The thermophysical properties of raw materials for ferromanganese production

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Abstract – Manganese ferro-alloys manufacturing involves a combination of quality raw materials and an energy source to produce high-quality products with low energy consumption. The thermal properties of manganese raw materials such as ores, sinters, and briquettes, are among the many factors that determine the amount of energy needed for processing. Thermal expansion, thermal diffusivity, conductivity, and apparent specific heat capacity of solid samples and compacted powder samples of manganese ores were examined from room temperature to 1000 °C. The effect of porosity (of the materials used) on the thermal properties was also investigated. The laser flash method and a pushrod dilatometer were used.

INTRODUCTION

The commercial production of ferromanganese or silico-manganese alloys involves the carbothermic reduction of manganese oxide ores. The process takes place in a submerged-arc furnace (SAF) where the three electrodes are submerged in the burden. The furnace is fed from the top with a mixture of different raw materials, which are previously weighed to obtain the desired composition of alloy and slag. The electric current runs through the zone below the electrode where electrical energy is converted to thermal energy.

The production rate, product quality, and stability of the furnace operation are the most important objectives during ferromanganese production. Raw material properties play a very important role in determining the whole process[1]. Knowledge about material properties, such as chemical composition, Mn/Fe ratio, reactivity, and mechanical strength of raw materials, is essential to having good control of the ferromanganese furnace.

There are not many publications where thermal properties of manganese ores and agglomerates are investigated. In this paper, properties such as thermal conductivity, thermal diffusivity, thermal expansion, and apparent specific heat capacity of ores are presented. The motivation for this research work is the

possibility of exploring and supplying new information about the thermal properties of manganese ores and how that can affect the process where continuous energy transfer between hot gases and solid materials occurs. The research work is based on the flash method for the measurement of thermal diffusivity.

EXPERIMENTAL

It has been almost 50 years since Parker published a paper introducing the flash method as a technique used for the measurement of thermo-physical properties of solid materials[2]. Due to the accuracy and reliability of the results, fast measurement time, easy sample preparation, and efficiency of the measurements, this method became the most popular, worldwide. Since the introduction of the method by Parker, many developments and significant improvements have been made to the non-contact, non-destructive testing technique[3]. The main idea of the technique is relatively simple. The front face of a small, usually disc-shaped, sample is heated by a short energy pulse sent from the laser or a flash lamp. An infrared detector (ID) measures the temperature rise on the opposite (rear) surface of the sample versus time. Additionally, the most up-to-date systems have the capacity to define the thermal diffusivity α and the specific heat C_P. If the bulk density ρ of a specimen is known, the thermal conductivity can be computed according to Equation 1 [4].

$$\lambda(T) = \alpha(T) \bullet Cp(T) \bullet \rho(T) \qquad [1]$$

A schematic design of the LFA 457 MicroFlash is presented in Figure 1.
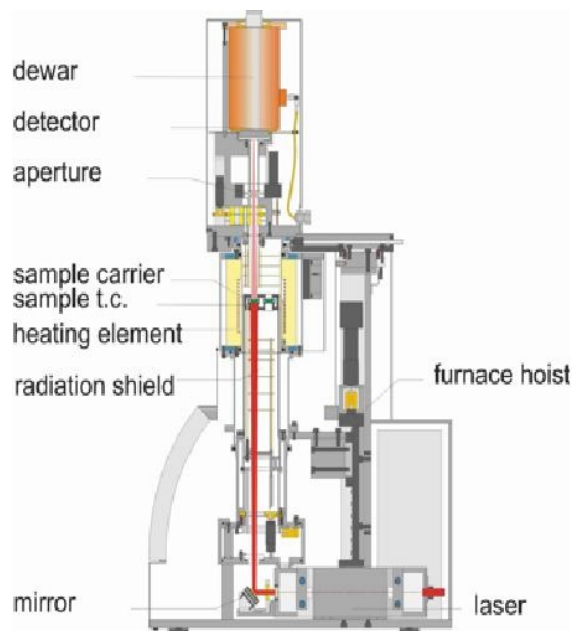

Figure 1: LFA 457 MicroFlash schema [4]

