MELTING PHENOMENON OF MANGANESE BEARING ORES

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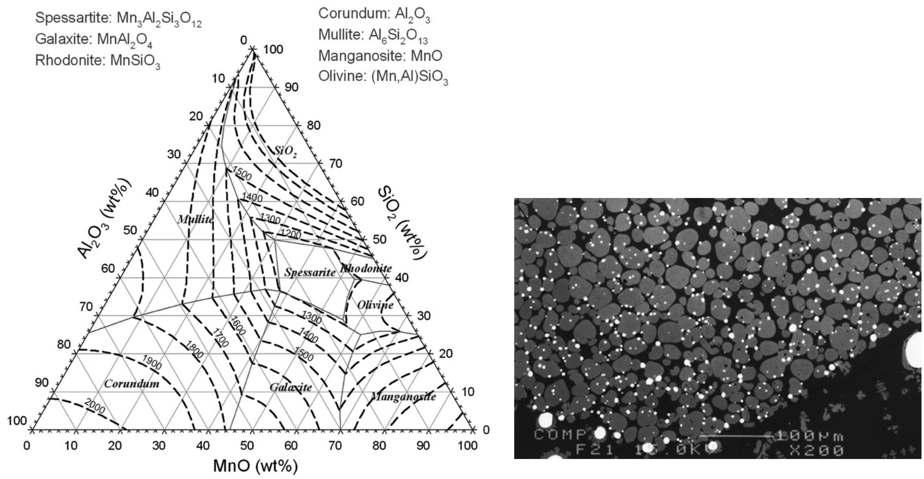
ABSTRACT

The melting phenomenon of various commercial manganese ores and sinters were studied in an experimental sessile drop furnace and a high temperature DTA/TGA. In the sessile drop furnace particles were placed on graphite substrates and then heated at a constant rate of 5°C/min in an atmosphere of carbon monoxide. Photographs of the particles were taken every second with a digital video camera to determine the softening and melting temperatures for each material. Some samples were also stopped at different stages of melting and analyzed with an EPMA to determine the composition as a function of temperature. It was found that the different materials had melting points ranging from 1200°C to 1600°C, with some phases melting above 1800°C. Generally sinter melted at a lower temperature than ore. Since manganese ore is generally not a homogeneous material, a certain variation in the measured melting point is expected and discussed. The experimentally determined softening and melting temperatures of each material are also compared to the relevant phase diagrams. Some implications of these properties on the furnace operation are discussed.

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, 2], but due to the time required to cool a furnace 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.



(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]

This paper discusses the use of complementary methods, where small samples of various raw materials can be studied while they are heated within a controlled environment. From this information it is then possible to attempt to understand the behavior of materials within an industrial furnace.

At temperatures above 1100°C, in an atmosphere of carbon monoxide, it can be assumed that manganese will exist as MnO and ores such as Comilog and CVRD can be presented in the MnO-SiO_2-Al_2O_3 phase diagram, as shown in Figure 1a. As the temperature increases, a liquid phase will be formed in co-existence with a solid MnO phase, as shown in Figure 1b. As the temperature continues to increase, reduction of the MnO will begin. 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.

Another issue not completely understood is the influence of the electrical conductivity of manganese ore on the operation of a submerged arc furnace. Other studies [5] have found that for highly conductive materials such as metallurgical coke, the contact resistance dominates. The electrical conductivity of manganese ore is expected to be even lower at modest temperatures, so it is reasonable to assume that the electrical conductivity will be very poor until the ore has softened sufficiently to allow good contact. The electrical conductivity is therefore not an isolated property, but must be studied with the softening/melting point of the ore.

The physical properties of the ore during 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.

METHODOLOGY

Two different methods were used to investigate the behavior of manganese ore while being heated in an atmosphere of carbon monoxide. The sessile drop furnace allowed the materials to be visually observed to determine when they softened and melted, and when the first gas bubbles were observed. The high temperature DTA/TGA was used to measure the energy required to heat the manganese ore and the resulting change in weight.

Sessile Drop Furnace

The sessile drop furnace, as shown in Figure 2, was designed to measure the contact angle of a liquid drop on a 10 mm 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.

All of the heated furnace parts, including the element and heat shields, were 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 2.6 µm per pixel.

A manganese ore sample of about 25 mg was placed in the centre of a graphite substrate, 10 mm diameter and 3mm high, which was located on the sample holder. After inserting the sample, the entire furnace was sealed, evacuated and backfilled to atmospheric pressure with carbon monoxide. The furnace was then continuously purged with 0.5 Nl/min of gas while the sample was heated at 250°C/min to 950°C, then 30°C/min to 1100°C and finally at 5°C/min until the test was stopped, typically at 1600°C.

