INVESTIGATION ON A POSSIBLE REVIEW ON THE THERMODYNAMIC PREDICTIONS ON THE CARBON SOLUBILITY IN Mn-Fe MELT DURING CARBOTHERMIC REDUCTION USING NCHWANENG MANGANESE ORES

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Abstract

The high carbon ferromanganese process produces an alloy saturated with carbon. The alloy contains Mn metal, Fe and C. Carbon dissolves into the alloy, and therefore it is important to calculate the activity of manganese in the alloy. Data dealing with the solubility of carbon in liquid ferroalloy are available but only applied to specific melts. Because the dissolution of carbon into the manganese alloy was not as obvious as in steel production, the behaviour of carbon in steel production was considered the archetype and became the accepted tradition in the manganese alloy production. The assumption was considered because of the solubility of carbon in liquid. Mn, Fe and Mn-Fe present similarities in their interaction parameters. In this investigation, two different equations linear regression that are used in the steel production were tested to establish their validity when using a basic manganese ore. The deviations of the experimental carbon solubility values obtained in this study are narrow such that the fitting of the model albeit revisited but strongly reconducted and cautiously adopted, therefore not reviewed. Therefore, Turkdogan's (1956) and Tuset and Sandvik's (1970) thermodynamic predictions on the carbon solubility in Mn-Fe melt remain valid and reliable for the production of high carbon ferromanganese using basic manganese ores.

Keywords: Metallurgy, high carbon ferromanganese, carbon solubility

1. INTRODUCTION

In a liquid state carbon and manganese are completely miscible. High carbon ferromanganese alloys are saturated with carbon. Carbon solubility in liquid Mn and Fe melts has been largely reported. However, the studies conducted applied to specific working conditions or to acidic manganese ores not to when basic manganese ores. A number of research works have been conducted to establish the correlation between iron in the alloy and the temperature [1-3]. In the Mn-C system, at higher manganese content the deviation to Raoult's law was found positive [4], whereas found close to Raoult's law [5].

Researchers do not agree on whether the Mn-Fe system is ideal or not. A group found that the system almost ideal [6] and others found it to be ideal [7] while it was concluded that the system was actually better than the accepted ideal [8] and the deviation was found negative [9].

In the Mn-Fe-C system, the measurements on manganese activity obtained by [4] and the calculated values fitted well when investigated in the same region [9].

Investigations have been conducted by several researchers: at 1400 °C [4], at 1523 °C [11], at 1500 °C [12-13], have all measured the activities of Mn in the system Mn-C and have all come to the same conclusion that the activity of Mn increases with the decrease of the activity of C. In high carbon ferromanganese the silicon content is usually below 0.1 %. Because it is low in the manganese alloy, its influence is not taken into account. Activities of Mn and Fe were measured in the Mn-Fe system at 1427 °C [11] while same activities were measured in the same system at 1600 °C [9]. Both groups found that there is a complete miscibility in liquid state and that the deviation from the ideal was minute. Investigations on the thermodynamics of Mn-Fe-C and

Mn-Si-C systems at 1400 °C and 1500 °C found that the solubility of carbon in the alloy decreased with silicon increase in the alloy [3]. This was confirmed by other researchers at 1430 °C [8] and aligned well with what was measured elsewhere [1,14]. The silicon in the alloy is generally less than 1 % and the lowest Si content is said to be 0.6 % [15]. The current paper focused on whether previous conclusions that were conducted in different systems is different when using basic manganese ores.

2.   METHODOLOGY

2.1   Material and equipment

The manganese ore used in the current investigation is a basic ore from South Africa while silica of 99.9 % sourced from the university of Johannesburg, Department of Metallurgy chemical laboratory; was used to adjust the basicity to unity. Coke was used as reductant. Argon (99.96 %) and carbon monoxide (99.06 %) sourced from Afrox were used. XRD, XRF, SEM and EPMA were used as analytical techniques. A THM 15 vertical furnace equipped with an alumina tube was used for the experiment.

2.2   Experimental procedure

100 g of manganese ores were used to which 5 wt% of coke and silica to adjust the basicity to unity were added. The mix was milled together for 15 minutes to ensure better homogenization. The mix was then placed in a graphite crucible which was placed in a silica crucible to avoid spillages in case the graphite crucible ceased due to possible reaction with the manganese ore. Argon was blown in the furnace from room temperature to 600 °C then carbon monoxide was switched on while argon was off until the aimed temperature was reached. Thereafter, the furnace was switched-off while carbon monoxide was still blown in till 600 °C then switched-off and argon switched on until room temperature. The feeds were analysed using XRD, XRF and SEM while the alloys produced were analysed using Electron Microprobe analysis (EPMA).