The laser, which is located in the bottom part of the instrument, is powered by an external capacitor bank. The laser pulse energy output is up to 15 J/pulse,

with the pulse length of 330 μs. Software can adjust the output of the laser via the voltage level of the capacitor bank and/or via a filter system located before the laser. The laser beam diameter is adjusted by an optical system to the required sample's diameter. Just after the optical system, the laser beam is reflected by the mirror and through the window to reach the sample chamber. The sample carrier is located inside the vacuum-tight sample chamber. It is possible to perform testing with a single or multiple sample arrangement, with an accurate sample carrier suitable for a particular condition, as presented in Figure 2.
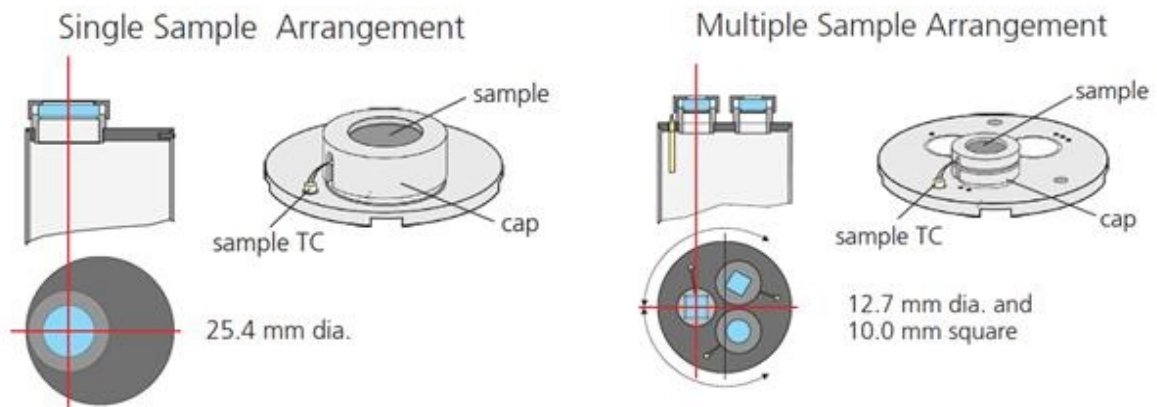

Figure 1: Single and multiple sample arrangement [LFA 457 Netzsch users manual]

Using the laser flash method, the specific heat of the material can be measured during the diffusivity measurement. By comparing the temperature rise of the tested sample to the temperature rise of a reference sample with a known specific heat value, it is possible to compute the C_P of the sample[5]. The C_P measurement of manganese ore, and manganese ore powder compacts, was calculated on the assumption that the mass of the sample was constant during the test. Therefore, the presented data are apparent C_P values. Moreover, measurement of thermal diffusivity by LFA 457 requires information about dimensions, density, and the tendency of the material to change in length in response to temperature change. To determine the linear thermal expansion of a material, a pushrod dilatometer 'Dill 402 E', made by the Netzsch company, was used.

The flash technique is strongly dependent on the quality of the sample, so the sample preparation plays an important role[6]. Pores, cracks, and parallelism of the sides of the disc-shaped sample can have a strong effect on the results. The manganese ores and agglomerates are relatively hard, porous, and brittle materials, with a tendency to being crushed. Therefore, the specimen preparation was a challenging and time-consuming part of the research. Sample preparation work for LFA measurement was divided into two main parts. The first part considered the solid materials (Assmang and Gabonese ores). The second part was focused on the powder materials obtained by crushing down the Assmang and Gabonese, briquette and sinter, to particles sized less than 63 μm. The main reason for crushing the original material into

powder was the difficulty experienced with the preparation of disc-shaped samples prepared from sinters and briquettes, which are shown in Figure 3.
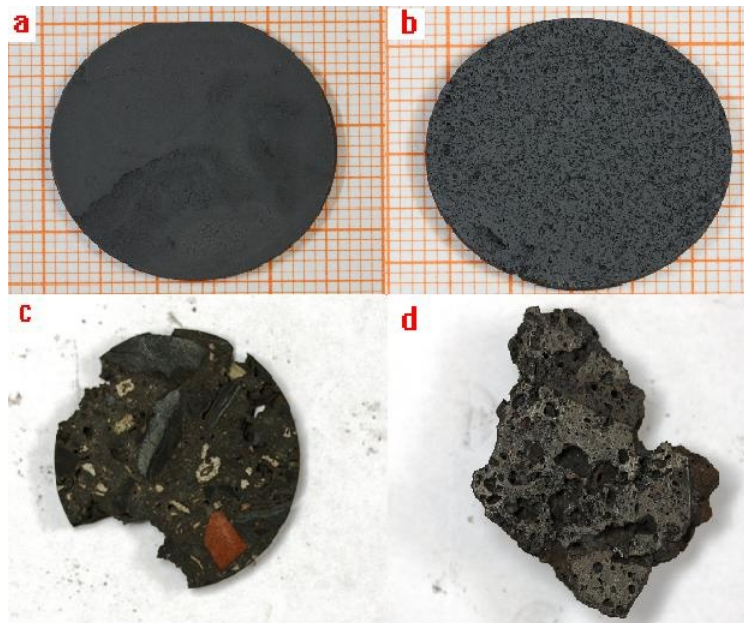

Figure 3: Specimens obtained after the mechanical working;
a) Assmang, b) Gabonese, c) briquette, d) Gabonese sinter

The porosity of the samples used is presented in Table I. Table II presents the chemical compositions of the raw materials used in the tests.

