fact that the molten products do not flow despite being fully molten has also been observed in previous works [5]. This can be explained by the fact that the gravity forces on the drop do not overcome the surface forces at the interface with the solid material. An example of how the surface tensions affect the flow of a molten fluid is shown in Figure 6. For a non wetting slag the flow into the coke bed in an industrial furnace will also be very limited.

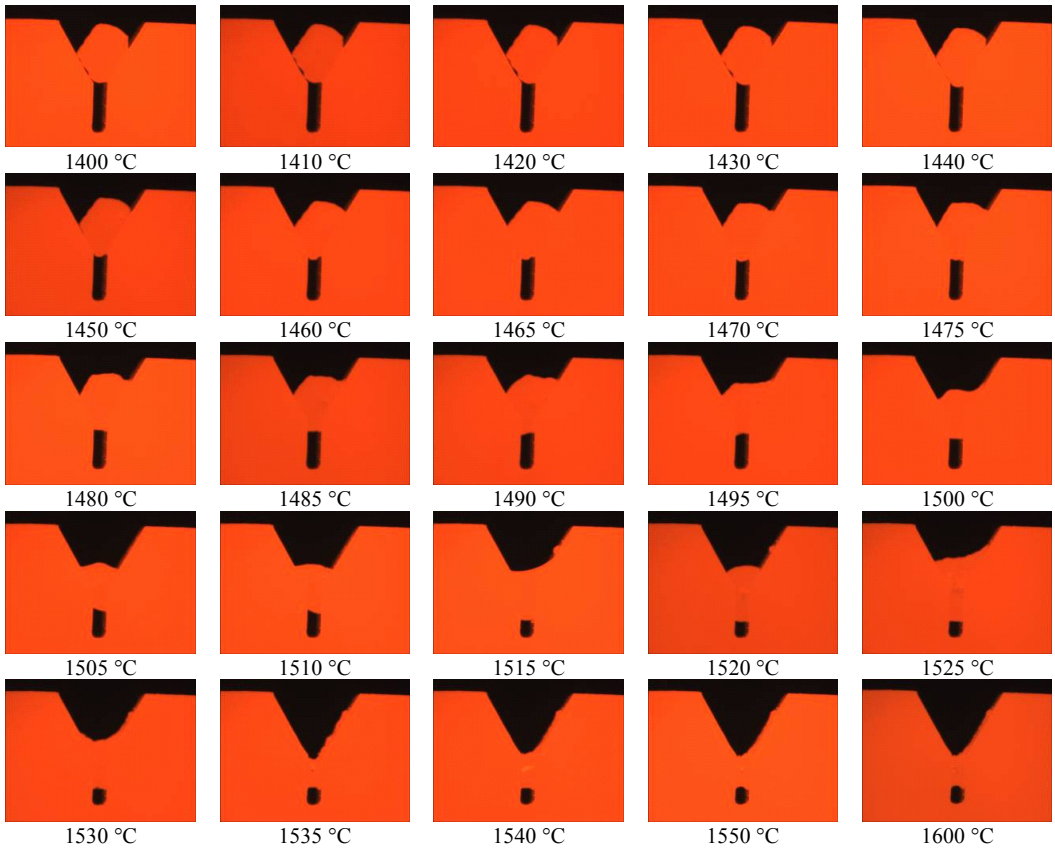
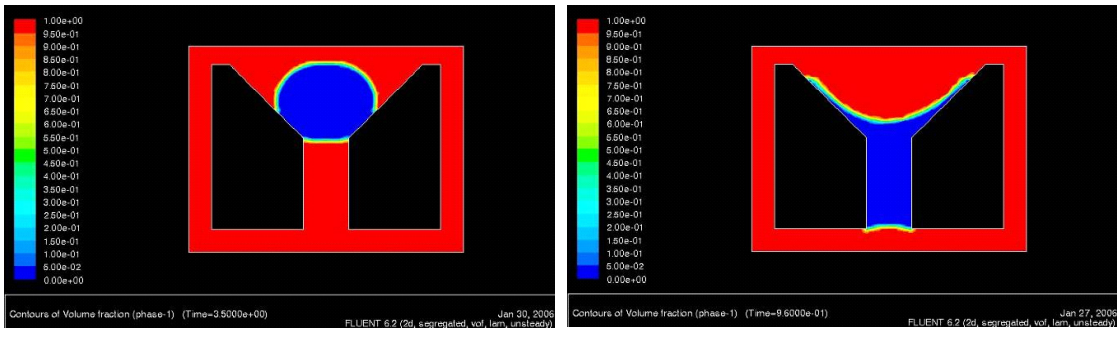