3.   RESULTS AND DISCUSSION

The XRD in **Figure 1** depicts the mineralogy of the manganese ore used in this project. Braunite, hausmannite and bixbyite are the major manganese minerals in the sample while hematite is the iron carrier.
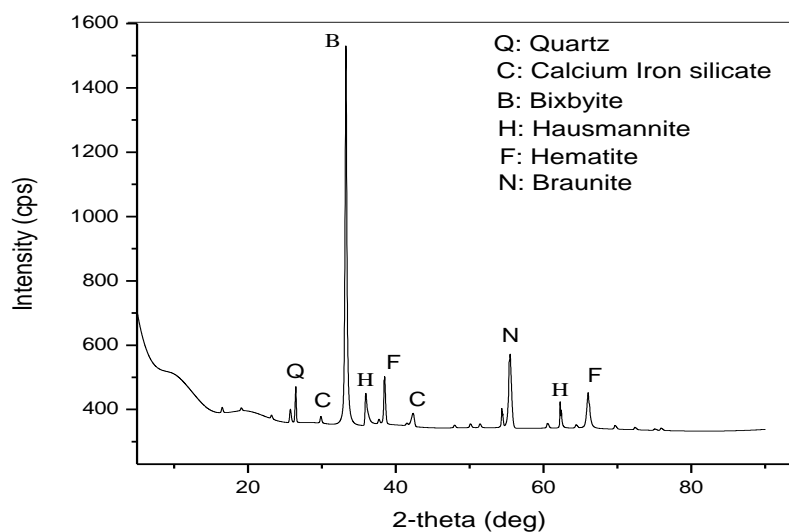

Figure 1 XRD results of the manganese ore

Figure 2 shows SEM while **Table 1** and **Table 2** provide the compositions of different spectra analysed with SEM and XRF results respectively.
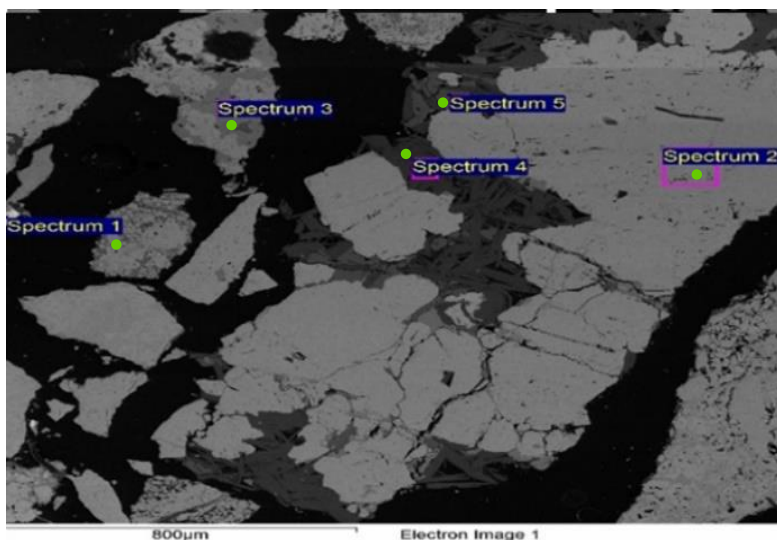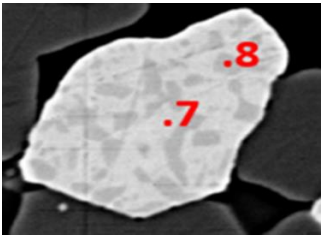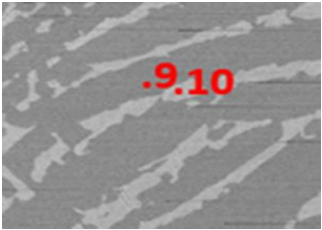
Figure 2 SEM of the manganese ore

Table 1 Analysis of the spectra in **Figure 2** (at%)

Spectrum	Mn	Fe	Al	Si	Ca	Mg	Phases	Formulas
1	6.7	-	-	-	1.05	-	Braunite	$Mn.Mn_6(SiO_4)O_8$
2	56.27	11.13	-	4.07	4.01	-	Bixbyite	$(Fe,Mn)_2O_3$
3	1.21	15.43	1.21	20.75	22.82	-	Hausmannite	$(Mn_3Fe)O_4$
4	0.46	0.57	9.87	18.25	-	24.71	Calcium iron silicate	$CaFeSi_2O_6$
5	1.1	-	2.34	3.34	53.66	7.18	Quartz	SiO_2