Table I: Porosity of samples

Material	Porosity, %
Assmang ore	3.7
Assmang powder compact	32.3
Gabonese ore	32.8
Gabonese powder compact	34.4

Table II: Chemical composition of raw material, mass %

Material / Compound	Gabonese	Assmang	Sinter	Briquette
Mn total	49	46.5	56.3	38.2
Fe total	2.3	9.8	3.8	5.3
SiO_2	5.9	6.8	7.6	9.8
Al_2O_3	6.4	0.3	6.5	4.9
CaO	0.14	6.8	0.34	10.6
MgO	0.01	0.94	0.01	3.8
TiO_2	0.14	0.01	0.17	0.15
P	0.1	0.03	0.11	0.11
S	0.01	0.05	0.01	0.24
K_2O	1.13	0.02	0.8	0.69
BaO	0.17	0.16	0.31	0.09

The mineralogy of manganese ore is complex. The most common manganese minerals are oxides, carbonates, or silicates. Table III presents an overview of common manganese minerals in manganese ore deposits[7].

Table III: Common manganese minerals in manganese ore deposits

Mineral	Chemical formula
Pyrolusite	MnO_2
Ramsdellite $MnO2$	MnO_2
Nsutite	$Mn(O,OH)_2$
Hollandite	$Ba_x(Mn^{4+},Mn^{3+})_8O_{16}$
Cryptomelane	$K_xMn^{4+}_{8-x}Mn^{2+}$ xO_{16}
Manjiroite	$Na_x(Mn^{4+},Mn^{3+})_8O_{16}$
Coronadite	$Pb_x(Mn^{4+},Mn^{3+})_8O_{16}$
Romanechite	$Ba_{.66}(Mn^{4+},Mn^{3+})_5O_{10} \cdot 1.34H_2O$
Todorokite	$(Ca,Na,K)X(Mn4+,Mn3+)_6O_{12} \cdot 3.5H_2O$
Lithiophorite	$(Li,Al)MnO_2(OH)_2$
Chalcophanite	$ZnMn_3O_7 \cdot 3H_2O$
Birnessite	$(Na,Ca)Mn_7O_{14} \cdot 2.8H_2O$
Vernadite	$MnO_2 \cdot nH_2O$
Manganite	$MnOOH$
Groutite	$MnOOH$
Feitknechtite	$MnOOH$
Hausmannite	$Mn^{2+} Mn_2^{3+}O_4$
Bixbyite	Mn_2O_3
Pyrochroite	$Mn(OH)_2$
Manganosite	MnO

To obtain the desired sample diameter, cylindrical cores were drilled out from the ore lumps. Then the core was cut into 2 mm slices. Sides were gently ground in order to have smooth surfaces. Drilled core and disc-shaped samples (12 mm in diameter) ready to be tested are shown in Figure 4.

Figure 4: Assmang drilled core and disc-shaped samples (12 mm in diameter)

Before the test, the solid samples were covered on both sides by thin layers of graphite. This was done in order to increase absorption of the laser beam by the front of the sample, and to improve the temperature response from the rear side of the disc[8]. The amount of energy received by the samples should be equal to the energy received by the standard during the measurement. Briquettes and sinter were too porous and brittle to drill out the cores. Therefore, materials (including the manganese ores) were milled, and sieved to the appropriate fractions, as described in previous publications[9]. Powder with particles sized less than 63 μm was used in most of the experiments. A hydraulic press and pressing tools were used to form powder compacts with ½ inch diameter and 2 mm thickness. The same pressing pressure was applied to all powder compacts. Quality and strength of the compacts was surprisingly good. Compacts were coated by a thin graphite layer before measurement. All measurements were carried out in a nitrogen atmosphere. The heating rate applied was 10 K/min from room temperature up to 100°C, and from 100°C to 1 000°C the heating rate was 20 K/min.

RESULTS AND DISCUSSION

Property of solids ore

The main purpose of the research presented here was to determine the thermal conductivity of manganese ores versus temperature. Moreover, the other thermophysical properties, such as thermal expansion, heat capacity, and diffusivity, have been examined and will also be discussed. Figure 5 presents the thermal conductivity of Assmang ore versus the temperature. Characters placed next to the name of the sample indicate the sample density in g/cm^3. Before the experiments, three samples were preheated up to 400, 600, and 800°C respectively, in a reducing atmosphere, based on previous research about the CO reactivity of manganese ore[10]. One sample (Assmang 3.8) was examined twice, once from room temperature up to 1 000°C in a N_2 atmosphere and the experiment was repeated.