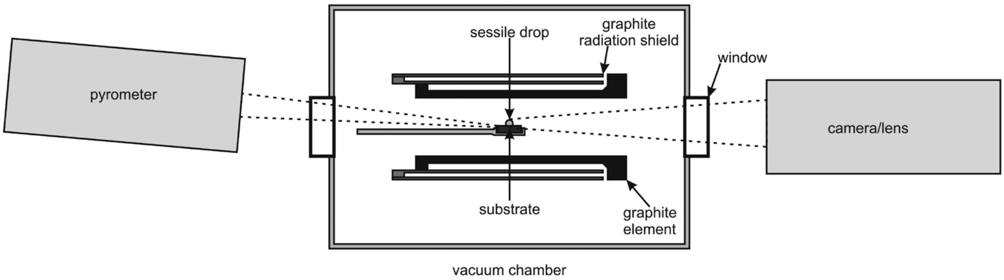


Figure 2: Schematic of sessile drop furnace

Differential Thermal Analyser and Thermal Gravimetric Analyser (DTA/TGA)

The combined DTA/TGA was a SetSys Evolution 2400, supplied by Setaram. To produce a representative sample, 500 g of each manganese ore was ground in a ball mill to less than 100 μm. A sample of approximately 35 mg of manganese ore was then placed in a graphite crucible 5 mm in diameter and 8 mm high, and loaded onto the DTA rod. The furnace was then sealed, evacuated and backfilled with carbon monoxide. The sample was then heated at 20°C/min to 1600°C, held for 5 minutes and then cooled at 20°C/min. The furnace was flushed with 100 ml/min of carbon monoxide during the experiment.

Materials

The substrate and crucibles were made from ISO-88, a high density iso-statically pressed graphite supplied by TANSO. Industrial manganese ores were used within this investigation, which were provided by ERAMET Norway and RDMN Norway. Before testing, the manganese ore was pre-reduced by heating to 1100°C over 2 hours in 70% CO / 30% CO_2, and then quenched in Ar. Some information on the composition of the materials is provided in the Table below.

Table 1: Analysis of materials after pre-reduction at 1100 °C in 70% CO / 30% CO_2 (wt%)

	Assmang	Comilog	CVRD ore	CVRD sinter
MnO (wt%)	73.9	82.5	75.1	75.6
FeO (wt%)	14.4	4.4	10.0	8.4
SiO_2 (wt%)	6.1	5.1	3.4	5.8
Al_2O_3 (wt%)	0.4	7.0	11.1	9.4
CaO (wt%)	0.3	0.9	0.3	0.5
MgO (wt%)	4.8	0.3	0.1	0.2

RESULTS AND DISCUSSION

Sessile Drop Furnace

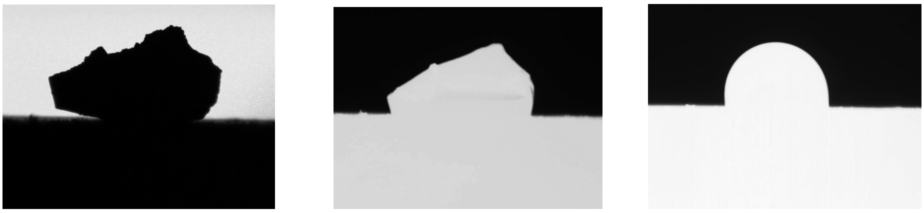
The results from the sessile drop furnace are summarized in Table 2 below. The melting of the manganese ore was assessed in three different ways.

- Start melting, the temperature at which liquid was visible on the surface of the manganese ore
- Finish melting, when the manganese ore appeared to be completely liquid
- Start reduction, when the first gas bubbles were visible on the surface of the manganese ore.

The final temperature is the temperature at which the experiment was stopped. This analysis was determined by observing the images taken during each test. An example of these images at the different stages of melting is given below in Figure 3.

Table 2: Results from sessile drop experiments, including the average and standard deviation for each manganese ore