Figure 5: Experiment 9. Comilog ore sitting in a graphite canyon heated in CO. The temperature is labelled below the photograph. The heating rate was 5 °C/min. The ore melts from 1425 °C to 1506 °C, after which it continues to react with the graphite



(a) (b)

Figure 6: Final drop shape from CFD simulations at constant viscosity and interfacial tension (with gas). (a) Non wetting fluid (high surface tension). (b) Wetting fluid (low surface tension)

3.2.1 Shrinkage of Comilog from 1000 °C to 1200 °C

Figure 7 indicates the extent of shrinkage of the Comilog ore particle in experiment 9. Mineralogically, Comilog consists mostly of pyrolusite and cryptomelane [6]. The expected volume decreases for cryptomelane and pyrolusite are respectively 25-28% and 6-10% in air, and 38% and 23% in reducing conditions [7-9]. Some of the contraction must have taken place during the pre-reduction, prior to the sessile drop experiment. Probably, the thermal transformations were not complete when the pre-reduction finished at 1100°C, and then continued when this temperature was reached in the sessile drop furnace. In our experiments, we could not observe that reducing conditions promoted a greater contraction.

No data was found concerning the thermal transformation of braunite II, which is the main phase in Asman 48.

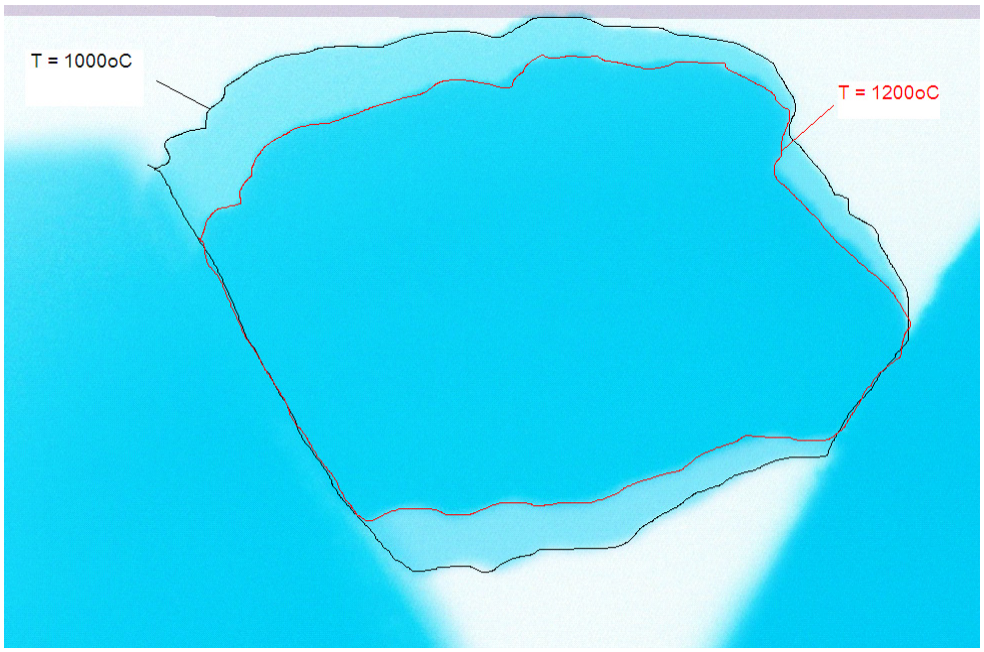


Figure 7: Contraction of the ore between 1000 and 1200°C for the Comilog ore in the canyon experiment (Experiment 9)

3.3 Two Asman particles on a graphite substrate heated in CO

In Figure 8 two pieces of Asman ore were heated in an atmosphere of CO on a graphite substrate. On the left side was a grey particle, while on the right was a black particle. In this experiment the particles started to melt at 1360°C and were completely molten at 1550°C.