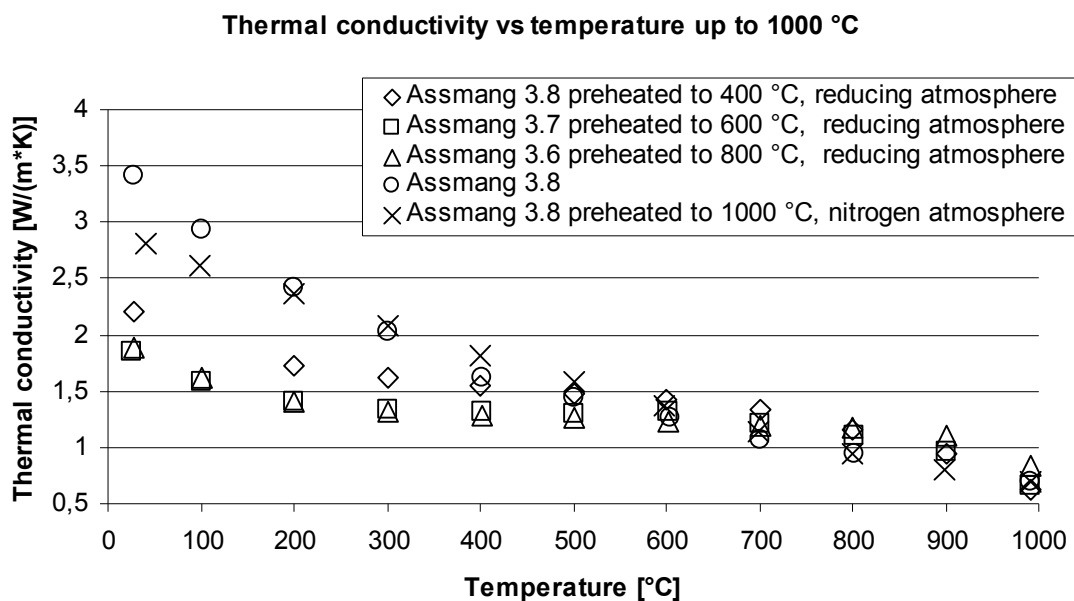**Thermal conductivity vs temperature up to 1000 °C**

Figure 5: Thermal conductivity of solid Assmang ore vs temperature

In all cases, thermal conductivity decreased with an increase in temperature. Assmang 3.8 heated from room temperature up to 1 000°C has the highest value. Samples that were preheated and pre-reduced have much lower conductivity, especially in the temperature range from 25 to 500°C. Above 500°C, the conductivity has similar values for all samples. A reducing atmosphere seems to have a strong influence on the conductivity values, particularly for the temperature range from 25 up to 500°C. 'Assmang 3.8 preheated to 400°C' was exposed to a mixture of CO (70%) and CO_2 (30%) for 40 minutes, while 'Assmang 3.591 preheated to 800°C' was heated and pre-reduced for 80 minutes. Reduction of ore caused a mass loss that affected the density. Two samples (one preheated and pre-reduced) have the same density, but the thermal conductivity varies significantly.

Figure 6 shows the thermal conductivity of Gabonese ore versus the temperature. Similar to Assmang ore, Gabonese ore conductivity decreases with a rise in temperature. The large 'drop' occurs from 3.4 $Wm^{-1}K^{-1}$ to 1.4 $Wm^{-1}K^{-1}$ between 500 and 600°C. This phenomenon appears only during the testing of the solid ore under a nitrogen atmosphere. It was not found when powders and solids were tested under vacuum. This effect needs to be more deeply investigated. Gabonese ore preheated in nitrogen has a much lower thermal conductivity then the primary ore, which was not observed in the case of Assmang ore. A test run under vacuum conditions gave unexpected results, with the lowest conductivity values. It is believed that these low values are an outlier and may be caused by a significantly lower density of specimen.
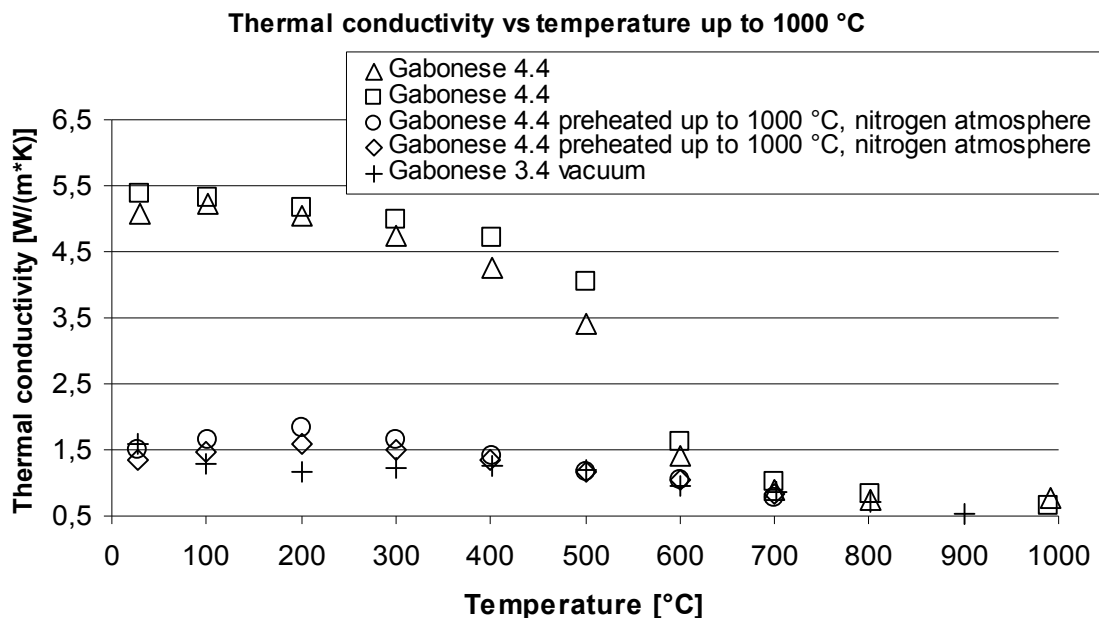