Exp. No.	Material	Final temperature	Start melting	Finish melting	Start reduction
1	Assmang ore	1600°C	1545°C	1596°C	1590°C
2	Assmang ore	1600°C	1444°C	1469°C	1445°C
3	Assmang ore	1600°C	1404°C	1499°C	1441°C
4	Assmang ore	1700°C	1390°C	1486°C	1420°C
Average for Assmang ore			**1446±70°C**	**1513±57°C**	**1474±78°C**
5	Comilog ore	1450°C	1277°C	1332°C	-
6	Comilog ore	1500°C	1471°C	-	-
7	Comilog ore	1500°C	1479°C	-	-
8	Comilog ore	1550°C	1478°C	1549°C	1484°C
9	Comilog ore	1550°C	1500°C	1538°C	1511°C
10	Comilog ore	1600°C	1485°C	1528°C	1493°C
11	Comilog ore	1600°C	1496°C	1537°C	1496°C
Average for Comilog ore			**1485±11°C**	**1538±9°C**	**1496±11°C**
12	CVRD ore	1370°C	1331°C	1365°C	1306°C
13	CVRD ore	1500°C	1470°C	-	-
14	CVRD ore	1550°C	1451°C	1479°C	1457°C
15	CVRD ore	1550°C	1455°C	1482°C	1452°C
16	CVRD ore	1600°C	1458°C	1488°C	1445°C
17	CVRD ore	1600°C	1479°C	1528°C	1502°C
Average for CVRD ore			**1485±13°C**	**1538±23°C**	**1496±26°C**
18	CVRD sinter	1400°C	1398°C	-	-
19	CVRD sinter	1500°C	1425°C	1497°C	1471°C
20	CVRD sinter	1600°C	1232°C	1260°C	1375°C
21	CVRD sinter	1600°C	1481°C	1362°C	1387°C
Average for CVRD sinter			**1354±85°C**	**1413±132°C**	**1411±52°C**



a) 20 °C b) 1404 °C c) 1499 °C

Figure 3: Images of Assmang ore heated at 5°C/min in carbon monoxide (experiment No. 3 in Table 2). a) cold sample, b) initial melting, c) completely molten

The results in Table 2 indicate that there is a significant variation in the properties of Assmang ore and CVRD sinter, although the Comilog ore and CVRD ore are relatively consistent. This indicates that some materials are highly inhomogeneous, which has been discussed previously [6] for Assmang ore which contains two distinct phases, one nearly pure MnO and the other containing significant quantities of iron. However, if experiment number 1 is excluded from the analysis, the results are much more consistent.

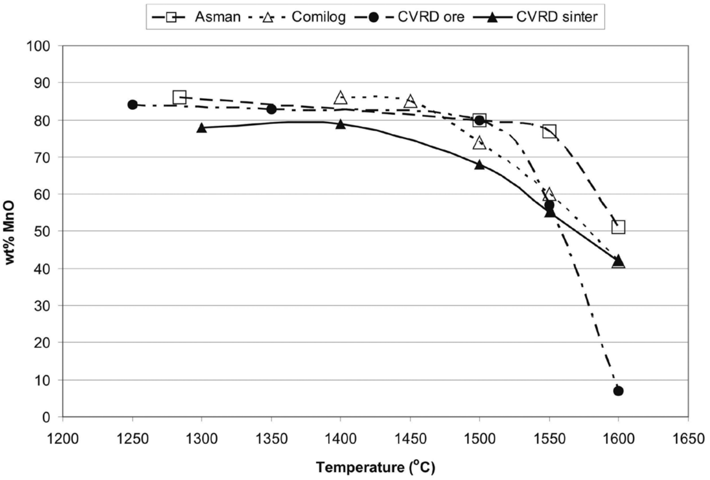


Figure 4: The composition of each ore as a function of temperature, as measured by an electron microprobe

After each experiment the composition of the sample determined with an electron microprobe, to determine the MnO content. The composition of each manganese ore was then plotted as a function of temperature, as shown in Figure 4. This shows the temperature at which reduction begins for each manganese source, and it agrees well with the averages in Table 2, except for Assmang ore which is about 80°C higher in Figure 4.

DTA/TGA

Both Comilog and CVRD sinter were also analyzed with a DTA/TGA, where the manganese ore samples were heated in a CO atmosphere at 20°C/min to 1600°C. Both the energy required to heat the sample and the resulting mass change were recorded, as shown in Figure 5.

These samples are more repeatable and provide more of an average result, as the manganese ore was ground to a fine powder in a ball mill, which also provided good mixing. The results shown in Figure 5 indicate that reduction of the Comilog ore begins at about 1290°C, as indicated by the loss in weight. The DTA response for Comilog indicates the principle melting points are 1450°C and 1570°C. The initial melting point corresponds reasonably well with the results from the sessile drop furnace. The endothermic dips at 1200 and 1250°C are due to the phase change from cryptomelane and pyrolusite [8, 7, 9].

The CVRD sinter is simpler to interpret, with reduction beginning at about 1400°C. CVRD sinter also contains minerals such as cryptomelane, lithiophorite and todorokite [10], which are probably responsible for the endothermic signals at 1160 and 1220°C. There is a strong signal at 1400°C for both melting and reduction which occur simultaneously.