3.3.1 Microprobe Analysis of Experiment 13

After heating to 1600 ºC the droplet was analysed in the microprobe, as shown in Figure 9. The "droplet" is actually a bubble, where the walls consist of slag and metal surrounding the gas. The slag is almost completely reduced in MnO and FeO (under 0.05%): it consists of 65% CaO and 30% SiO_2 with some additional minor elements. The metal consists of two phases, one phase has approximately 75% Fe, 20% Mn, 1% C, 1.5% Si and 0.1% P while the other has 60% Fe, 30% Mn, 4% C, traces of Si and no P. It is uncertain why the large metal drops are to be found in the upper part of the sample. Since significant amounts of carbon have been consumed, direct reduction must have taken place. Therefore, the big metal drops must have been at least partly formed at the bottom. This is confirmed by experiment 14 and 15 where the largest metal drops are found at the very bottom of the particle. The small holes at the bottom of the sample are bubbles that were under

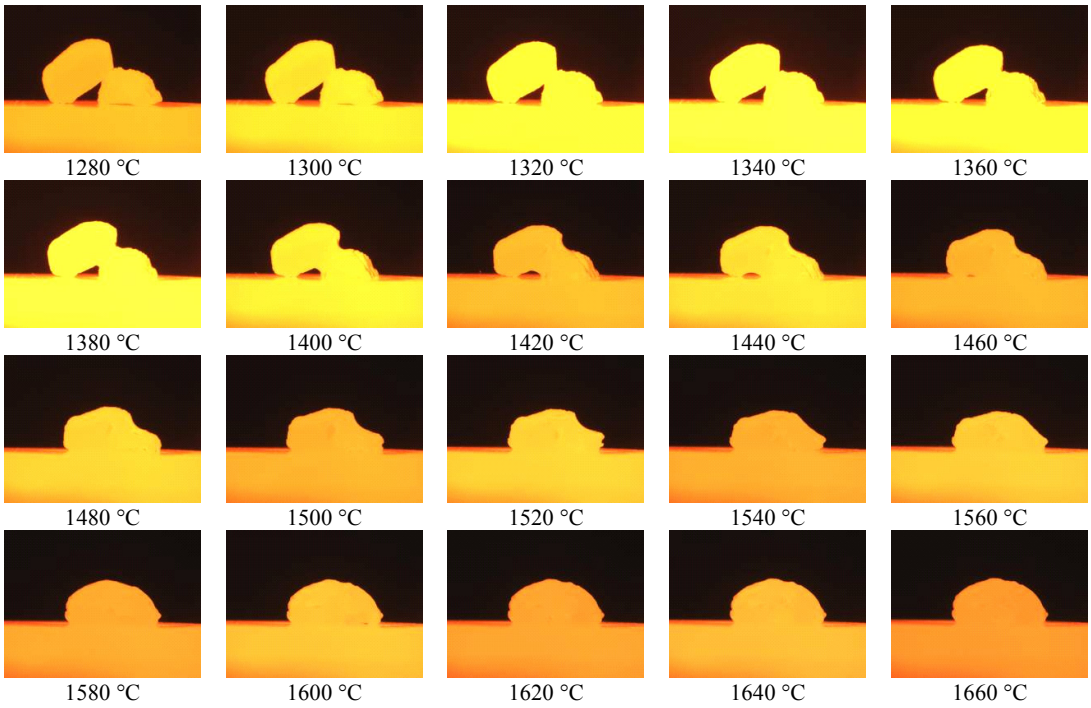


Figure 8: Experiment number 13. Asman ore on a graphite substrate heated in CO. The temperature is labelled below the photograph. The heating rate was 5 ℃/min