Table 2 XRF analysis of the manganese ore

Oxide	MgO	Al_2O_3	SiO_2	CaO	MnO_2	Fe_2O_3	Basicity	Mn/Fe
wt%	1.03	0.93	4.89	5.29	66.85	19.56	1.1	3.1
Element	Mg	Al	Si	Ca	Mn	Fe		
wt%	0.97	0.77	3.56	5.89	65.80	21.31		

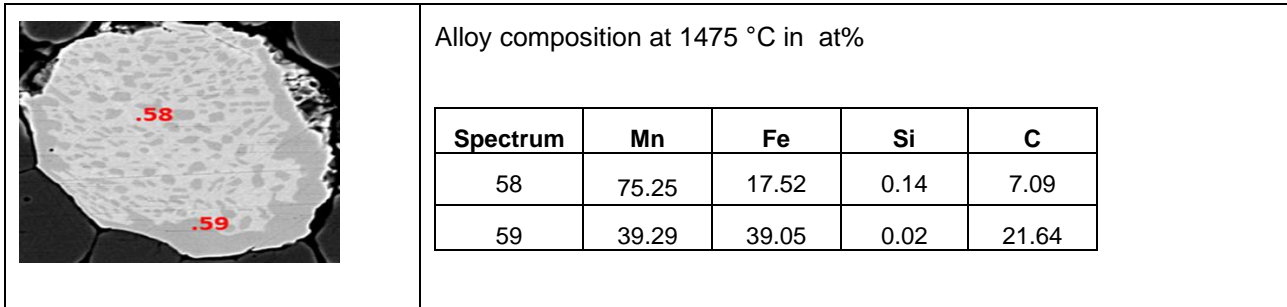|	
	Alloy composition at 1400 °C in at% <table><tr><td>Spectrum</td><td>Mn</td><td>Fe</td><td>Si</td><td>C</td></tr><tr><td>7</td><td>75.17</td><td>17.74</td><td>0.09</td><td>6.93</td></tr><tr><td>8</td><td>69.96</td><td>23.14</td><td>0.11</td><td>67.97</td></tr></table>
	Alloy composition at 1450 °C in at% <table><tr><td>Spectrum</td><td>Mn</td><td>Fe</td><td>Si</td><td>C</td></tr><tr><td>9</td><td>37.3</td><td>46.18</td><td>0.11</td><td>15.4</td></tr><tr><td>10</td><td>75.10</td><td>17.87</td><td>0.09</td><td>6.94</td></tr></table>

Alloy composition at 1475 °C in at%

Spectrum	Mn	Fe	Si	C
58	75.25	17.52	0.14	7.09
59	39.29	39.05	0.02	21.64

Figure 3 EPMA analysis of alloys (at%) obtained at different temperatures

The model review of the metal system based on the dissolution data of Mn and Fe melts from the EPMA results at different temperatures are presented in **Table 3** whereas the EPMA spectra composition are presented in **Figure 3**. On one hand, it was found that alloys produced had an average Mn content of about 75 at.% and Fe of about 17.5 at.% on average. The Mn/Fe ratio remained constant at about 4.2 and was not dependent on the temperature change.

On the other hand, it was found that there was a decrease in carbon solubility with temperature increases, whereas silicon increased with increasing temperature.

However, although there was an increase in silicon, its amount remained below the 1 at% mark. It was also observed that the carbon dissolved in the metal increased when Mn/Si increased.

The carbon solubility in the Mn-Fe alloy produced in this research was calculated using the linear regression analysis below for possible review:

$$\text{Log \%C} = (1.065 - 614/T(K) + 0.18 \text{ \%Mn}/(\text{\%Mn} + \text{\%Fe}) \tag{1}$$

$$\text{Log \%C} = (1.005 - 478/T(K) + 0.147 \text{ \%Mn}/(\text{\%Mn} + \text{\%Fe}) \tag{2}$$

The calculated carbon solubility values and experimental values are presented in **Table 3**.

Table 1 Calculated log %C compared to log %C calculated as per Turkdogan and Tuset&Sandvik models

Temperature (°C)	Comparison 1		Comparison 2	
	Calculated as per Turkdogan (1956)	Experimental log %C	Calculated as per Tuset and Sandvik (1970)	Experimental log %C
1400	0.84	0.84	0.84	0.84
1450	0.85	0.84	0.85	0.84
1475	0.86	0.85	0.85	0.85

In order to easily estimate the variation of the carbon solubility in the Mn-Fe melt, the best configuration was to present the inverse of temperature in Kelvin for a better configuration of the scale. Therefore, although the trend of carbon solubility shows a decrease, it was observed that the solubility of carbon in Mn-Fe melt is directly proportional to the temperature.