Figure 6: Thermal conductivity of solid Gabonese ore vs temperature

Assmang ore from room temperature up to 600°C has a much lower thermal conductivity (1.5 – 3.5 $Wm^{-1}K^{-1}$) than the Gabonese ore (3.5 – 5.5 $Wm^{-1}K^{-1}$), while the porosity of solid Assmang ore (3.4%) is much lower than solid Gabonese ore (32.8%). This indicates that the porosity is not the main property

affecting the thermal conductivity of those two materials. From 600°C to 1 000°C, the thermal conductivities are similar.

LFA 457 calculates the specific heat capacity by comparing the temperature rise of the sample with the temperature rise of the standard with a known C_P. The C_P value is essential, in order to compute the thermal conductivity according to Equation 1.

Specific heat capacity vs the temperature up to 1000 °C
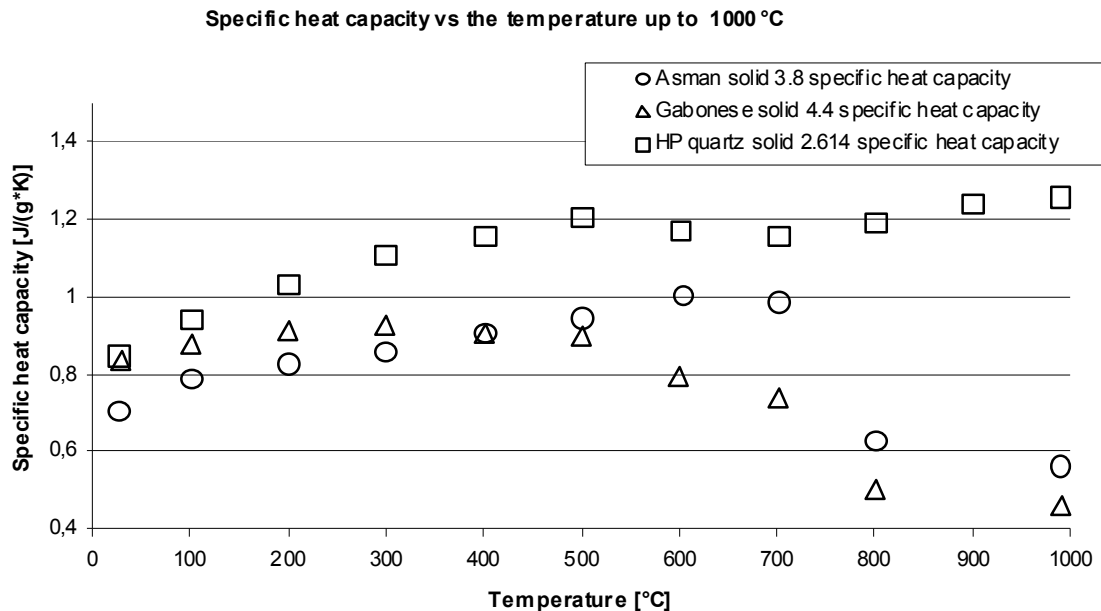

Figure7: Specific heat capacity of solids vs temperature

Figure 7 presents the apparent heat capacity of the solid Assmang ore and Gabonese ore, determined under a nitrogen atmosphere. In addition, the specific heat capacity of HP silicon dioxide is presented for comparison. Assmang ore increases in specific heat up to 700°C. Above that temperature, values decrease drastically. This can be caused by decompositions of higher oxides, or there is a measurement error due to the mass loss of the sample. A similar trend exists for Gabonese ore; initially the apparent specific heat increases up to 500°C and then values start to drop. It is believed that, in the case of Gabonese ore, the curve shape is correlated to the mass loss during heating. Instability of higher oxides MnO_2 (510°C) and Mn_2O_3 (981°C) during the heating could possibly have caused the observed changes. Quartz, which is a more stable dioxide than manganese ores, keeps increasing in specific heat up to the end of the measurement.