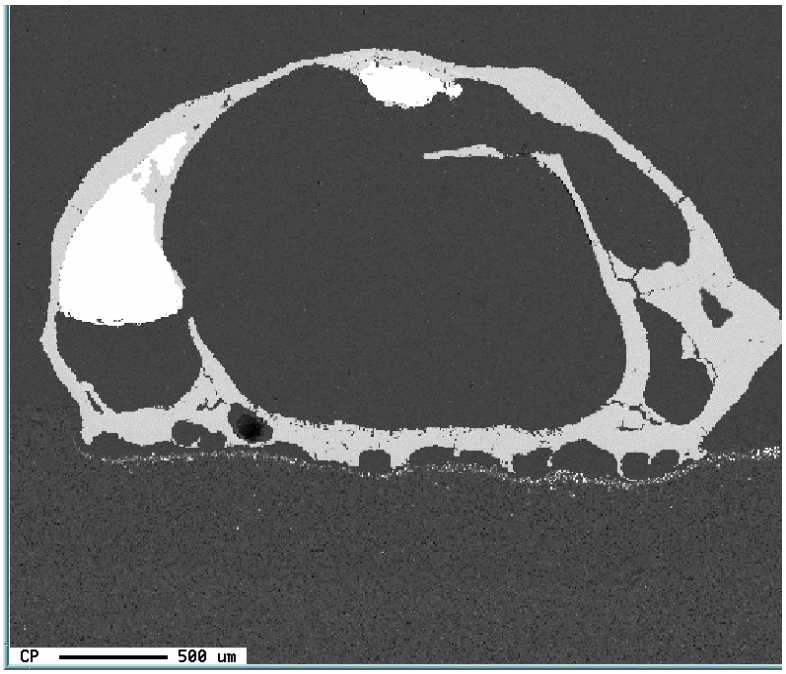


Figure 9: Microprobe image from Experiment 13. The result after two particles of Asman ore were heated on a graphite substrate in CO. The brighter phase is metal, the grey phase is oxide and the dark phase at the bottom is graphite

formation. These bubbles coalesce to make larger bubbles and build up pressure. Once the pressure overcomes the surface tension of the slag, the bubble will burst.

Some much smaller iron rich drops are found in the upper part of the droplet. The fact that all metal appears in the upper part of the sample indicates that this metal has been transported there, probably as a result of the strong bubbling activity that resulted in stirring the molten materials. Smaller metal drops must have coalesced to larger ones. Because of the higher metal density, we expect the metal drops to be attracted to the bottom. However, under cooling, the metal drops may have been stuck at the top because of the large viscosity of the freezing slag that prevented their flowing down. A similar phenomenon seems to have taken place in experiment 11 for the Asman in a canyon, for which bubble formation resulted in a big bubble that caused the two phases to separate with metal on top.

3.4 Smelting Range of Materials

Within this study smelting designates the change of phase from solid to liquid coming from both chemical reactions; MnO reduction and continuously decreasing MnO content in slag, as well as phase change due to heating (which would happen independently of chemical reactions in an inert environment). The phase composition of the ore, that is the amount of solid MnO phase and liquid phase, is dependent on the temperature as well as the MnO content, which decreases with temperature and time. The temperature where the first liquid phase is visible, and the temperature where the ore particle behaves as a liquid, is hence dependent on the heating rate. However, even if these temperatures are somewhat different in an industrial furnace, the trends are expected to be the same in this apparatus as in the industrial furnace.

3.4.1 Comilog

In nitrogen, the smelting temperature of Comilog (to get a round drop) was found to be 1520°C [10]. This is in the smelting range observed in this study for Comilog on graphite in argon (1450-1575°C). In a CO atmosphere on graphite, the melting range has been reported to be 1440-1450°C [11]. In the present work, under similar conditions, the range was 1450-1490°C.