From the possible review of previous carbon dissolution models as discussed in the modelling, it transpired from **Figures 4** and **5** below that the experimental carbon solubility values obtained in this study are in good agreement with both [1] and [8].
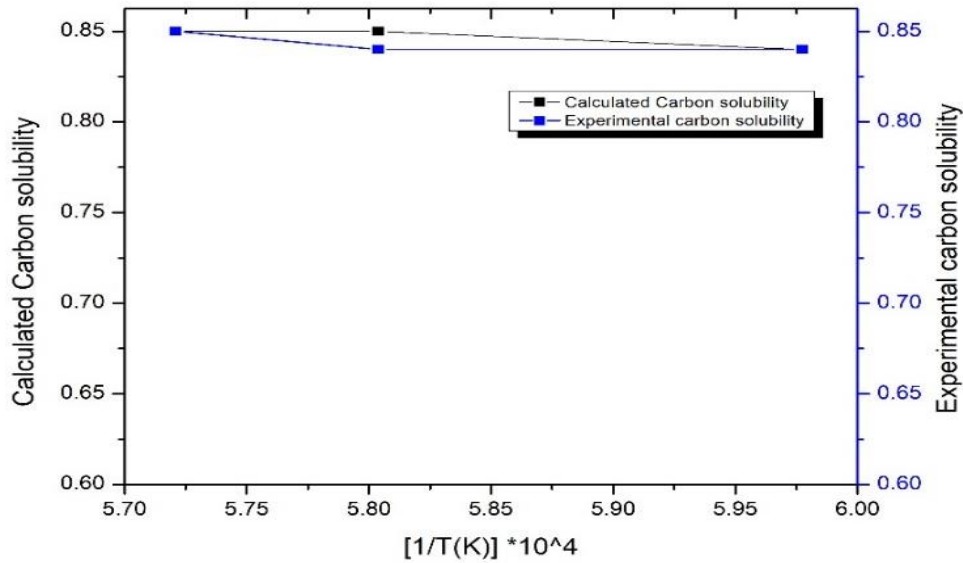
Figure 1 Comparison between experimental and Turkdogan (1956) calculated carbon solubility(at.%)
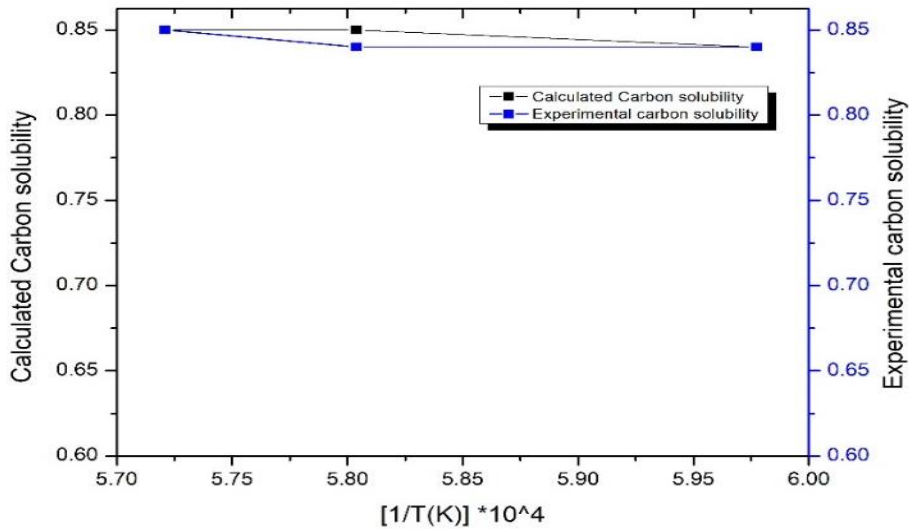

Figure 5 Comparison between experimental and Tuset and Sandvik (1970) calculated carbon solubility(at%)

The deviations in **Figure 4** shows that the highest difference between the calculated values using the Turkdogan model and the values obtained experimentally is 0.01 at% at 1450 °C. At 1400 °C and 1475 °C no deviations were noted. **Figure 5** depicts the comparison between the calculated values of carbon solubility using Tuset and Sandvik model and the experimental values. Results show that the highest deviation was obtained at 1450 °C of 0.01 at% while for 1400 °C and 1475 °C no deviation was noted.

4. CONCLUSION

The deviations of the experimental carbon solubility values obtained in this study are considerably narrow such that the fitting of the model albeit tested with the intention to be revisited are adopted, therefore not reviewed. Therefore, the linear regressions of Turkdogan's (1956) and Tuset&Sandvik's (1970) thermodynamic predictions on the carbon solubility in Mn-Fe melt remain valid and reliable for the production of high carbon ferromanganese using any of basic manganese ores.

ACKNOWLEDGEMENTS

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