Comparison of solid and powdered materials
One of the objectives of this work was to find the way to test various manganese ores and agglomerates by using LFA 457. Briquettes and sinter were too porous and brittle to drill out the cores. Therefore, materials (including the manganese ores) were milled, sieved, and pressed to applicable disc-shaped samples. Figure 8 shows a comparison of thermal conductivity and apparent specific heat of Gabonese ore and powder compacts.
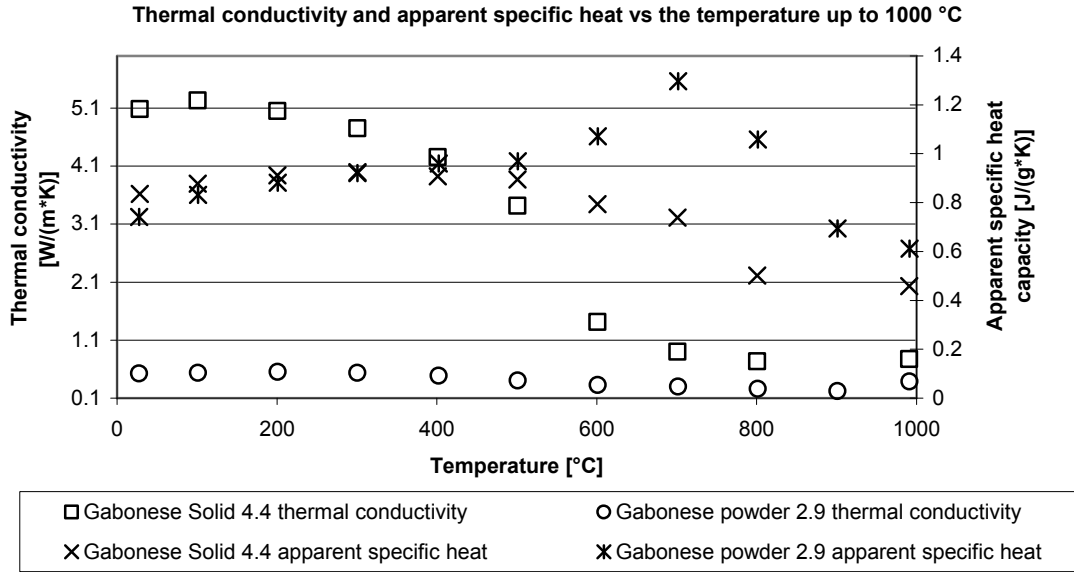
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Thermal conductivity and apparent specific heat vs the temperature up to 1000 °C

- □ Gabonese Solid 4.4 thermal conductivity
- ○ Gabonese powder 2.9 thermal conductivity
- ✕ Gabonese Solid 4.4 apparent specific heat
- ✳ Gabonese powder 2.9 apparent specific heat

Figure 8: Thermal conductivity and apparent specific heat of Gabonese ore and Gabonese powder compact