3.4.2 Asman

Asman consists of one grey and one black phase that are easy to identify by eye. The grey phase is almost pure MnO while the black one is rich in ferrous oxides. The grey phase started melting around 1830°C (Experiment 10). This is in agreement with melting temperatures for MnO as reported in [12]; 1844°C[13], 1875°C[14] and 1830°C (in vacuum)[15]. In a more recent study, the melting temperature of MnO in equilibrium with a Si-Mn alloy was evaluated to be 1842°C[16]. In the present study, the black phase of Asman melted in the region between 1300 and 1450°C in CO, while a mixture of grey and black Asman melted in the range 1430-1570°C. This corresponds well with the 1410-1450°C observed under similar conditions, though the proportion between black and grey Asman in these experiments is unknown [11]. According to the phase diagrams, it is expected that a homogeneous mixture of Asman ore will behave as a fluid at a higher temperature compared to Comilog ore due to a higher amount of basic oxides, and hence a higher quantity of solid MnO spheres. However, the experimental results show that the mineralogy and the distribution of phases may affect the smelting temperature more than the chemical composition in itself.

3.4.3 FeMn slag

From Experiment 3, the smelting point was determined to be 1230°C, which is similar to previous measurements: 1210°C [10] and 1220-1240°C [5]. As the HCFeMn slag has a MnO content close to the liquidus composition, it is expected that it would melt rapidly at a relatively low temperature.

3.4..4 Atmosphere

The atmosphere was controlled by maintaining a low flow rate of gas (0.5 Nl/min). Carbon monoxide and argon were tested when a graphite substrate was used (experiments 1 and 2 with Ar, experiment 5 with CO). In both cases, Comilog started smelting at 1450°C. The surface of the particle exposed to the atmosphere clearly softens faster in the presence of CO. A round-shaped drop, indicating complete melting, is achieved

at 1575°C in Ar and at 1490°C in CO. There are several possible reactions between CO and higher manganese oxides and iron oxide that could explain the observed difference.

3.4.5 Additional particles

The presence of low melting point materials, such as HCFeMn slag in contact with high MnO ores, promotes the smelting of materials that typically require a higher smelting temperature. This means that an ore with a high smelting point in contact with a lower smelting point material, will generally smelt earlier and faster.

4. CONCLUSIONS

Sessile drop experiments allowed the observation of ores as they were heated on carbon substrates. The substrates were either flat or had a canyon shape to simulate what may be experienced by ore on top of the coke bed of an industrial furnace. Chemical reactions were analyzed, in some cases by studying microprobe pictures of the final products.

The smelting ranges obtained in the present work are in good agreement with earlier studies. Typical smelting ranges on graphite in a CO atmosphere are 1450-1490°C for Comilog, 1430-1570°C for Asman and 1230°C for HC FeMn slag. The main difference is due to the MnO content, as well as the mineralogy of the ore. For the high MnO ores, like Asman and Comilog, the difference in smelting range is low compared to materials with low MnO contents like HCFeMn slag. However, the mineralogy of the ore may also affect the smelting temperature, as well as distribution of minerals and elements.

A CO atmosphere promoted an earlier and faster smelting, compared to argon. When an ore with a high smelting point is in contact with materials with a lower smelting point (slag or another ore), it smelts earlier and faster, after it is wetted by the adjoining particle. Consequently, it may be possible to adjust the smelting range of a given mix by varying its composition by blending it with lower smelting point materials.

Between 1100 and 1200°C (before melting), the volume of Comilog is reduced by 5 to 15%. This may be explained by thermal transformation to MnO.

Because of the small size of the samples (20 mg), we observed some variations in the composition for samples made of the same ore, that resulted in different contact angles and composition of the final products.

5. ACKNOWLEDGMENTS

The authors would like to thank Dr Marc Dhainaut for modelling the behaviour of a liquid drop melting within a canyon, as presented in Figure 6.

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