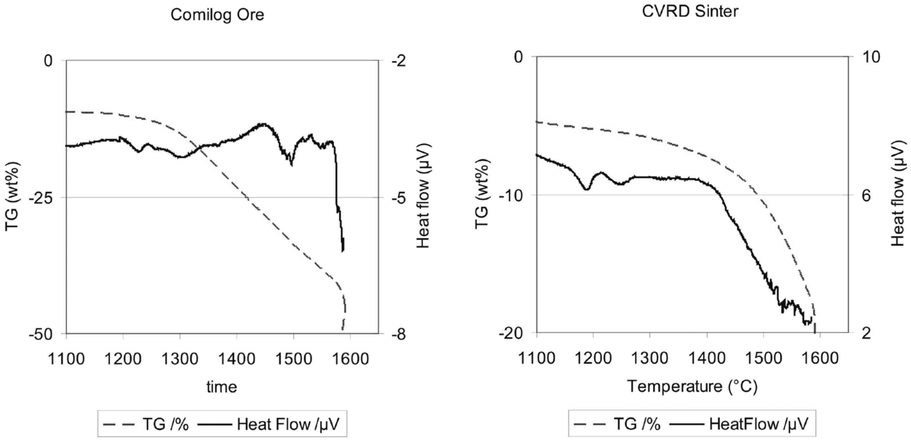


Figure 5: The heat flow and weight change of Comilog ore and CVRD sinter when heated in a CO atmosphere at 20°C/min to 1600°C

Assmang Ore

The non-reducable oxides in Assmang ore are more basic than the other ores studied. Using a suitable phase diagram [3], the expected initial melting point is about 1350°C. The sessile drop experiments found that the initial melting point varied from 1390 to 1545°C, with an average temperature of 1450°C, although if the first experiment is excluded, the data is more consistent. However, this ore has large variations in composition [6] and the phase diagram indicates that this will result in large variations in the initial melting point. Figure 4 showed that reduction began at about 1550°C, which is relatively high, as gas bubbles were visible from 1420°C in some experiments.

Comilog Ore

Previous studies have found that Comilog melted at 1440-1450°C [11] and 1450-1490 °C [6]. The phase diagram indicates that the initial melting point for Comilog ore is about 1430°C, which is about 50°C lower than observed in the sessile drop furnace and 20°C lower than the DTA indicated. The results for Comilog are relatively consistent, with a small variation in each of the measured properties. Comilog melts at about 1485°C, and reduction is visible from 1500°C. Weight loss begins at 1280°C, although Figure 4 indicates that reduction of MnO begins at about 1450°C.

CVRD Ore

From the phase diagram the initial melting point of CVRD ore is expected to be about 1500°C, which agrees with the behavior observed in the sessile drop furnace. Reduction was also observed from about the same temperature, and Figure 4 indicates that the MnO content decreases rapidly from 1500°C, which is why it is completely molten by about 1540°C. The results for CVRD ore are relatively consistent.

CVRD Sinter

CVRD sinter is more acidic, with an initial melting point of 1420°C from the phase diagram. This is higher than the average result observed in the sessile drop furnace, but within the range. Reduction was observed from about 1410°C in the sessile drop furnace, which corresponds with an endothermic heat flow and a mass loss in the DTA/TGA. Although CVRD sinter melts at a lower temperature than the ore, the reduction rate is much more gradual.

Furnace Operation

The observed differences in the melting and reduction of the different manganese ores investigated will affect the performance of the submerged arc furnace. The choice of ore depends on the specific conditions and constrictions of the furnace operation, especially the combined properties of all of the materials in the charge mix. The melting properties of the manganese ore will influence the coke bed size and temperature at the top of the coke bed, which will affect the heat balance within the furnace. For example, if the ore melts at a low temperature it will flow more quickly through the coke bed, resulting in a larger coke bed with a lower temperature at the top. Also, the temperature at which the MnO in the ore is reduced will influence the heat balance in the furnace, as an ore which is reduced at a lower temperature will consume more energy in the upper zones of the furnace. These issues are also discussed by Ringdalen *et al.* [12].

However, the choice of ore depends on several factors including the ore strength, oxygen content, mineralogy, porosity, metal composition, energy requirements and slag to metal ratio. It is critical to have an understanding of all of the ore properties and their influence on the operation of the SAF when selecting the ores to be used within the furnace.

CONCLUSIONS

The softening/melting point and reduction of manganese ore in contact with graphite in an atmosphere of carbon monoxide was determined with a sessile drop furnace and a DTA/TGA. It was found that the initial melting point of Assmang, Comilog and CVRD ores was between 1450 and 1500°C, while CVRD sinter melted at 1350 to 1400°C.

Reduction of MnO started at about 1300 °C for Comilog, while CVRD sinter was slowly reduced from 1400°C, CVRD ore was quickly reduced from 1500°C and Assmang was not reduced until above 1550°C.

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