There is a significant difference between solid and powdered compacts in thermal conductivity values. This fact suggests that the compacted powder samples are not representative for investigation of the conductivity of solids. Solid Gabonese ore decreases in conductivity during the temperature rise, with a large drop from $3.4\,Wm^{-1}K^{-1}$ to $1.4\,Wm^{-1}K^{-1}$, between 500 and 600°C. The Gabonese compact maintained its conductivity in the range from $0.5\,Wm^{-1}K^{-1}$ at room temperature to $0.2\,Wm^{-1}K^{-1}$ at 1 000°C. A significant drop of values between 500 and 600°C was not observed. The powder compact made from Assmang ore increased its conductivity value up to 200°C then started to decrease with the temperature rise, while the solid Assmang sample decreased in conductivity continuously to 1 000°C.
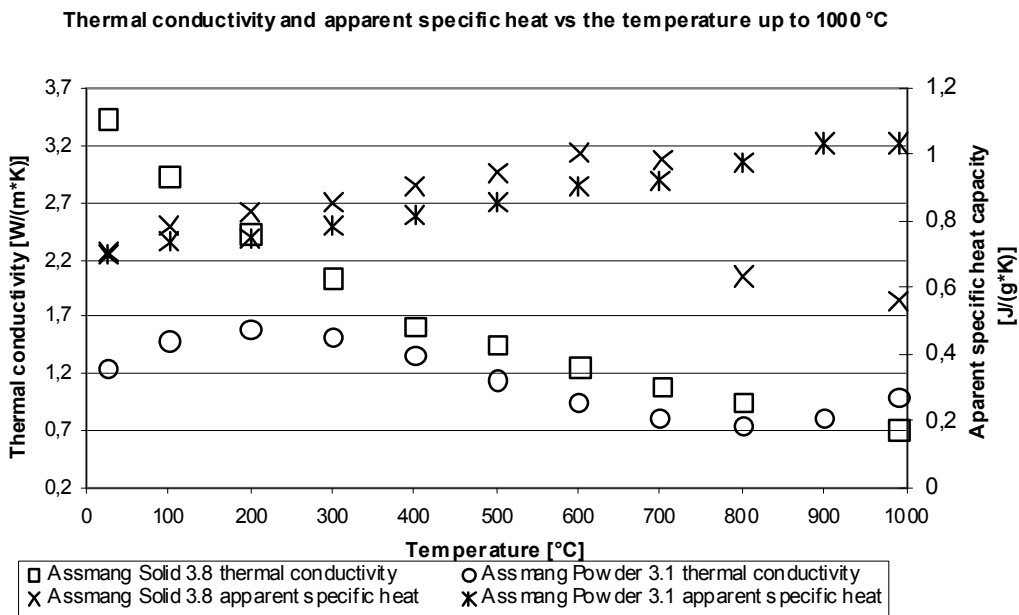
Thermal conductivity and apparent specific heat vs the temperature up to 1000 °C

- □ Assmang Solid 3.8 thermal conductivity
- ○ Assmang Powder 3.1 thermal conductivity
- ✕ Assmang Solid 3.8 apparent specific heat
- ✳ Assmang Powder 3.1 apparent specific heat

Figure 9: Thermal conductivity and apparent specific heat of Assmang ore and Assmang powder compact

Figure 8 and Figure 9 show that the Assmang ore, from room temperature up to 600°C, has a much lower thermal conductivity than the Gabonese ore, while the porosity of solid Assmang ore (3.4%) is much lower than that of solid Gabonese ore (32.8%). This indicates that the porosity is not the main property affecting the thermal conductivity of those two materials. It is also worth mentioning that the compacts used in the tests had a porosity of around 32% before heating, and 35% after the test, which is close to the porosity of solid Gabonese ore.

The C_P values presented in Figure 8 and Figure 9 are obtained by comparing the temperature rise of the sample with the temperature rise of the standard with known C_P. The possibility of error can be high if mass loss occurs, or if the amount of energy absorbed by the surface of the sample is different from the energy absorbed by standard. From room temperature, up to 500°C for Gabonese, and 600°C for Assmang, solid materials achieve the same values as the powdered materials. This confirms the accuracy of the tests, as the values presented in Figures 8 and 9 are intensive properties. Above 500°C, Gabonese ore and compact exhibit a decrease in C_P values up to the end of the test. The Assmang ore compact keeps showing an increase in apparent specific heat up to 1 000°C, while Assmang ore above 700°C starts to show a decrease in its apparent specific heat capacity. This can be caused by decompositions of higher oxides, or there might be a measurement error due to the mass loss of the sample.

Additionally, thermal expansion tests were run. Figure 10 presents the tendency of solid ore and powdered compacts to change in length in response to temperature change. The heating rate in all tests was 2 K\min. It is essential, for the measurement of thermal diffusivity, to know how the thickness of the disc-shaped sample changes versus the temperature.
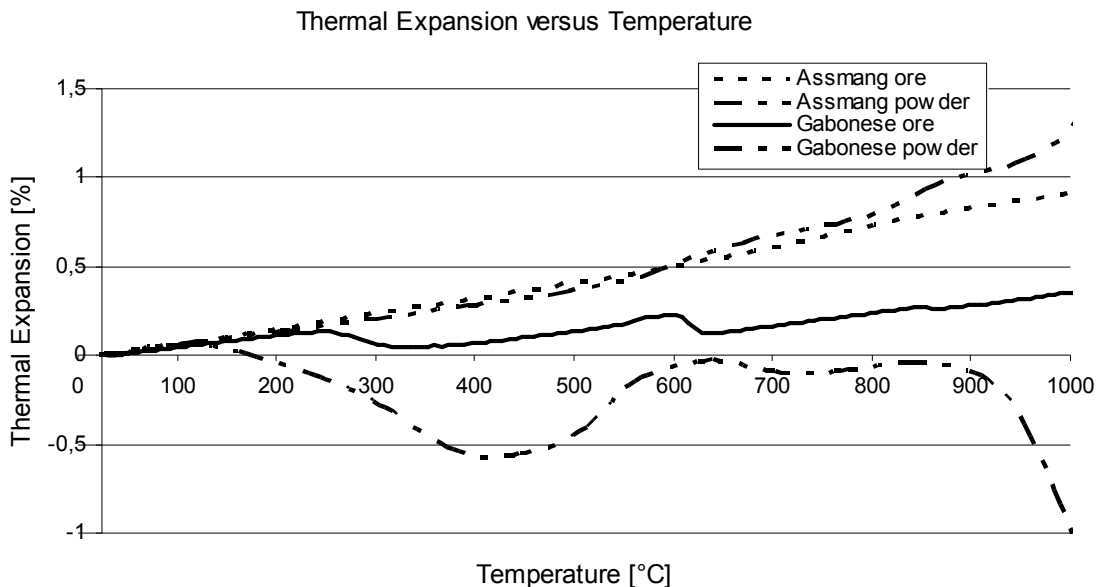

Figure 10: Thermal expansion in length of solid ore and powdered compacts

Solid Assmang and Assmang powdered compacts expand progressively from room temperature to 1 000°C. It is worth mentioning that, during the five tests, three Assmang ore samples broke just above a temperature of 400°C. The thermal expansion curve of solid Gabonese material follows a similar trend as a powdered sample, increasing and decreasing length in particular temperature ranges. The Gabonese powdered compact changed its length surprisingly. From 100°C, the Gabonese compact drastically started shrinking up to 400°C, where after it started to expand again. Solid Gabonese ore, from room temperature up to 250°C, expands, then drops in value and starts to increase again up to 600°C. In the solid state, there is no shrinkage effect, where the sample length is shorter during the heating than the initial sample length. It is believed that the shape of the Gabonese curve is correlated with mass loss and the release of gases (CO_2 and O_2) during heating. Also, instability of higher oxides MnO_2 (510°C) and Mn_2O_3 (981°C) during the heating in an air atmosphere should be taken into consideration[1]. However, both the Gabonese ore and Gabonese powder have very low expansion values (~ 0.5%).

CONCLUSIONS

Thermal expansion, thermal diffusivity, conductivity, and apparent specific heat capacity of solid samples and compacted powder samples of manganese ores were examined from room temperature to 1 000°C. A laser flash method and pushrod dilatometer were used.

1) The diffusivity and conductivity of compacted powder are different from that of solid samples. This indicates that the compacted powder samples do not provide representative values for materials that were not solid enough to prepare into disc-shaped samples for LFA investigation.

2) It was found that all the presented properties are strongly dependent on temperature. Moreover, a reducing atmosphere has a strong effect on the change of thermal conductivity of Assmang ore. On the other hand, only pre-heating and a vacuum atmosphere caused significant changes in the conductivity of Gabonese ore. It has been shown that the density is not the main factor affecting thermal conductivity. Two Assmang ore samples with similar density, around 3.8 g/cm^3, showed a variety of conductivity values.

3) The thermal conductivity of solid Assmang ore and Gabonese ore decreases with increasing temperature. The drop of the Gabonese ore's thermal conductivity from 3.4 Wm^{-1}K^{-1} to 1.4 Wm^{-1}K^{-1} between 500 and 600°C has to be more deeply examined to explain this phenomenon.

4) The authors believe that the C_P values presented, up to 500°C for Gabonese ore, and 600°C for Assmang ore, are quite accurate. It has been shown that, at temperatures up to 500°C, Gabonese ore requires a higher amount of energy to increase one gram of material by a temperature of one Kelvin. Data presented for temperatures up to 600°C are similar to data found in the literature for pure Mn oxides.

5) More porous Gabonese ore, with a porosity of 32.8%, has a higher thermal conductivity than Assmang ore, with a porosity around 3%. Moreover, the thermal conductivity decreases with a temperature rise in both cases, which shows similarity to the thermal conductivity of iron ores investigated by Akihama *et al*. The results presented here exhibit the relationship typically found for rocks. Rocks with a thermal conductivity higher than 2 Wm^{-1}K^{-1} at room temperature decrease in value with a temperature rise.

6) The thermal expansion of two manganese ore and powder compacts was investigated. Assmang and Gabonese ore have a thermal expansion less then 1% in the temperature range from 25° up to 1 000°C. The various samples showed different trends. The Assmang powder compact follows the trend and values similar to the solid Assmang ore, while the Gabonese powder compact shrinks and then increases its length at particular temperatures.

7) As a part of future work, a comparison of thermal conductivity with the mineralogy of manganese ore will be investigated.

ACKNOWLEDGEMENTS

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